AROMATICITY

SEM- II

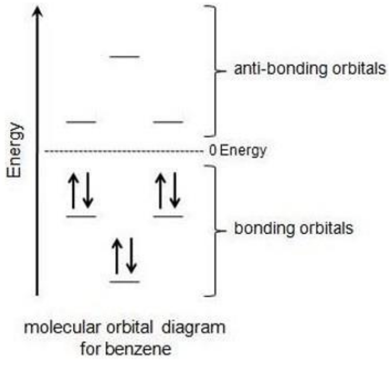
In 1931, German chemist and physicist Sir Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties .This is a very popular and useful rule to identify aromaticity in monocyclic conjugated compound. According to which a planar monocyclic conjugated system having (4n +2) delocalised (where, n = 0, 1, 2, ...) electrons are known as aromatic compound . For example: Benzene, Naphthalene, Furan, Pyrrole etc.

Criteria for Aromaticity

1) The molecule is cyclic (a ring of atoms)
2) The molecule is planar (all atoms in the molecule lie in the same plane)
3) The molecule is fully conjugated (p orbitals at every atom in the ring)
4) The molecule has 4n+2 π electrons (n=0 or any positive integer

Why 4n+2π Electrons?

According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. - This is true of aromatic compounds, meaning they are quite stable. - With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n), leaving all bonding orbitals filled and no anti-bonding orbitals occupied. This gives a total of 4n+2π electrons. - As for example: Benzene has 6π electrons. Its first 2π electrons fill the lowest energy orbital, and it has 4π electrons remaining. These 4 fill in the orbitals of the succeeding energy level.



The criteria for Antiaromaticity are as follows:

1) The molecule must be cyclic and completely conjugated
2) The molecule must be planar.
3) The molecule must have a complete conjugated π-electron system within the ring.
4) The molecule must have 4n π-electrons where n is any integer within the conjugated π-system [positive integer (n = 0,1,2,3 etc.)]

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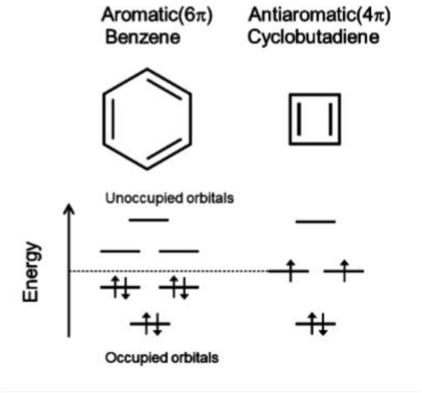


