Huckels rule :⇒

Planar, monocyclic, completely conjugated hydrocarbons would be aromatic when the ring contains $(4n+2)\ \pi$ electrons, where n is any integer including zero.

Limitations :⇒

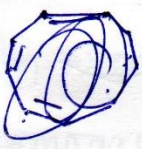
(a) ∴ Monocarboxylic conjugated system

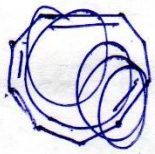
But heterocyclic compds are considered aromatic

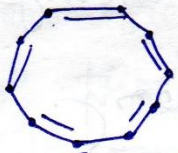
∴ bicyclic, polycyclic aromatic hydrocarbons like naphthalene, phenanthrene are considered to be aromatic

(b) [10] annulene contains $10\ \pi$ e⁻s, but it is not aromatic

Although it contains 10 π electrons, but the molecule cannot adopt the necessary planar conformation If all the double bonds are all cis (a) or one is trans (b), the angle strain is excessive



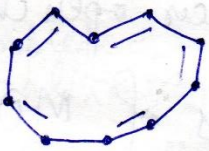




(a)

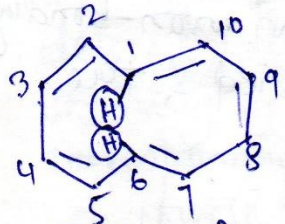
Internal ∠c-c-c = 144°

Suffers from serious angle strain - unstable



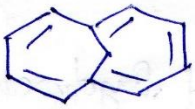
(b)

Suffers from angle strain also.



(c) → Isomer with two trans double bonds cannot be flat because two of the H-atoms interface with each other.

Suffers from strong steric crowding between the two H atoms at C₄ and C₆ - unstable.



Yes, this is aromatic. Because the internal "Hs" in [10]-annulene which prevent it from achieving coplanarity, are replaced by methylene bridge permitting it to be flat.

Since the bridgehead 'C's are still sp^2 hybridised their "p" electrons are available for extended delocalization in a 10-electron system.

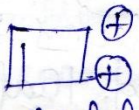
// Antiaromatic ⇒ Planar, conjugated, carbocyclic polyenes that are especially less stable than their open chain analogs are called antiaromatic $4n\pi$ electron system.

// Non-aromatic ⇒ Completely conjugated, non-planar carbocyclic polyenes whose stability are comparable to their open chain analogs are called non-aromatic

Examples of aromatic compd

2π electronic system.

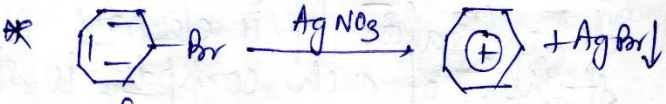
Cyclopropenyl cation
(smallest hydrocarbon that is aromatic)



Cyclobutenyl dication

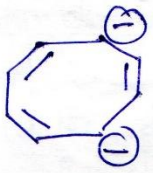
6π e^- system

Tropylium cation
Cycloheptatrienyl cation

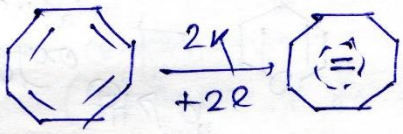


Tropylium bromide gives yellow ppt on treatment with $AgNO_3$

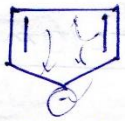
10 π – electrons.



Cyclooctatetraenyl dianion

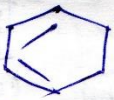


*

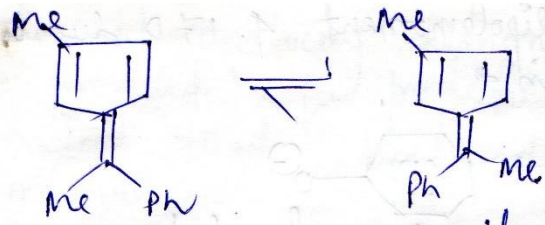


H of $-CH_2-$ of cyclopentadiene is more acidic than 1,3-cyclohexadiene

6 delocalised π e⁻s. This aromaticity stabilizes the cyclopentadienyl anion, causing cyclopentadiene to be much more acidic.

