M.Sc. Semester-I
Core Course-II (CC-II)
Reaction Mechanism in Organic Chemistry

Nature of Bonding in Organic Molecules

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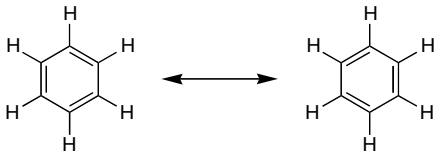
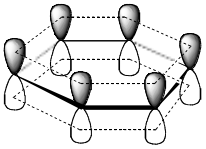
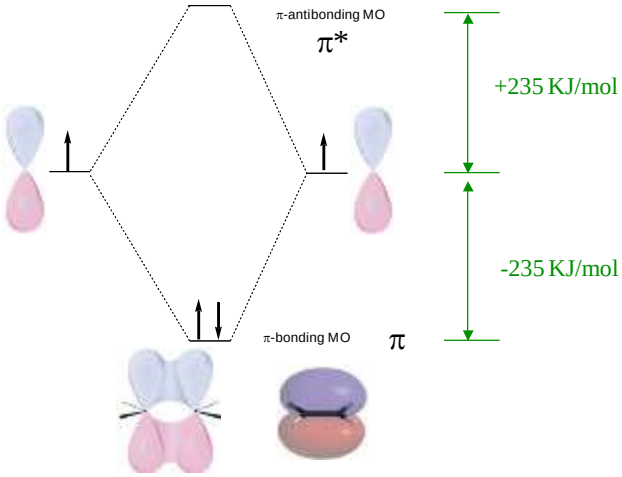
Aromaticity



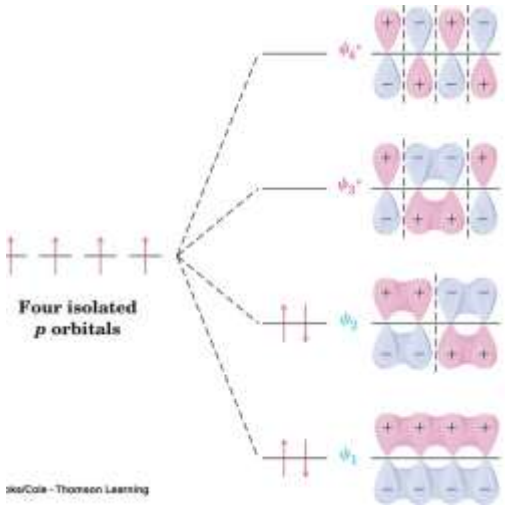
C_6H_6



MO's of a C=C π-bond



π-molecular orbitals of butadiene



3 Nodes
0 bonding interactions
3 antibonding interactions
ANTIBONDING MO

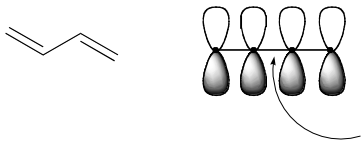
2 Nodes
1 bonding interactions
2 antibonding interactions
ANTIBONDING MO

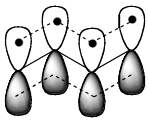
1 Nodes
2 bonding interactions
1 antibonding interactions
BONDING MO

0 Nodes
3 bonding interactions
0 antibonding interactions
BONDING MO

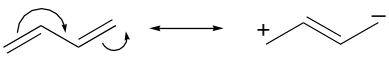
ψ_2 is the Highest Occupied Molecular Orbital (HOMO)
ψ_3 is the Lowest Unoccupied Molecular Orbital (LUMO)

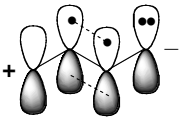
ψ_1 of Butadiene (no nodes, bonding MO)





