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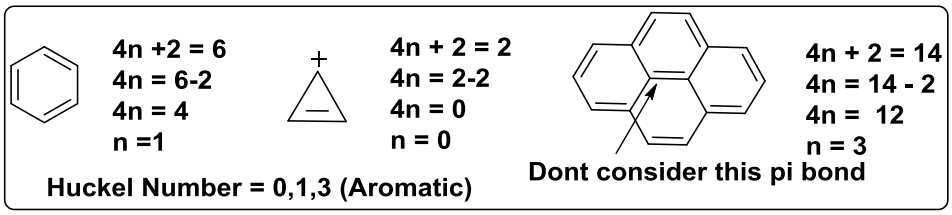
Aromaticity notes | Pritesh Sharma Notes

Aromaticity.

The name 'aromatic' was originated from the characteristic odor or 'aroma' of Benzene like compounds, chemists now have a completely different method of deciding whether a compound is aromatic or not. Based on the analysis of a number of compounds with unusual resonance stabilization energies, the following characteristics have been accepted as **criteria for aromaticity.**

1. Cyclic, containing some number of conjugated π bond, planar with uninterrupted cloud of π electrons above and below the plane of the ring.
2. Each atom in the ring must have an unhybridized p orbital. (The ring atoms are usually sp2 hybridized or occasionally sp hybridized.)
3. The Chemist Erich Huckel was the first one to recognize that an aromatic compound must have an odd number of pairs of π electrons in cyclic structure (1, 3, 5, 7), which can mathematically be written as 4n+2 (n = 0,1,2,3 etc.).



4. Delocalization of the pi electrons over the ring must lower the electronic energy and increases the stability.
5. Aromatic compounds will have all occupied bonding molecular orbitals completely filled and the relative energies of p molecular orbitals in planar cyclic conjugated systems can be determined by a simplified approach developed by A. A. frost in 1953 (FROST CIRCLE).
6. Aromatic systems exhibit a diamagnetic ring current, which causes protons on the outside of the ring to be shifted downfield while any inner protons are shifted upfield (eg-18-annulene), in sharp contrast to a paramagnetic ring current, which causes shifts in the opposite directions. Compounds that sustain a diamagnetic ring current are called diatropic; and are prevalent in 2, 6, 10, 14, 18… electron system.
7. Commonly it shows electrophilic substitution reaction which is a characteristic of saturated compounds and not electrophilic addition reaction which is characteristic of

unsaturated compound and hence it will not decolorize bromine water solution and Baeyer's reagent (dil KMnO4).

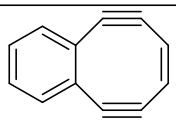
➢ Criteria for Antiaromatic Compounds.

1. Cyclic, containing some number of conjugated π bond, planar with uninterrupted cloud of π electrons above and below the plane of the ring.
2. Each atom in the ring must have an unhybridized p orbital. (The ring atoms are usually sp2 hybridized or occasionally sp hybridized.)
3. Delocalization of the pi electrons over the ring increases the electronic energy and decreases the stability.
4. According to Huckel Antiaromatic compound must have an even number of pairs of π electrons in cyclic structure (2, 4, 6, 8) which can mathematically be written as 4n (n = 1,2,3 etc.).

4n = 4
n = 1

4n = 8
n =2

Considered Planar
6 Pi electron
1 Pair of electrons
Total = 8 electrons



4n = 12
n = 3

In case of Triple bond
count only 2 pi electron per triple bond.

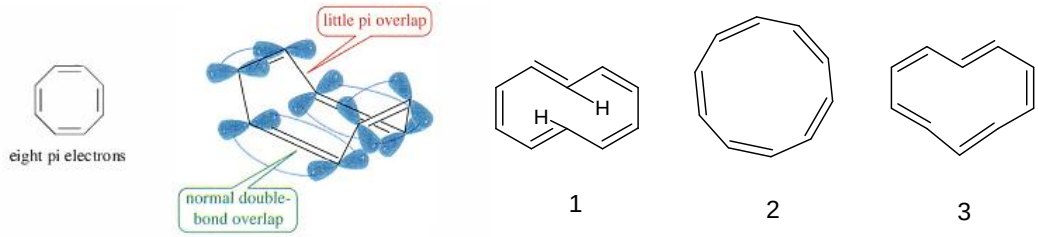
Huckel Number = 1,2,3 (Antiaromatic)

5. Aromatic structures are more stable than their open-chain counterparts. For eg, benzene is more stable than 1, 3, 5-hexatriene. Cyclobutadiene meets the first two criteria for a continuous ring of overlapping p orbitals, but delocalization of the pi electrons increases the electronic energy. Cyclobutadiene is less stable than its open-chain counterpart (l, 3-butadiene), and it is antiaromatic.
6. Antiaromatic systems exhibit a paramagnetic ring current, which causes protons on the outside of the ring to be shifted upfield while any inner protons are shifted downfield (eg-12-annulene), in sharp contrast to a diamagnetic ring current, which causes shifts in the opposite directions. Compounds that sustain a paramagnetic ring current are called paratropic; and are prevalent in 4, 8, 12, 16, 20… electron system.

7. Commonly it gives addition reaction or get dimerize/polymerize at room temperature. Most of the antiaromatic compounds are stable at cryogenic temperature only.