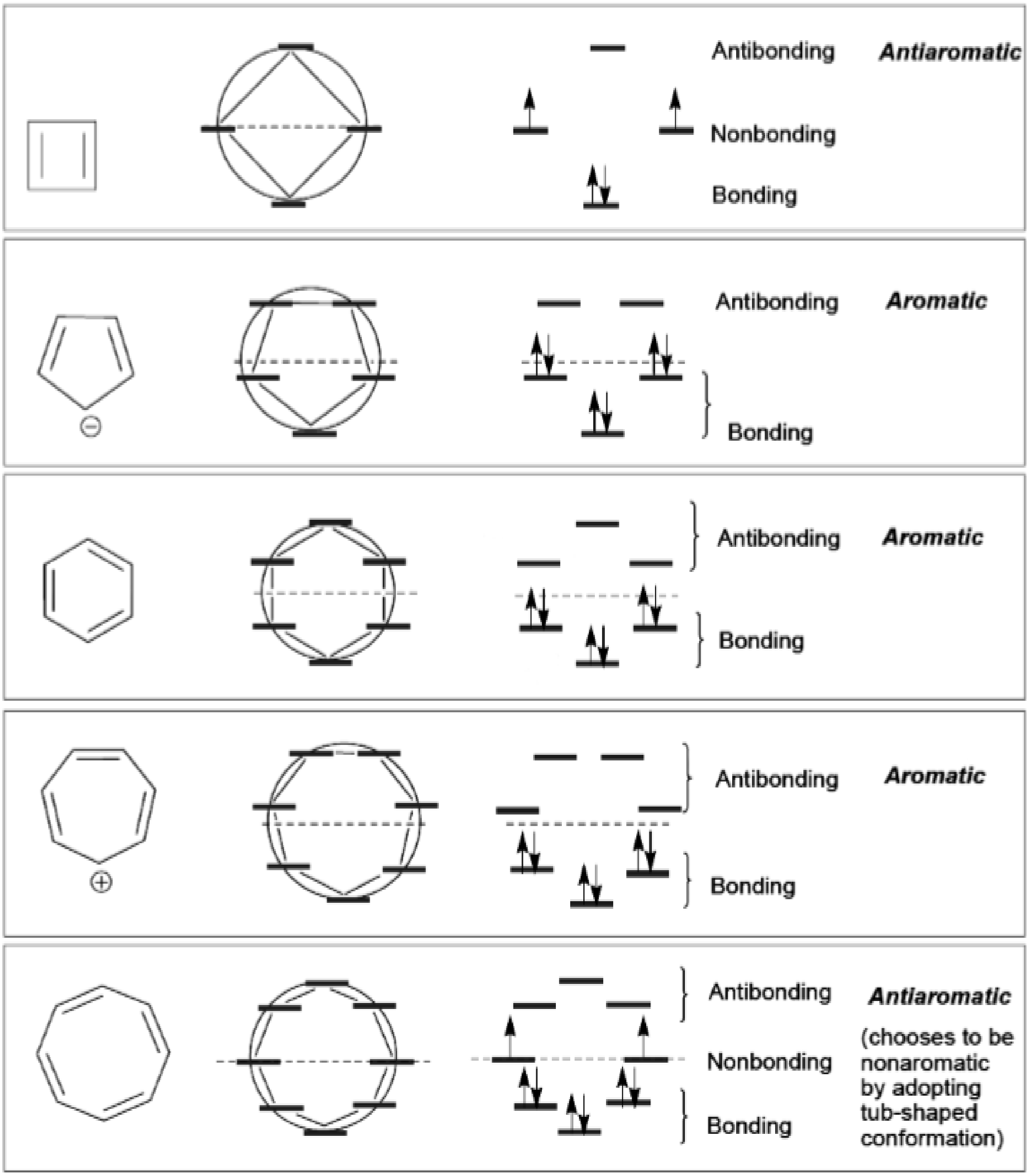
Whether or not a compound is aromatic may be determined by the so-called **Frost circle** An easy way to describe the molecular orbitals of a small conjugated ring is to draw the Frost Circle.

To do this , following steps are followed

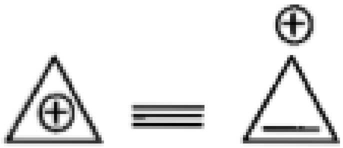
1. Draw a circle
2. Connect the carbon atoms to the circle such that one is always pointed at the bottom
3. Draw a horizontal line at each carbon this represent the pi bond molecular orbitals.
4. Draw a dotted line through the middle of the circle – this is the boundary between bonding and antibonding orbital

Any pi electrons occupying an orbital below the line are in a bonding orbital are STABLE

Any pi electrons on the line or above the line are in non-bonding & anti-bonding orbital and are UNSTABLE.

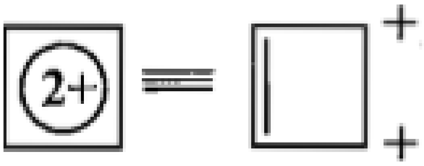

Antibonding
Nonbonding
Bonding
Antiaromatic
Antibonding
Bonding
Aromatic
Antibonding
Bonding
Aromatic
Antibonding
Bonding
Aromatic
Antibonding
Nonbonding
Bonding
Antiaromatic
(chooses to be nonaromatic by adopting tub-shaped conformation)

2π-electron system



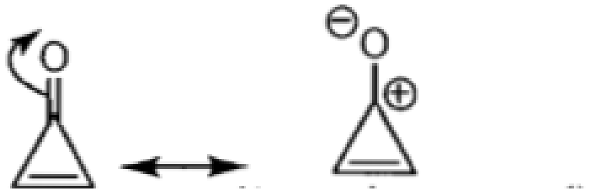
Cyclopropenyl cation

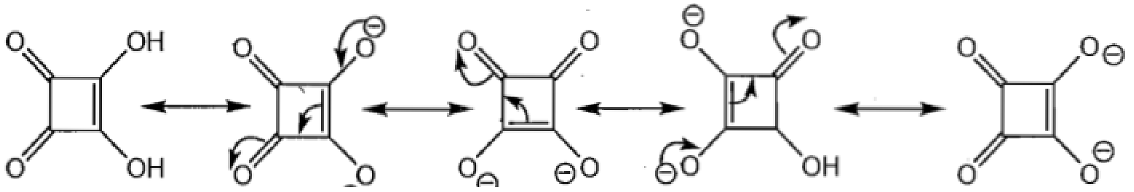
(Aromatic)