The four π-electrons in ψ_1 are delocalized over the four p-orbitals

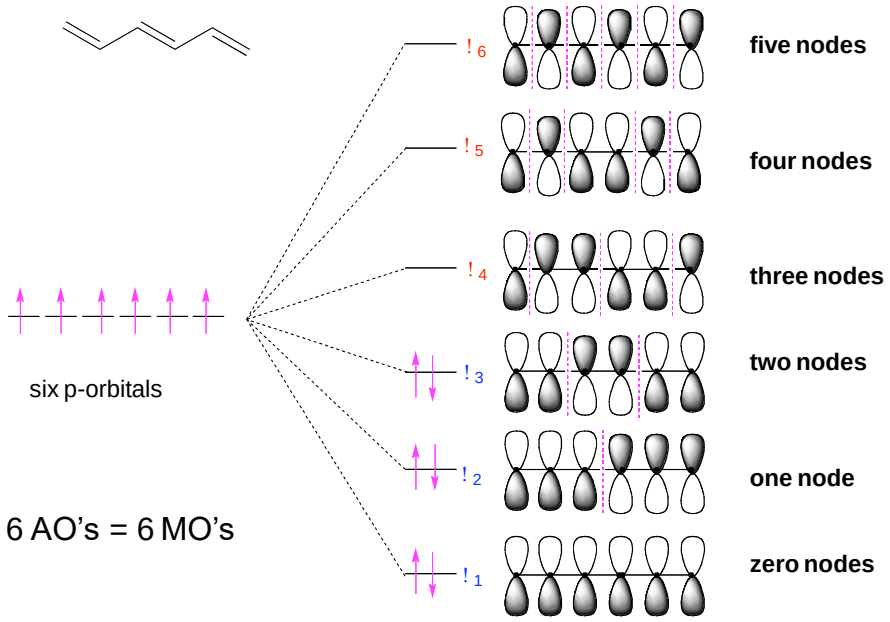




Bond lengths in pm

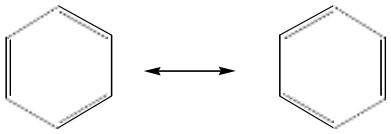
H_3C-CH_3	$H_2C=CH_2$	$H_2C=CH-CH_3$	$H_2C=CH-CH=CH_2$	$H_2C=CH-CH=CH_2$
154	133	149	148	134

π-molecular orbitals of hexatriene



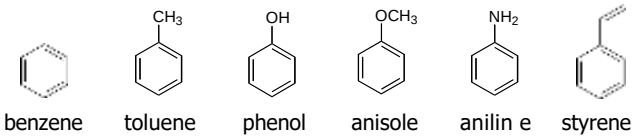
Conjugation: Series of overlapping p-orbitals

Aromaticity: Cyclic conjugated organic compounds such as benzene, that exhibit special stability due to resonance delocalization of π-electrons.



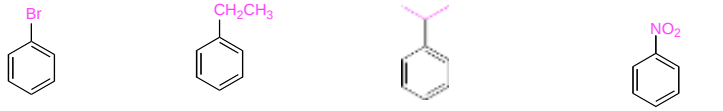
2. Naming aromatic compounds: (arenes)

Large number on non-systematic names:



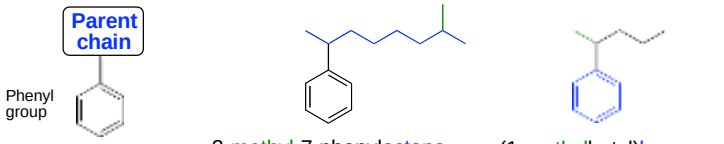
benzene toluene phenol anisole anilin e styrene

Generally, mono-substituted benzenes are named in a similar manner as hydrocarbons with -benzene as the parent name



bromobenzene **ethylbenzene** **(1-methylethyl)benzene (isopropylbenzene)** **nitrobenzene**

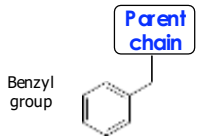
When the benzene ring is a substituent of a parent chain, referred to as a phenyl group. The benzene ring is is regarded as a substituent when the parent chain has greater than six carbons. The benzene ring is the parent when the longest alkyl chain substituent is six carbons or less