➢ **Criteria for Nonaromatic compound.**

1. A cyclic compound that does not have a continuous, overlapping ring of p orbitals cannot be aromatic or antiaromatic. It is said to be nonaromatic, nonplanar or aliphatic.
2. Its electronic energy is almost similar to its openchain counterpart. Eg - 1,3 Cyclohexadiene is as stable as cis, cis - 2,4 hexadiene.
3. Cyclooctatetraene is [8] annulene, with eight pi electrons (four double bonds) in the classical structure. It is a 4N sy stem, with N = 2. If Huckel 's rule were applied to cyclooctatetraene, it would predict antiaromaticity. However, cyclooctatetraene is a stable hydrocarbon with a boiling point of 153 °C. It does not show the high reactivity associ ated with antiaromaticity, yet it is not aromatic either. Its reactions are typical of alkenes.
4. Cyclooctatetraene would be antiaromatic if Huckel 's rule applied, so the conjugation of its double bonds is energetically unf avorable. Remember that Huckel's rule applies to a compound only if there is a continuous ring of overlapping p orbitals,usually in a planar system. Cyclooctatetraene is more flex ible then cyclobutadiene and it assumes a nonplanar 'tub shaped' conformation that avoids most of the overlap between pi bonds. Huckels rule simply not applicable for non planar structure.



5. There are three geometrically possible isomers of [10] annulene: the all-cis (2), the mono-trans(3), and the cis–trans–cis–cis–trans(1). If Huckel's rule applies, they should be planar. But it is far from obvious that the molecules would adopt a planar shape, since they must overcome considerable strain to do so. For a regular decagon (2) the angles would have to be 144 , considerably larger than the 120 required for sp2 angles. Some of

this strain would also be present in 3, but this kind of strain is eliminated in (1) since all the angles are 120 . However, it was pointed out by Mislow that the hydrogens in the 1 and 6 positions should interfere with each other and force the molecule out of planarity.

- **Criteria for Homo-aromatic compounds.**

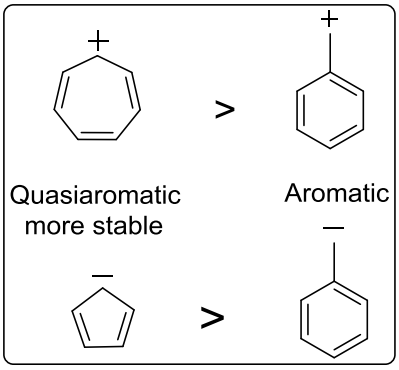
1. Compound that contain one or more sp3-hybridized C-atom in a conjugate cyclic ring but sp3-hybridized carbon atom are force to lie almost vertically above the plane (out of the plane) of the aromatic system for effective orbital overlapping in a closed loop known as homoaromatic compounds.
2. Homoaromatic compound involves delocalization of Pi electron cloud bypassing sp3 hybridized atom.

3. When cyclooctatetraene is dissolved in concentrated H_2SO_4, a proton adds to one of the double bonds to form the homotropylium ion. In this species, an aromatic sextet is spread over seven carbons, as in the tropylium ion. The eighth carbon is a sp3 carbon and so cannot take part in the aromaticity. The ^{1}H-NMR spectra show the presence of a diatropic ring current: Hb is found at -0.3 ppm; Ha at 5.1 ppm; H1 and H7 at 6.4 ppm; H2–H6 at 8.5 ppm. This ion is an example of a homoaromatic compound, which may be defined as a compound that contains one or more sp3-hybridized carbon atoms in an otherwise a conjugated cycle. Hb is directly above the aromatic sextet, and so is shifted far upfield in the NMR. All homoaromatic compounds so far discovered are ions, and it is questionable as to whether homoaromatic character can exist in uncharged systems. Homoaromatic ions of 2 and 10 electrons are also known.
4. Cyclobutenyl cation is the homoaromatic analog of cyclopropenium cation. This cation can be prepared from 3-acetoxy cyclobutene in superacid condition.

- **Criteria for Quasiaromatic compounds.**

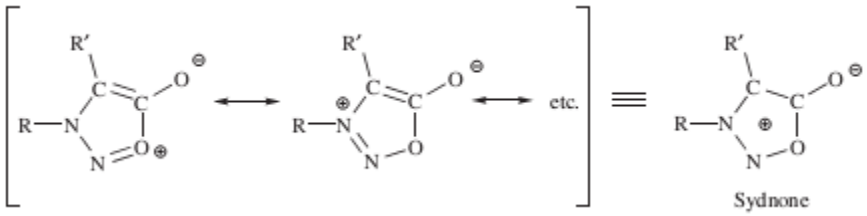
1. Aromatic compounds in which +ve or -ve charge is part of Huckle's rule or aromaticity, i.e., the charge is present in the ring, are called quasi aromatic compounds or most preferably quasi aromatic ions.

2. Thus, all quasi aromatic ions are aromatic compounds but the reverse is not true. Quasiaromatic compound are highly stable.



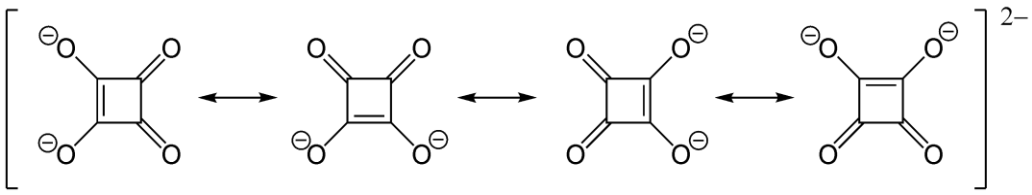
- **Criteria for Mesoionic compounds**.

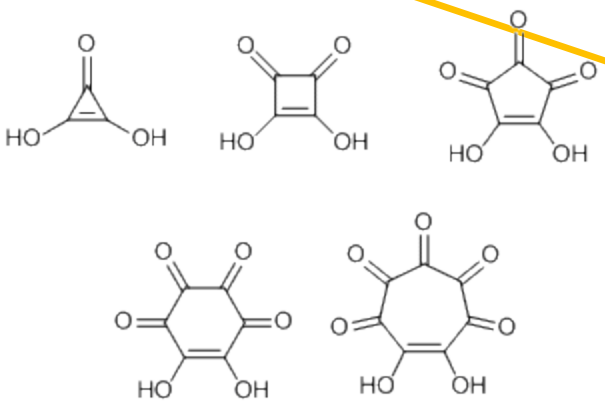
1. These compounds cannot be satisfactorily represented by Lewis structures not involving charge separation. Most of them contain five-membered rings. The most common are the sydnones, stable aromatic compounds that undergo aromatic substitution when R is hydrogen.