Cyclobutadienyl dication

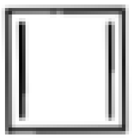
(Aromatic)



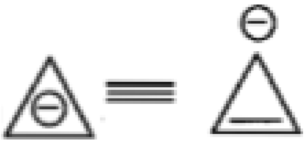


Aromatic

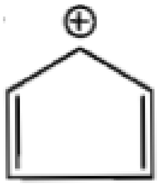
4π-electron system(anti- aromatic)



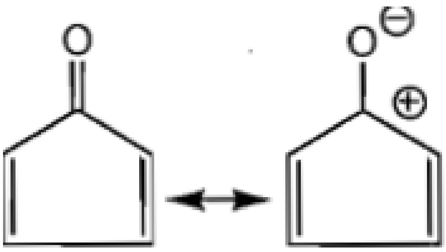
Cyclobutadiene



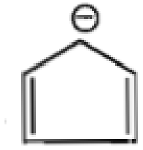
cyclopropenyl anion



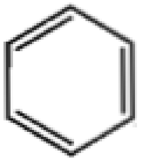
cyclopentadienyl cation



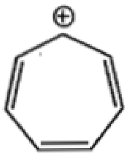
6π-electron system (aromatic)



Cyclopentadienyl anion

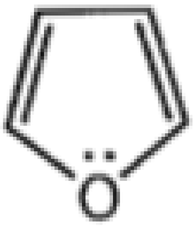


Benzene(aromatic)



cycloheptatrienyl cation

tropylium ion (aromatic)

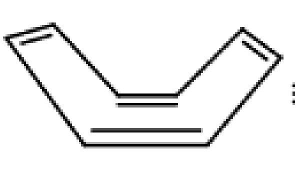


furan(aromatic)

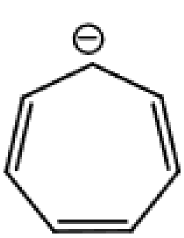
pyridine aromatic

pyrrole(aromatic)

8π-electron system

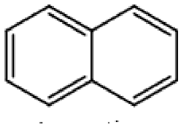


COT(tub shaped)

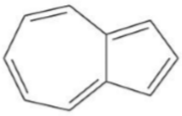


cycloheptatrienyi anion(anti aromatic)

10 π -electron system

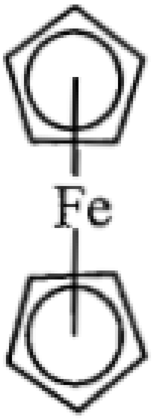


Naphthalene(aromatic)

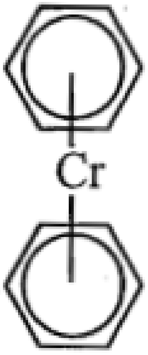


Azulene(aromatic)

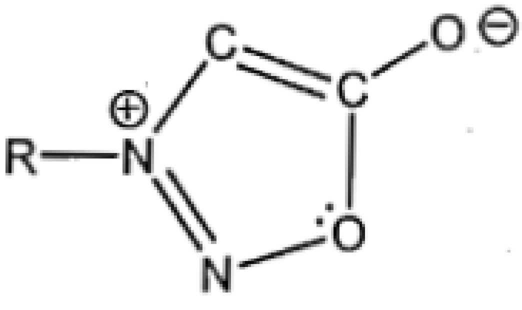
Organometallic aromatic compound



ferrocene

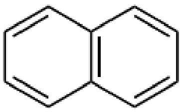


Dibenzene chromium

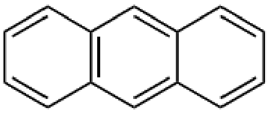


Sydons , meso ionic compound , aromatic

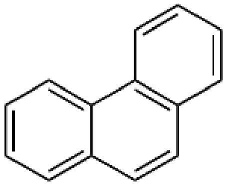
Polycyclic Aromatics



naphthalene



anthracene



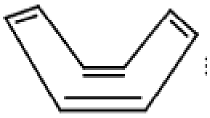
phenanthrene

Non aromatic

1.Cyclic

2.non planar(due to sp^3 hybridised atom or due to distorted planarity)