2-methyl-7-phenyloctane (1-methylbutyl)benzene

A phenyl substituent (C_6H_5-) is often abbreviates as Ph-

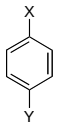
A C_6H_5-CH_2- susbtitutent is often referred to as a benzyl group (Bn-)



Disubstituted benzene: Relative position of the substitutents

1,2-disubstituted: *ortho* (*o*-)

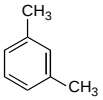
1,3-disubstituted: *meta* (*m*-)



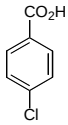
1,4-disubstituted: *para* (*p*-)

Note: ortho, meta, and para are not used in systematic nomenclaure

2-chlorotoluene
ortho-chlorotoluene
o-chlorotoluene



1,3-dimethylbenzene
meta-xylene
m-xylene

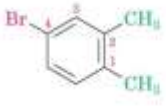


4-chlorobenzoic acid
para-chlorobenzoicacid
p-chlorobenzoic acid

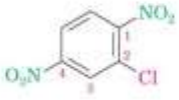
Benzenes with two or more substituents:

Choose numbers to get lowest possible values

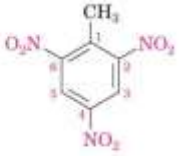
List substituents alphabetically with hyphenated numbers



4-Bromo-1,2-dimethylbenzene



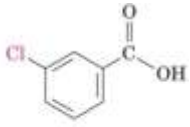
2-Chloro-1,4-dinitrobenzene



2,4,6-Trinitrotoluene (TNT)

Common names, such as “toluene” can serve as root name (as in TNT)

2,6-Dibromophenol

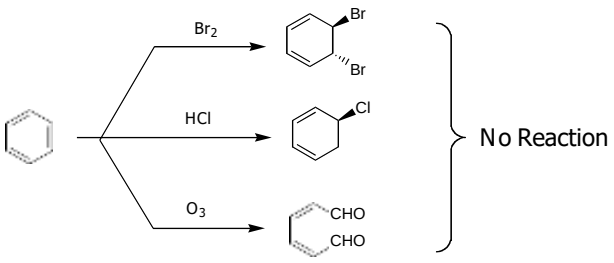


m-Chlorobenzoic acid

3. Structure and Stability of Benzene

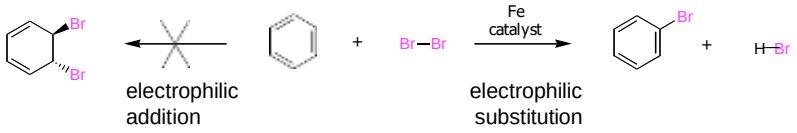
Formula: C_6H_6, four degrees of unsaturation (section 6.2)
three double bonds + one ring

The π-bonds of benzene are resistant to the normal reactions of alkenes and alkynes

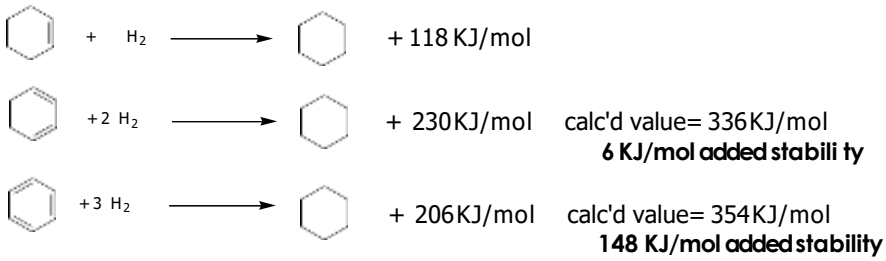


Benzene's cyclic conjugated structure gives it special stability

Benzene undergoes electrophilic substitution reactions (chapter 16) rather than electrophilic addition