The Dianion of Squaric Acid/ Oxocarbonic acid.

The stability of this system is illustrated by the fact that the pK1 of Squaric acid is 1.5 and the pK2 is 3.5, which means that even the second proton is given up much more readily than the proton of acetic acid, for example. The analogous three-, five-, and six-membered ring compounds are also known.



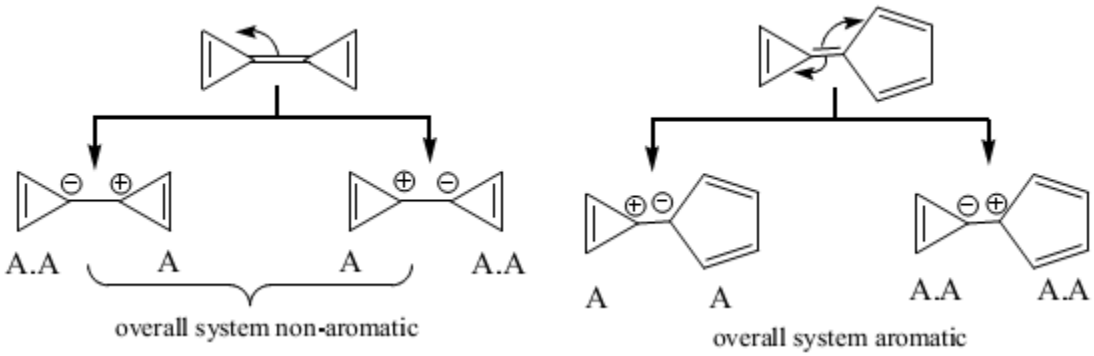


Oxocarbonic acid.

Aromatic Alltropes of Carbon –

Graphite and Fullerene are aromatic and confirmed from ^{13}C-NMR. Molecular-orbital calculations showed that ‘‘fullerene aromaticity lies within 2 kcal mol (8.4 kJ/ mol) per carbon of a hypothetical ball of rolled up graphite.

Fused Aromatic compounds.



Such fused fulvalene/calicene type rings are either aromatic or nonaromatic but never an antiaromatic. Need to polarize/displacement of the common double bond between two rings and check aromatic nature, if both rings are aromatic then overall molecule is aromatic. If even one ring is non aromatic/antiaromatic then overall molecule is nonaromatic. If fused aromatic compound is overall aromatic then there is low rotational barrier for center double bond and such molecule show free rotation compare to nonaromatic fused ring compound.

Stability Order.

Aromatic > Homoaromatic > Nonaromatic > Antiaromatic.

Energy Order.

Antiaromatic > Nonaromatic > Homoaromatic > Aromatic.

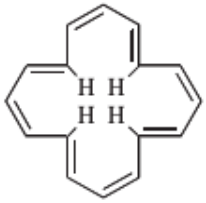
Annulene.

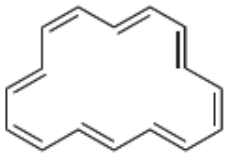
1 Hydrocarbons containing a single ring with alternating double and single bonds are Called annulene.

2. To name an annulene, indicate the number of atoms in the ring in brackets and add the word annulene. Thus, benzene is [6]-annulene. Both [14]-annulene and [18]-annulene are cyclic, planar, completely conjugated molecules that follow Hückel's rule, and so they are aromatic.[10] annulene fits the Huckel rule criteria but not planar so considered nonaromatic (already discussed above). [16] Annulene fits the criteria for antiaromatic but they are nonplanar so its nonaromatic.

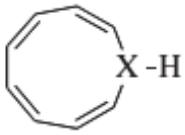
[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic

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

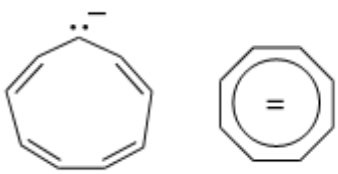




[16] Annulene

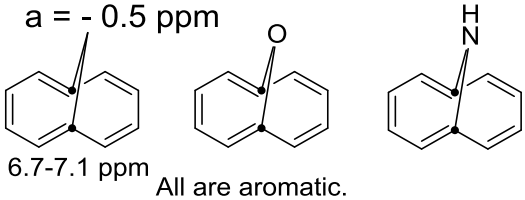


X = N - Aromatic.
X = O - Nonaromatic
X= CH2- Nonaromatic.

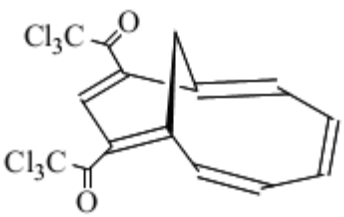


Aromatic

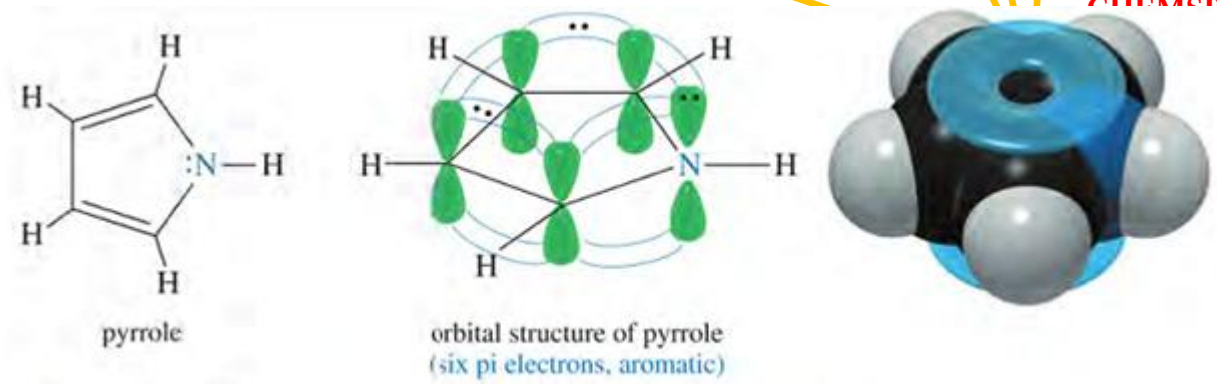
3. Bridged Annulene.