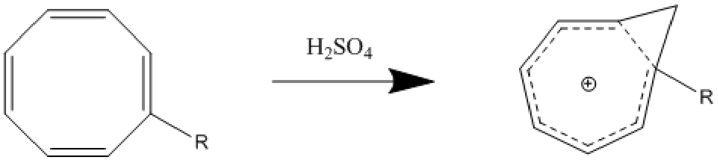
3.Huckel rule not applied



COT(tub shaped)

Homoaromaticity –

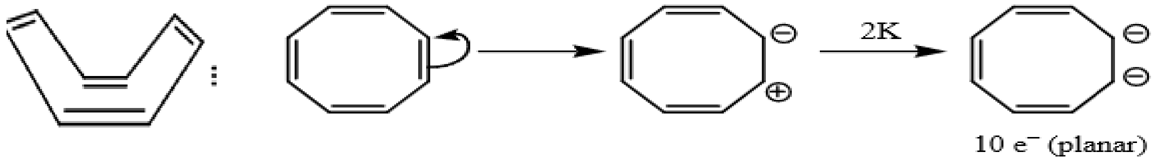
Homoaromaticity, in organic chemistry, refers to a special case of aromaticity in which conjugation is interrupted by a single sp3 hybridised carbon atom. - That means if a stabilized cyclic conjugated system (4n+2 e s) can be formed by bypassing one saturated atom, that lead to Homoaromaticity.



1-substituted homotropenylium cation

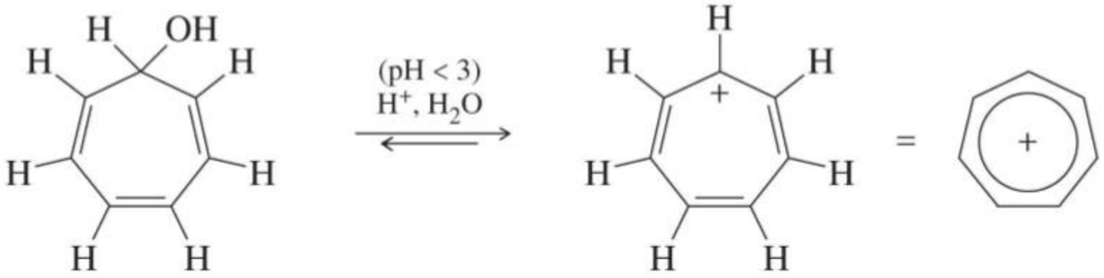
R = methyl, phenyl

Cyclooctatetraene Dianion



COT has tub shape and it is not planar, therefore it is non aromatic and not anti aromatic

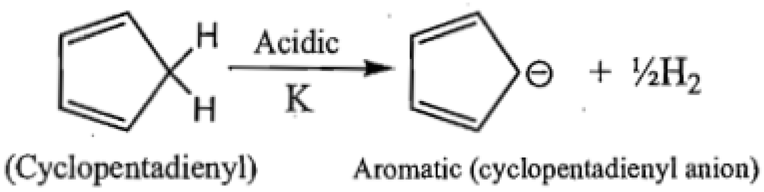
Reaction of cyclooctatetraene with potassium metal (a good electron donor), easily generates an aromatic dianion. The dianion has a planar, regular octagonal structure.



tropylium ion, six pi electrons

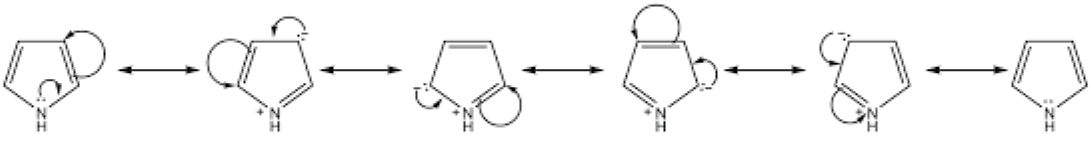
cycloheptatrienyl cation has 6π electrons, aromatic .Therefore it is easily formed, and is often called the tropylium ion.

Cyclopentadienyl Ions



Cyclopentadienyl Ions are acidic in nature due to aromatic character

Why is pyridine more basic than pyrrole ?