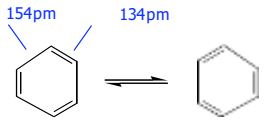


Stability of Benzene: Heats of Hydrogenations

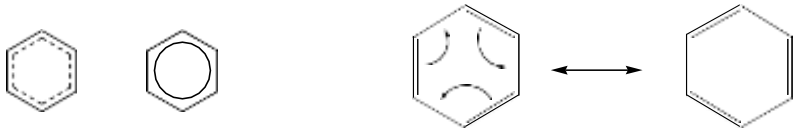


Structure of Benzene:

Kekule benzene: two forms are in rapid equilibrium



- All bonds are ~139 pm (intermediate between C-C and C=C)
- Electron density is distributed evenly between the six carbons
- Structure is planar, hexagonal
- C–C–C bond angles are 120°
- Each carbon is sp^2 and has a *p* orbital perpendicular to the plane of the six-membered ring



Arrows in organic chemistry

Reaction arrow

Equilibrium arrow

Resonance arrow

Mechanism arrows

Double-headed arrow

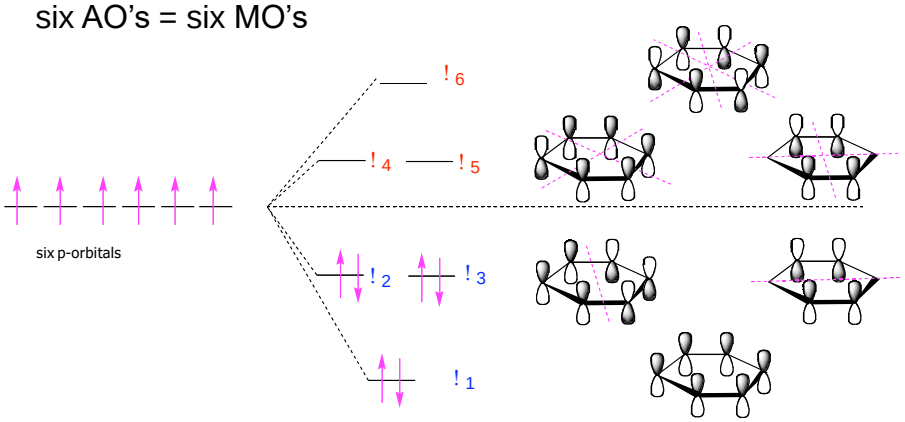
Single-headed arrow

Drawing and Interpreting Resonance Forms

1. No one resonance forms accurately depicts the structure of the molecule. The real structure is a composite or hybrid of all resonance forms
2. Resonance forms differ only by the placement of π- or non-bonding electrons. Neither the position or hybridization of the atoms changes.
3. Resonance forms are not necessarily equivalent. While all resonance forms contribute to the actual structure (resonance hybrid), some forms may contribute more.
4. All resonance forms must be proper Lewis structures.
5. The actual resonance hybrid is more stable than any single resonance form.
6. In general, the greater the number of resonance forms, the more stable the resonance hybrid.

4. Molecular orbitals of benzenes:

six AO's = six MO's



Degenerate orbitals: orbitals that have the same energy

Ψ_1: zero nodes
Ψ_2 and Ψ_3: one node

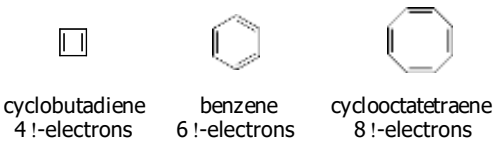
Bonding

Ψ_4 and Ψ_5: two nodes
Ψ_6: three node

Anti-bonding

5. Aromaticity and the Hückel 4*n* + 2 Rule

Cyclic conjugated molecules: not all cyclic conjugated systems are aromatic (no special stability)

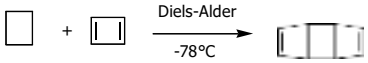


cyclobutadiene
4 !-electrons

benzene
6 !-electrons

cyclooctatetraene
8 !-electrons

Cyclobutadiene: highly reactive
two different C-C bonds



Cyclooctatetraene: reactivity similar to normal C=C

Exists in a boat-like conformation:
little overlap between
double bonds

Aromatic:

Cyclic
Conjugated: "alternating single and double bonds"
Flat: maximum overlap between conjugated π-bonds
Must contain 4*n*+2 π-electrons, where *n* is an integer
(**Hückel's rule**)

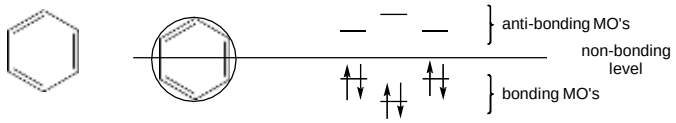
Anti-aromatic:

cyclic, conjugated, flat molecules that contain 4*n* π-electrons (where *n* is an integer).
Destabilized (highly reactive) relative to the corresponding open-chain conjugated system

6. Frost Circles: relative energies of the molecular orbitals of cyclic, conjugated systems

Inscribe the cyclic, conjugated molecule into a circle so that a vertex is at the bottom. The relative energies of the MO's are where the ring atoms intersect the circle

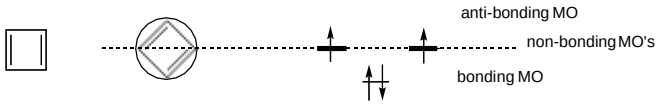
benzene:



Benzene
6 !-electrons

For aromatic compounds, such as benzene, the bonding MO's will be filled.

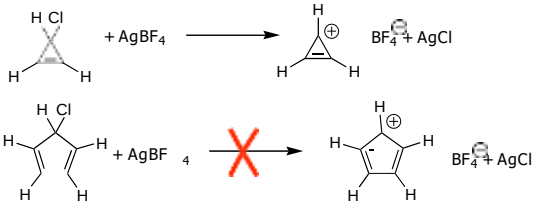
cyclobutadiene:

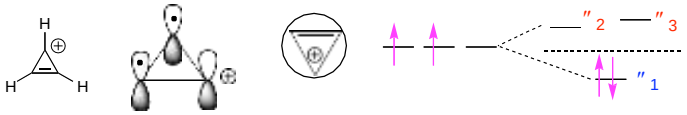


Cyclobutadiene
4 !-electrons

For anti- aromatic compounds, such as cyclobutadiene, there will be unpaired electrons in bonding, non-bonding or antibonding MO's.