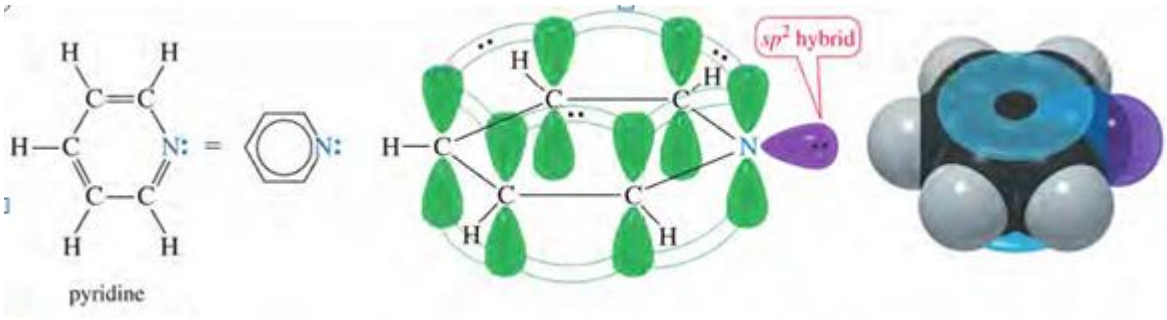
All are aromatic.



Aromatic.

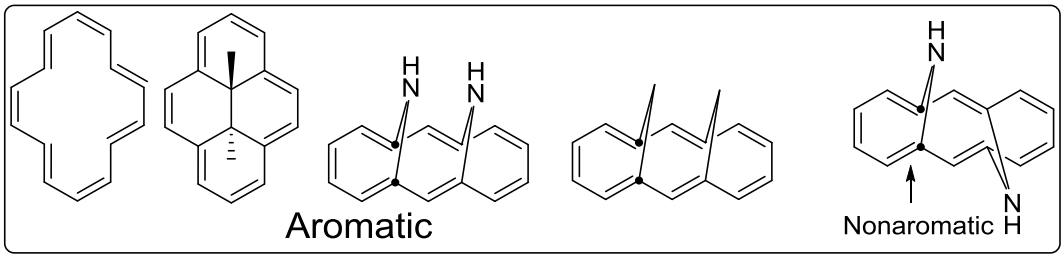


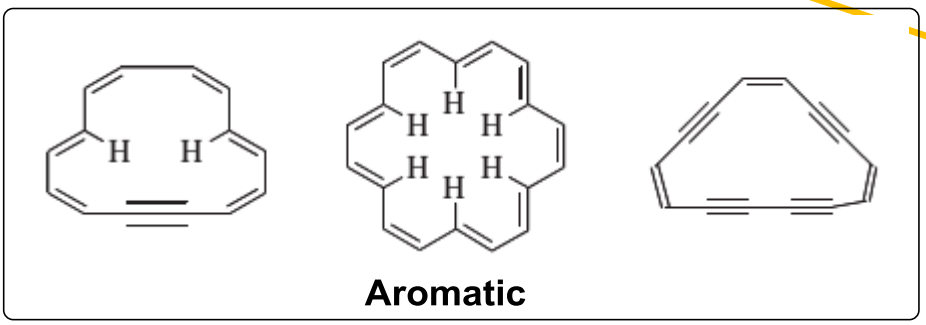
The pi bonding structure of Pyridine has six delocalized electrons in its cyclic pi system. The two nonbonding electrons on nitrogen in an sp^2 orbital, and they do not interact with pi electrons of the ring



The pi bonding structure of pyrrole. The pyrrole nitrogen atom is sp^2 hybridised with a lone pair of electron in p orbital. This p orbital overlaps with the p orbital of the carbon atoms to form a continuous ring. Counting the four electrons of the double bond

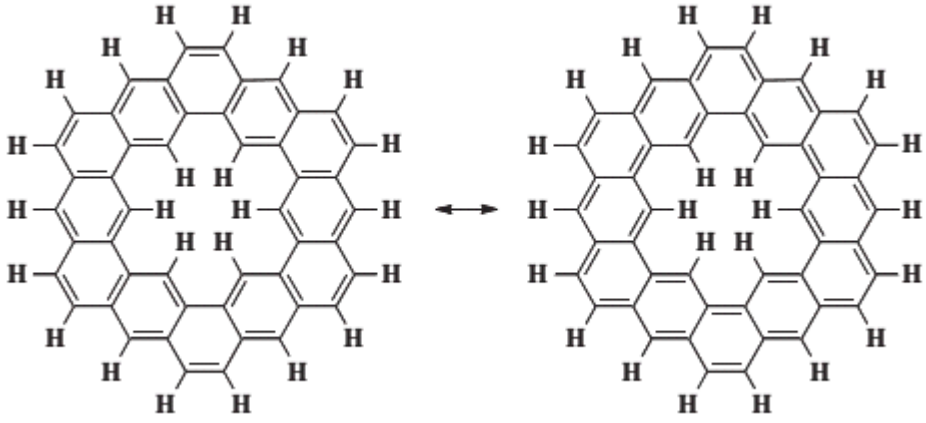
Mixed Examples.