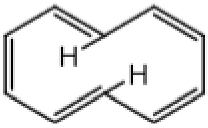


In case of pyrrole , the lone of electrons on nitrogen atom takes part in the resonance with the pi electron of pyrrole ring, through which pyrrole attain the Huckel's rule of aromaticity .

As a result, the availability of electrons for donation is not easy , which decrease the basicity of pyrrole.

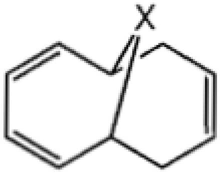
Because, pyridine contains three alternating pi bond . So resonance is not possible. In addition to , the p-orbital of carbon atom is mutually perpendicular to the lobe of p-electron orbital of nitrogen atom **.**

Therefore , it is impossible to occur resonance between p-orbital of carbon atom and p-orbital of nitrogen atom. Hence ,the lone pair on ‘N’-atom is available for donation to the electron deficient element, ion or group.



Not aromatic

Although it is cyclic , conjugated and has 10 electron, it is not flat due to the repulsion between the hydrogens that arise when it is flat conformation. So it is not aromatic.

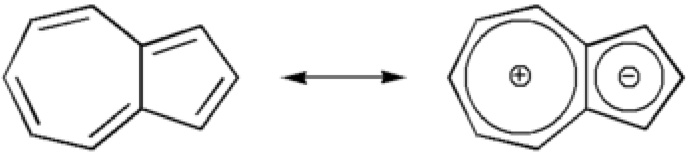


Aromatic

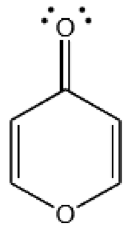
However replacing the hydrogens with the bonds to a bridging carbon allows all the c-c bond in the same plane. Hence it is aromatic

AZULENE

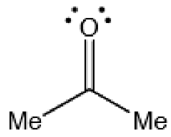
Dipole moment of azulene 1.08 D, in contrast with naphthalene, which has a dipole moment of zero. This polarity can be explained by regarding azulene as the fusion of a 6 π-electron cyclopentadienyl anion and a 6 π-electron tropylium cation: one electron from the seven-membered ring is transferred to the five-membered ring to give each ring aromatic stability by Hückel's rule. Reactivity studies confirm that seven-membered ring is electrophilic and the five-membered ring is nucleophilic.



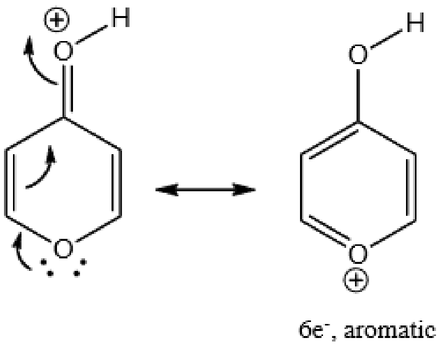
Which of the following compounds is more basic ?



4-pyrone

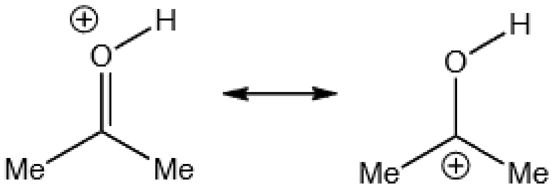


acetone



more basic

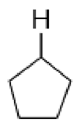
resonance structures stabilize the protonated form; the aromatic resonance structure is particularly stable

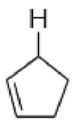


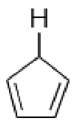
less basic

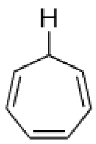
only one resonance structure stabilizes the protonated form

Problem : The following have enormous differences in acidity. (10-20, 10-42, 10-50, 10-56)

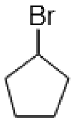


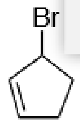


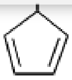


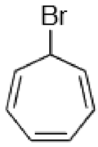


Problem : The following substrates have widely differing reactivity toward H_2O solvolyis . Rank the reactivity

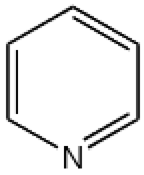




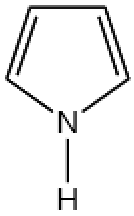




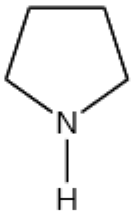
Problem : Rank the following compounds from most to least basic.



pyridine



pyrole



pyrolidine

Problem. Why does the following compound have a large molecular dipole?