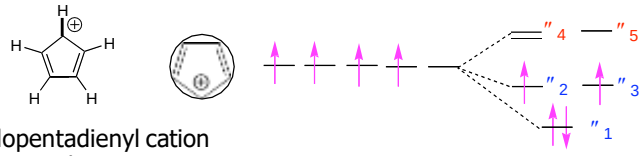
7. Aromatic ions





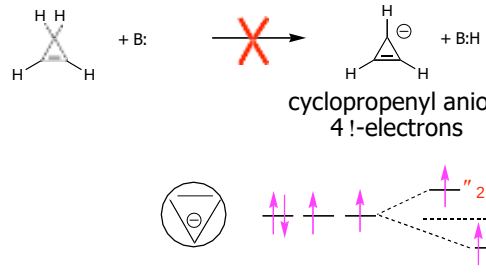
cyclopropenyl cation
2 !-electrons

$4n+2=2$
$n=0$
aromatic

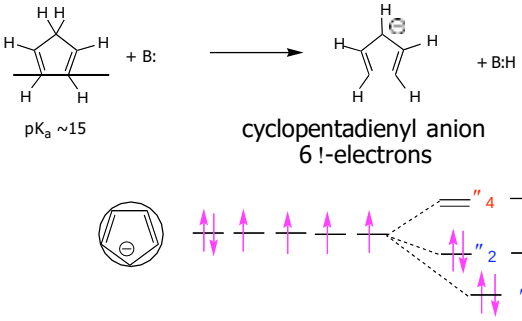


cyclopentadienyl cation
4 !-electrons

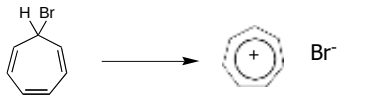
$4n=4$
$n=1$
anti-aromatic



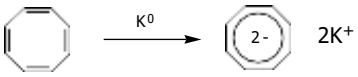
$4n=4$
$n=1$
anti-aromatic



$4n+2=6$
$n=1$
aromatic



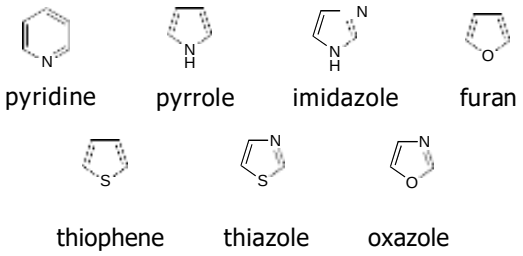
6 π-electron



10 π-electron

8. Aromatic Heterocycles

Heterocycle: any cyclic compound that contains ring atom(s) other than carbon (N, O, S, P)



Cyclic compounds that contain only carbon are called carbocycles

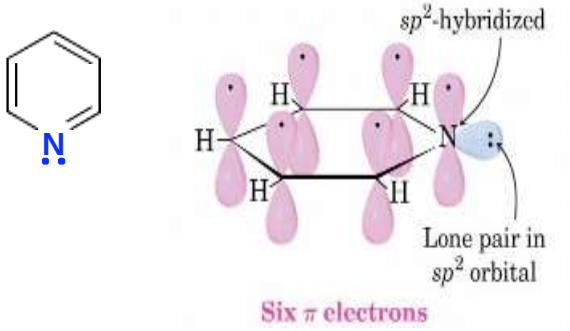
Heterocyclic aromatic compounds are numerous, common and a very important class of organic compounds

Nomenclature for heterocyclic compounds is specialized

Pyridine

π-electron structure resembles benzene (6 π-electrons)

The nitrogen lone pair electrons are not part of the aromatic system (perpendicular orbital)

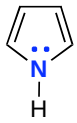


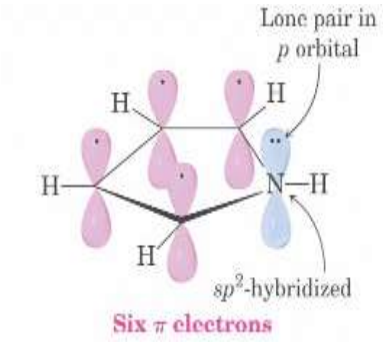
Pyrrole:

6 π-electron system similar to that of cyclopentadienyl anion

Four *sp*2-hybridized carbons with 4 *p* orbitals perpendicular to the ring and 4 p electrons

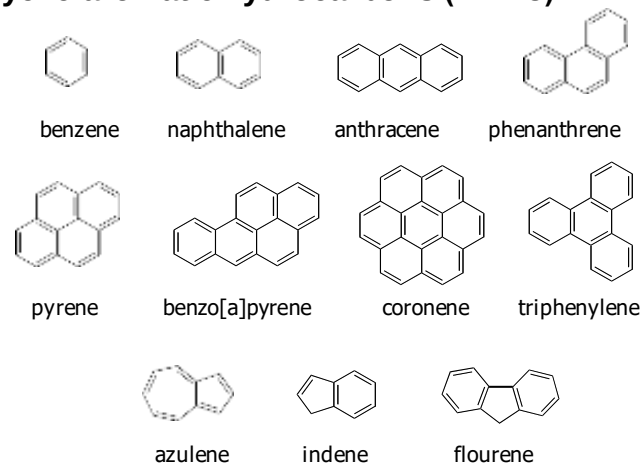
lone pair of electrons in an sp^2 orbital; part of the aromatic sextet



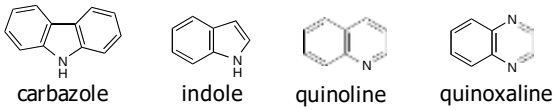


Pyrrole is much less basic than pyridine. Why?