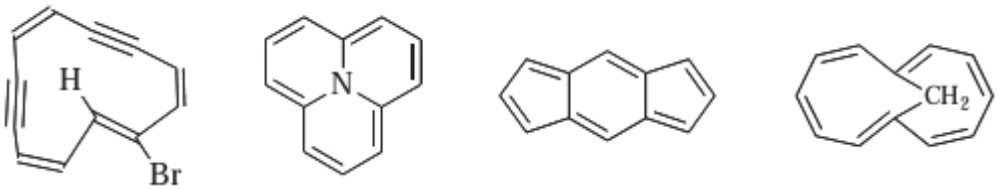


Aromatic

Homoaromatic



Aromatic.



Antiaromatic.

twist

boat

heart

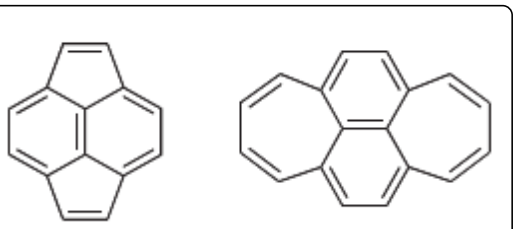
Z,E,Z,Z,E

E,Z,Z,Z,Z–

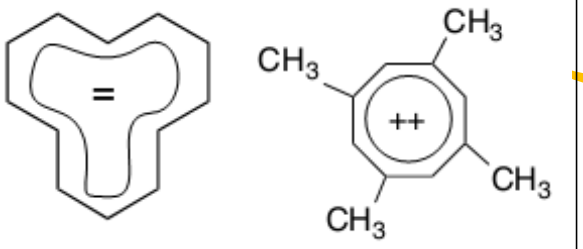
Z,Z,Z,Z,Z–

E,Z,Z,Z,Z-

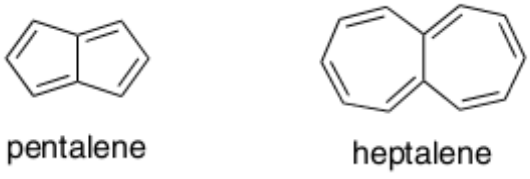
Nonaromatic.



Antiaromatic.

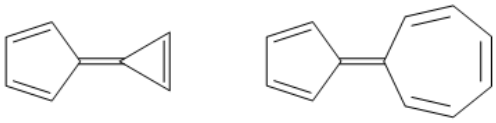


Aromatic



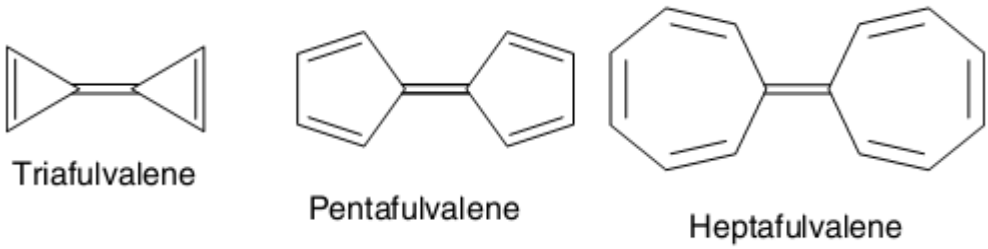
pentalene heptalene

Antiaromatic



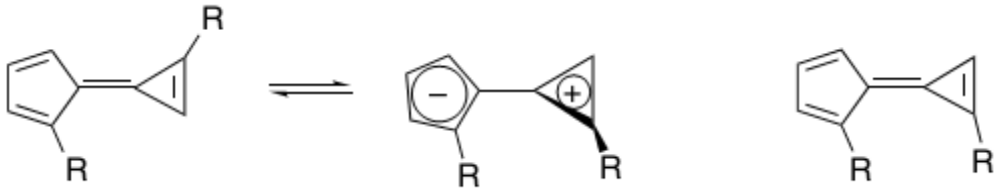
Calicene Cyclopentadienylidene-cycloheptatriene