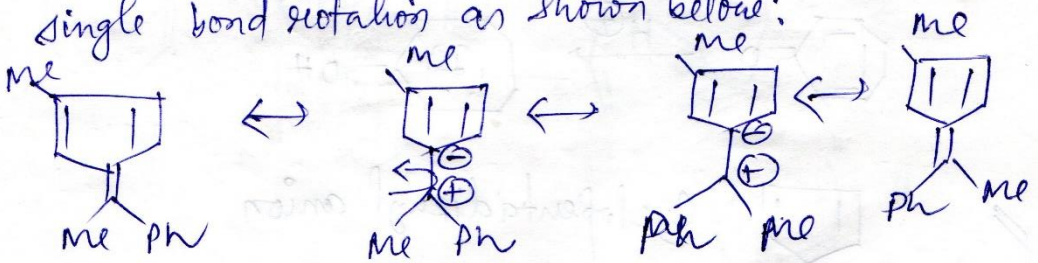


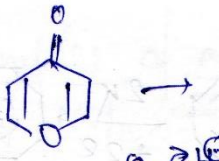
Removal of $H^{\oplus}$ from cyclohexadiene also gives anion with 6 e^- in a ring. However, presence of sp^3 C prevents continuous cyclic overlap & the anion is not aromatic



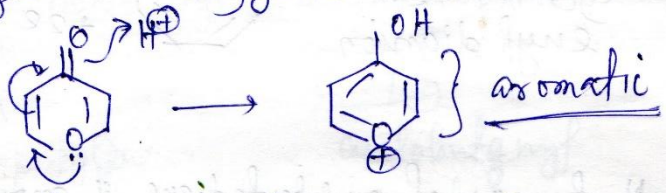
Due to gain in aromaticity, the exocyclic double bond has considerable single bond character.

Two isomers are easily interconvertible by 'C–C' single bond rotation as shown below:





Due to gain in aromaticity, the carbonyl oxygen is more basic

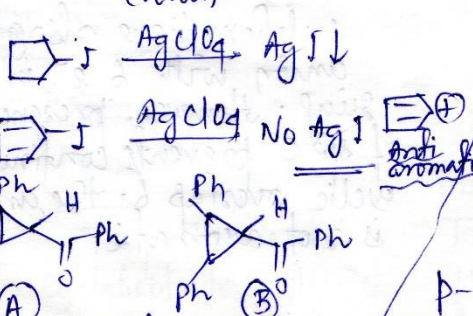


aromatic

Antiaromatic compound.

cyclopentadienyl cation

cyclobutadiene



Ag ClO4 → Ag I ↓

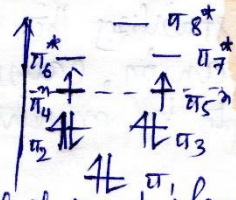
Ag ClO4 → No Ag I

anti aromaticity

(A) H-exchange several thousand time slow than (B)

Non-aromatic compd

cyclooctatetraene.



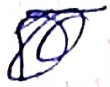
Since non-bonding orbitals are half-filled, it seems to be antiaromatic, energy it is not planar, it is tub shaped

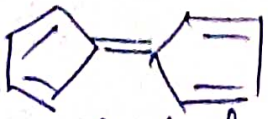
p-orbital of one C=C are not coplanar with that of a neighbouring C=C there can be no effective overlap for delocalization.

Exocyclic double bonds.