9. Polycyclic aromatic hydrocarbons (PAH's):



Polycyclic heterocycles

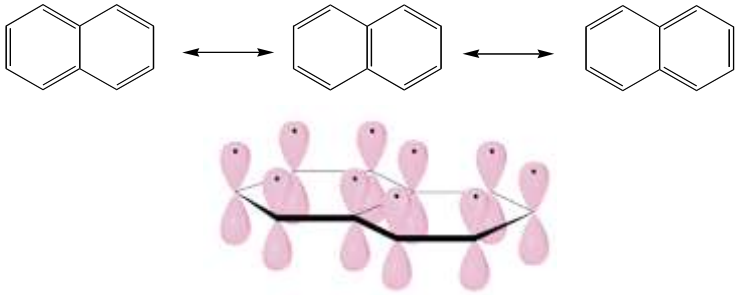


10. Polycyclic aromatic hydrocarbons

Aromatic compounds can have rings that share a set of carbon atoms (fused rings)

Compounds from fused benzene or aromatic heterocyclic rings are themselves aromatic

Naphthalene: $4n+2=10$, $n=2$ note: Hückels rule is strictly for monocyclic aromatic compound, its application to polycyclic aromatic compounds is tenuous.

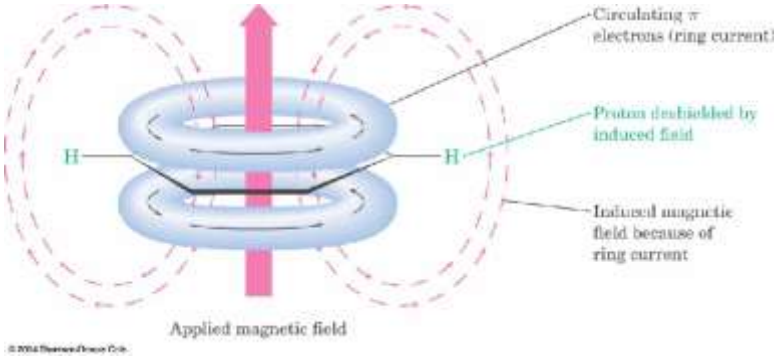


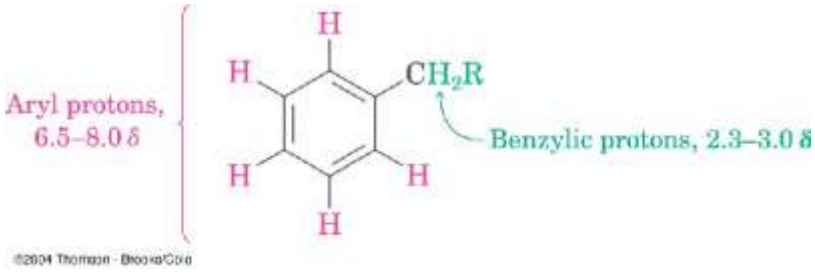
11. Ring Current:

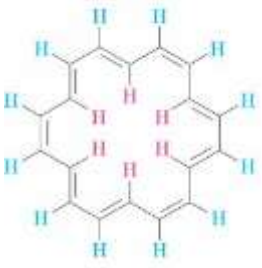
Aromatic ring oriented perpendicular to a strong magnetic field, delocalized π electrons producing a small local magnetic field

Opposes applied field in middle of ring but *reinforces* applied field outside of ring

Results in outside H's resonance at lower field



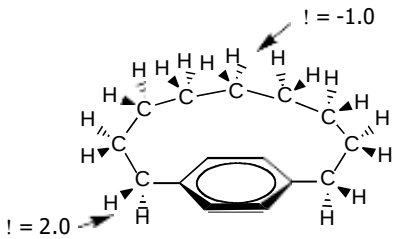




[18]Annulene

Inside H: −3.0 δ

Outside H: 9.3 δ



Thank You

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