Aromatic

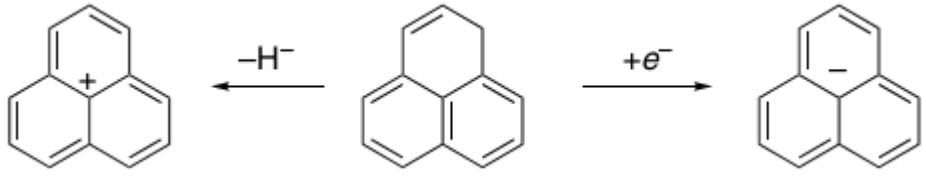


Triafulvalene Pentafulvalene Heptafulvalene

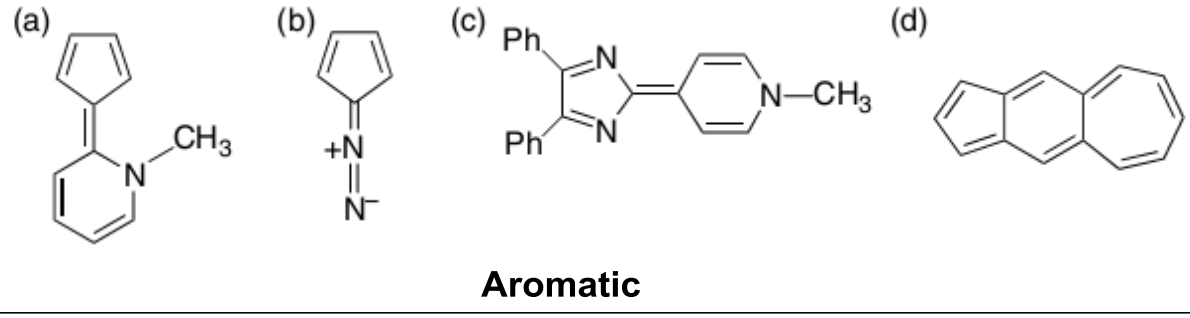
Nonaromatic



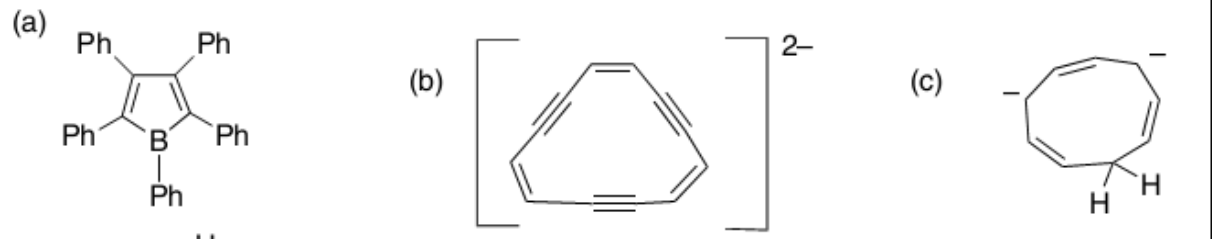
Due to Aromatic nature, cis-trans isomerization possible because reduced barrier to rotation around fused double bond.

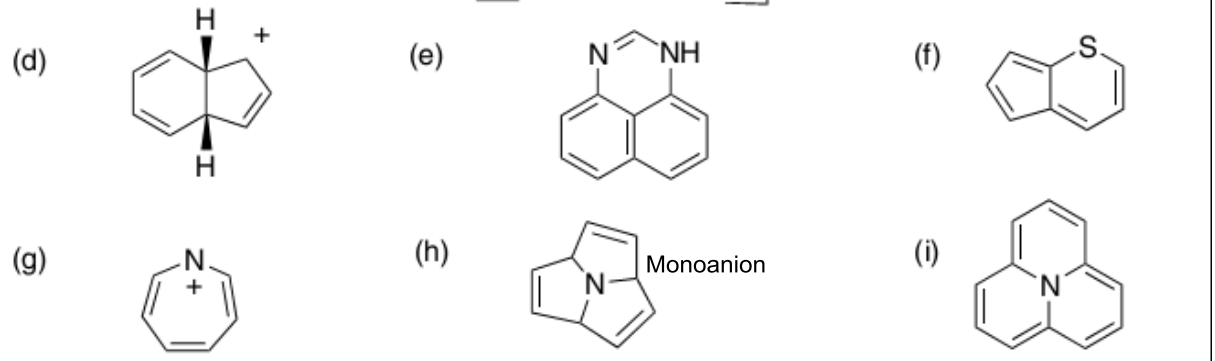


Aromatic Phenalene Nonaromatic Aromatic

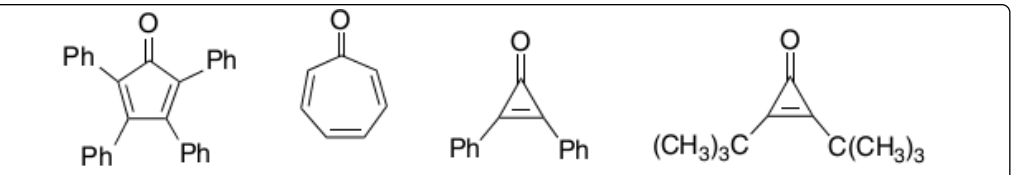


Aromatic

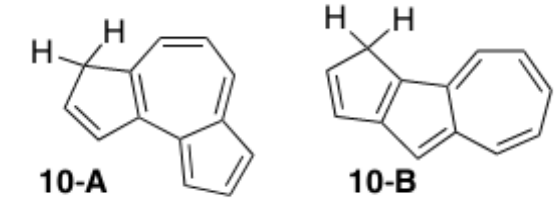




Aromatic - b, e, f, g, h **Antiaromatic-a, i**
Nonaromatic-c **Homoaromatic-d**



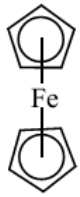
Basicity of Oxygen - More the basic, more is the stable carbocation after polarizatio of ketonic double bond due to aromatisation, more is the equilibrium constant



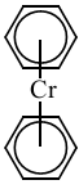
A is more acidic than B.

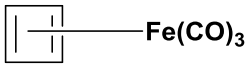
Organometallic Aromatic compound.

Ferrocence



Dibenzene chromium





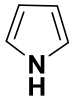
4 Pi electrons
2 electrons from Iron

Resonance energy of some aromatic compound.

36 kcal/mol

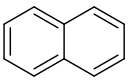
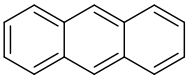
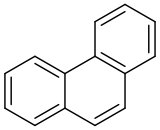
32 kcal/mol

29 kcal/mol

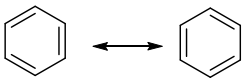


21 kcal/mol

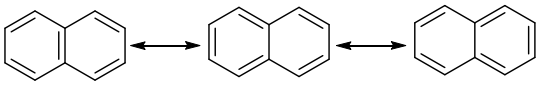
16 kcal/mol

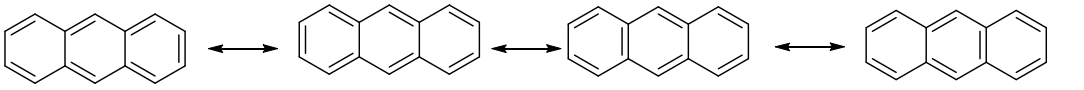
				
Resonance energy -	**36 kcal**	**61 kcal**	**83 kcal**	**91 kcal**
Resonance energy / No. of Cyclic ring	**36 / 1**	**61 / 2**	**83 / 3**	**91 / 3**
	36 / ring	**30.5 / ring**	**27.7 / ring**	**30.3 / ring**

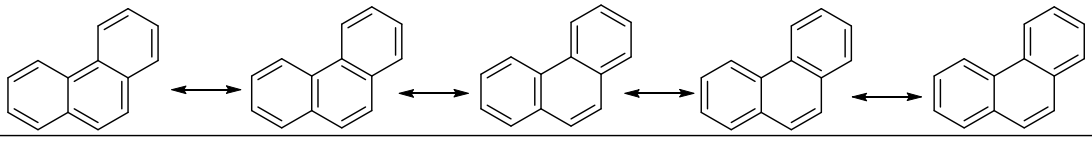
Higher the resonance energy per ring higher is the aromaticity of molecule.
Benzene > Naphthalene > Phenanthrene > Anthracene.