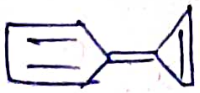
Pentafulvene

Hepta fulvene



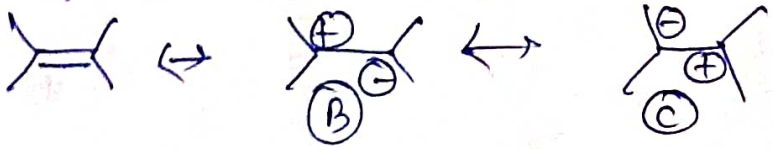


Penta fulvene

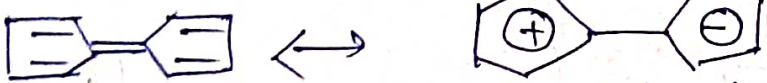


Calicene.

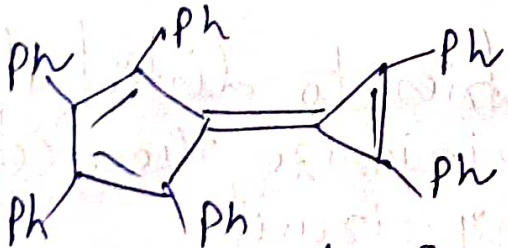
Such types of compounds are aromatic if resonance contribution like B or C makes both rings aromatic

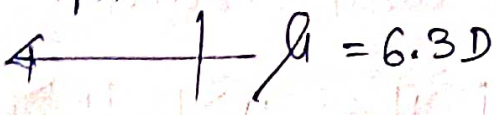


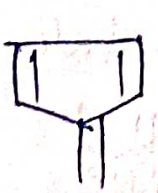
Aromatic



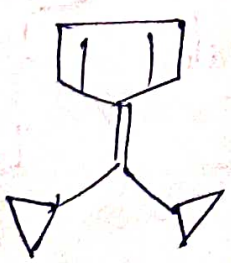
Not aromatic Antiaromatic Aromatic



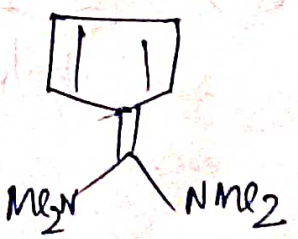




$\mu = 1.1D$



$\mu = 1.7D$



$\mu = 5.4D$

Fulvene is not very stable, but its dipolemoment can be enhanced by cyclopropyl group and NMe_2 group which are known to stabilize carbonium ions.

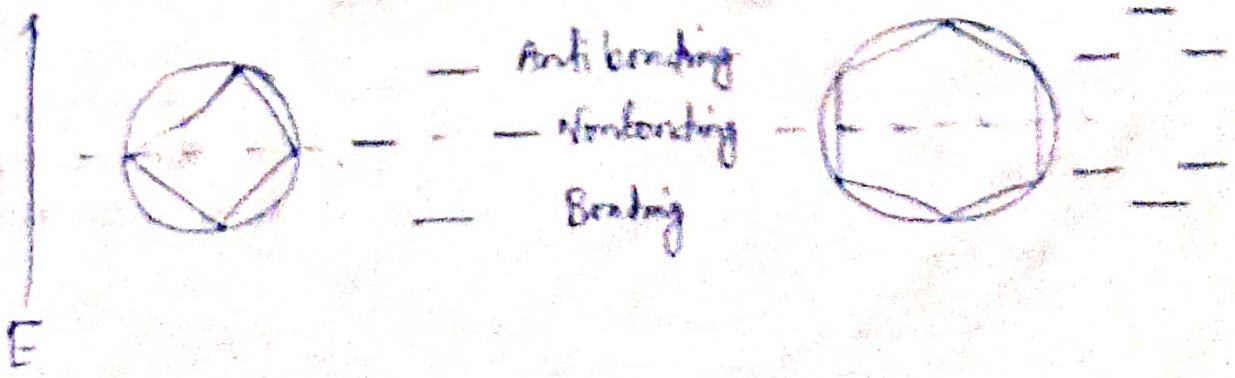
Frost principle

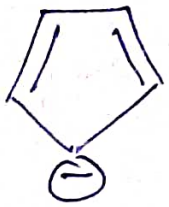
(i) Draw a circle.