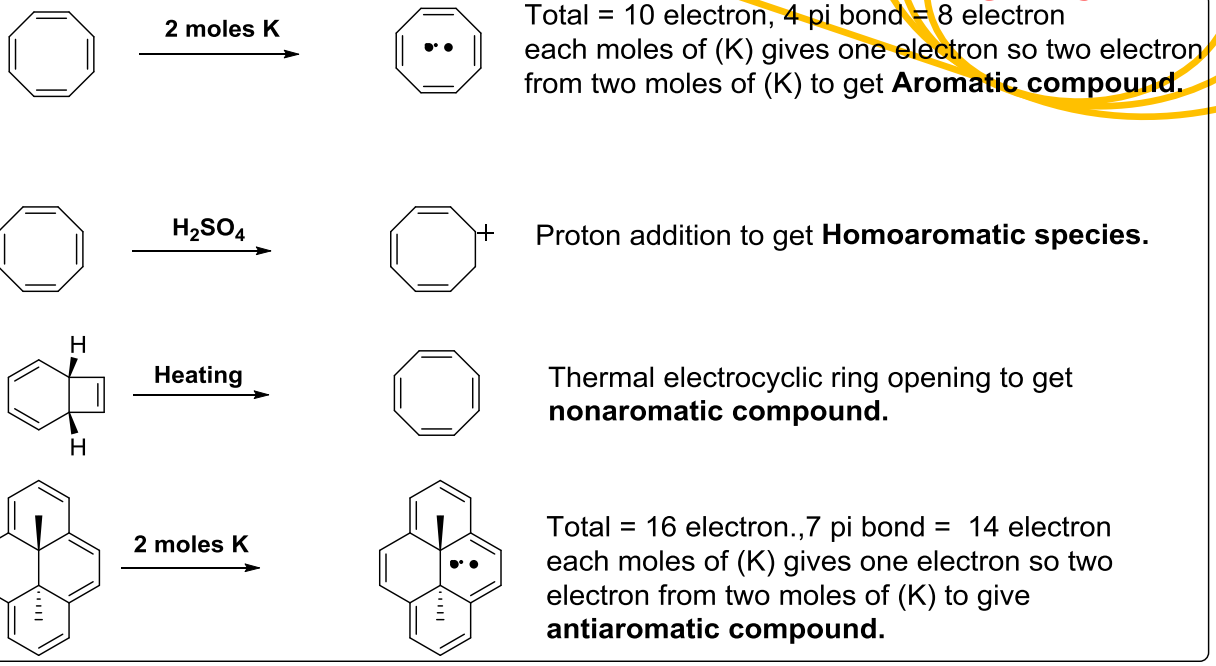


Resonating Structures

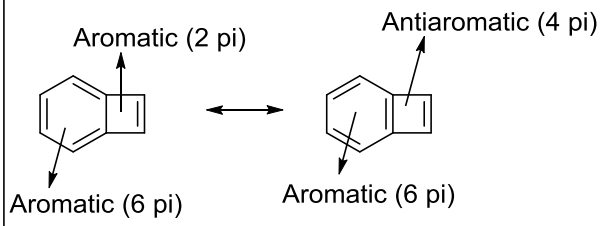






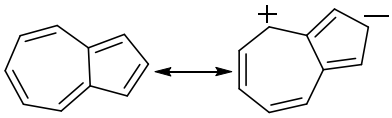


Benzocyclobutadiene.



According to Huckel rule its Antiaromatic if consider close loop of 8 pi electron.

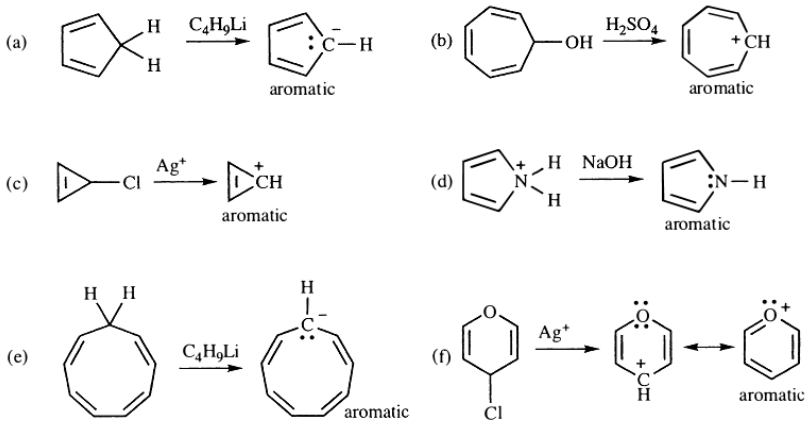
Azulene

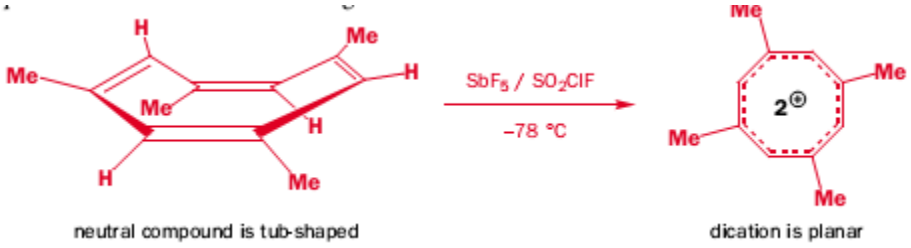


(Non benzenoid Aromatic compound with Dipole moment.

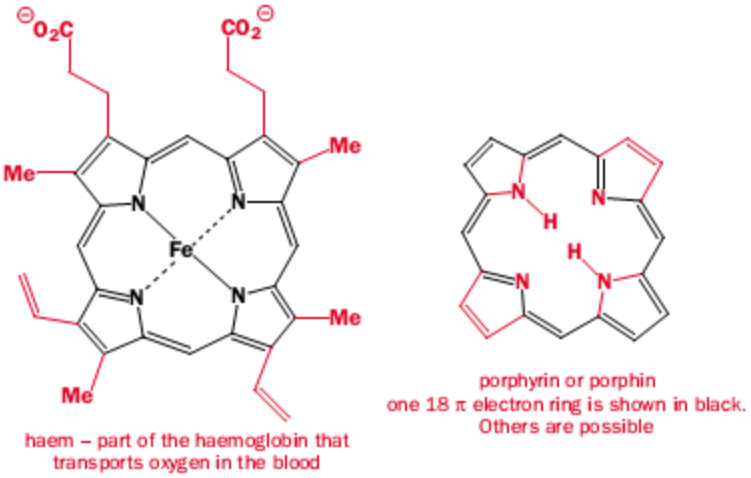
➢ Some Additional Information

Ways in which we can prepare Aromatic Compound



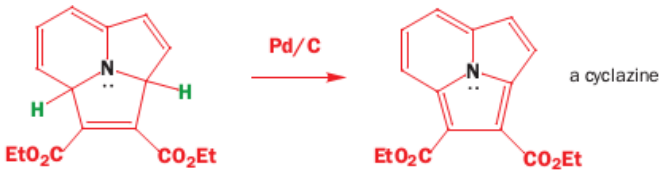


Aromatic



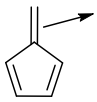
Aromatic

Nonaromatic

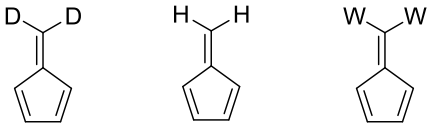


Aromatic

Fulvenes type.



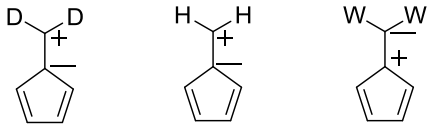
Exocyclic double bond not easily polarizable.

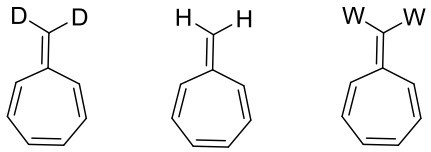


D = Donor group

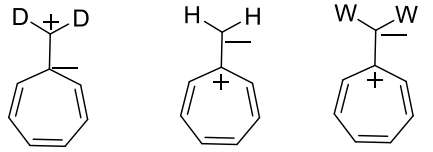
W = Withdrawing group

Aromaticity decreases





Aromaticity increase

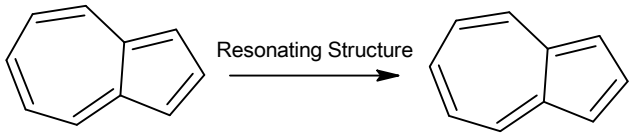


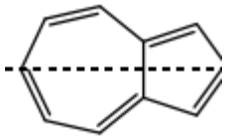
➢ Craig's Rule

This rule is applicable for polycyclic non benzenoid compounds. If molecule contain C2 Axis then count total number of double bonds (N) and calculate the value of N-1 which decide aromaticity in compound

If N-1 = odd compound is non aromatic

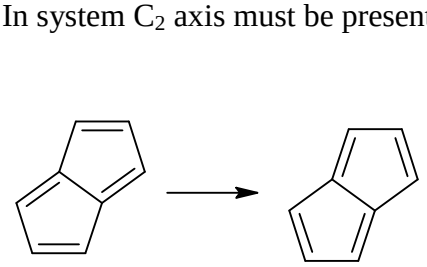
If N-1 = even compound is aromatic





C_2 axis N-1=4π bond aromatic

In system C_2 axis must be present

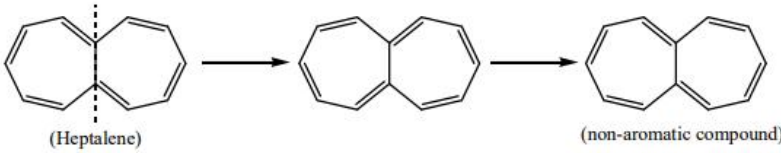


Non-Aromatic

N= 4

N-1= 3 odd, hence compound is non aromatic

N = 4
N–1 = 3, odd. Hence, compound is non-aromatic.



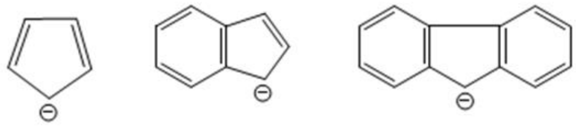
(Heptalene) (non-aromatic compound)

N = 6
N–1 = 5, odd. Hence compound is non-aromatic.

Pentalene and heptalene is a non-aromatic compound. Since it does not follow craig's rule.
The organic compound which show aromaticity are aromatic in nature or diatropic in nature and the protons (outside the rings) signal always exist away from the TMS (these protons are dishielded protons)

Annelation effect :

Each ring in fused system give the part of the aromaticity to the adjacent ring called **annelation effect**.

e.g. 

- Number of benzene ring increases
- Aromaticity decreases

TEST YOURSELF

1. Among the given molecules, identify Aromatic, Anti aromatic and