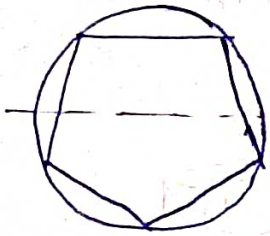
(ii) Place the ring in the circle with one of the vertices pointing down. Each point where polygon touches the circle represents an energy level.

(iii) Place the correct no. of electrons in the orbitals, starting with the lowest energy orbitals first, in accordance with Hund's rule.

If the polygon touches the circle at a horizontal diameter, the point would represent a nonbonding orbital. Energy levels below this line is bonding and those above this lines are antibonding.



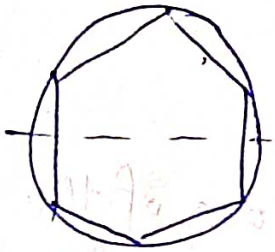




Antibonding

Aromatic

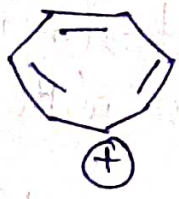
Bonding

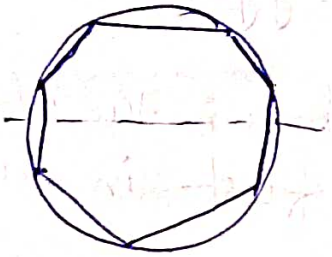


Antibonding

Aromatic

Bonding

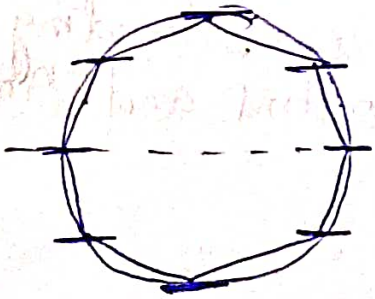




Antibonding

Aromatic

Bonding

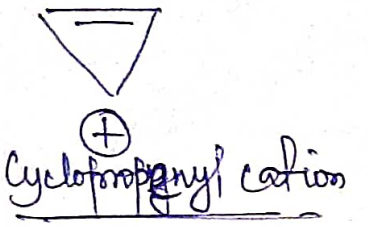


Antibonding

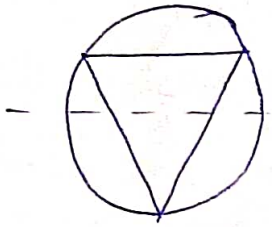
Non bonding

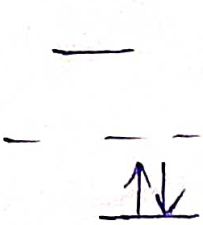
Bonding

It should be antiaromatic, but because of tub shaped conformation it is non-aromatic



Cyclopropenyl cation



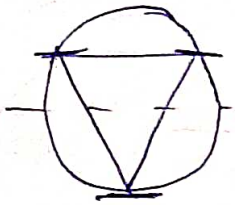


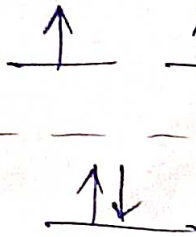
Antibonding

aromatic

Bonding

cyclopropenyl anion



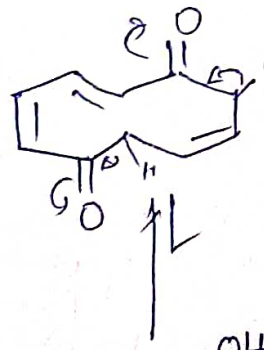


antibonding

antiaromatic

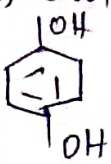
Bonding

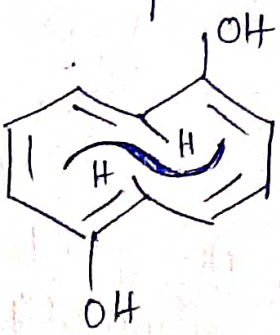
*



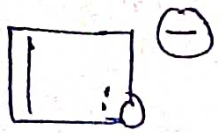
fails to enolize

gives enol





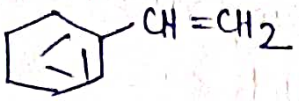
strong steric crowding between two protons inside the ring.

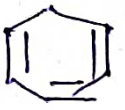
*  Aromatic $6\pi e^-$

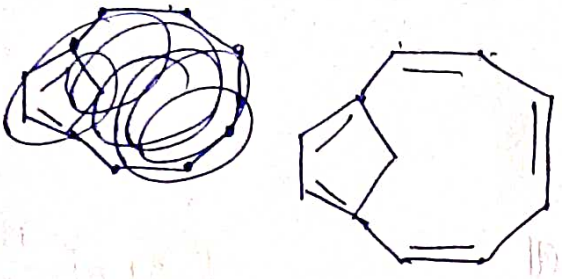
*  → $3\pi e^-$, not aromatic

* 
oxepin

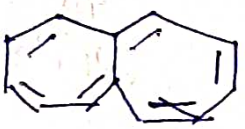
It is non-aromatic non-planar.

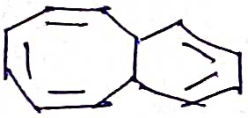
*  Aromatic, extra double bond is an irrelevant substituent, not being part of the cyclic system.

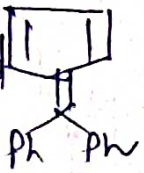
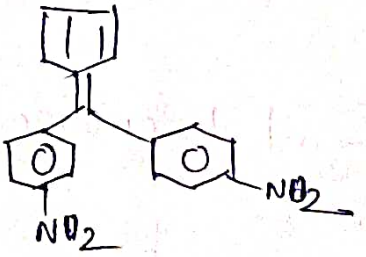
*  → NO sp^3 C breaking the circle of p-orbital

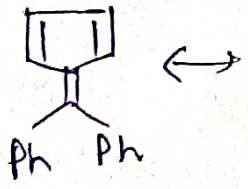
* 

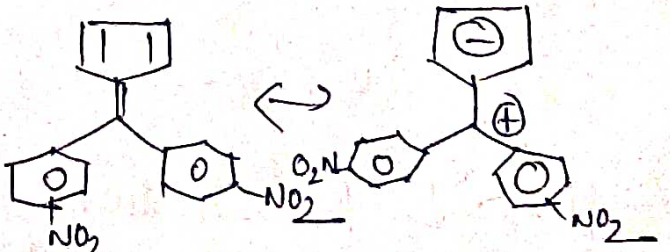
Yes. $10\pi e^-$, sp^3 C here is bridging & does not interrupt "p" orbital circle.

*  NO $12\pi e^-$

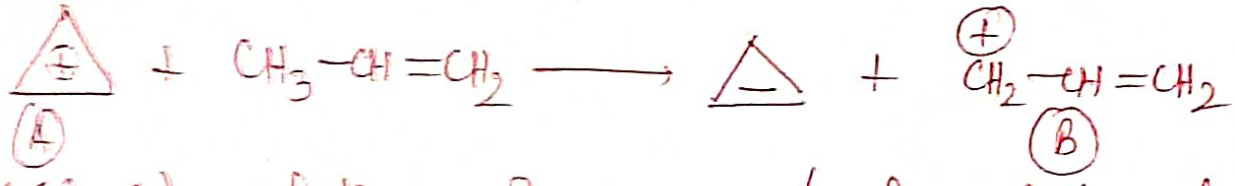
*  NO saturated ring fusion carbons interrupt circle.

* dipolemoment of  is higher than 

 Aromatic

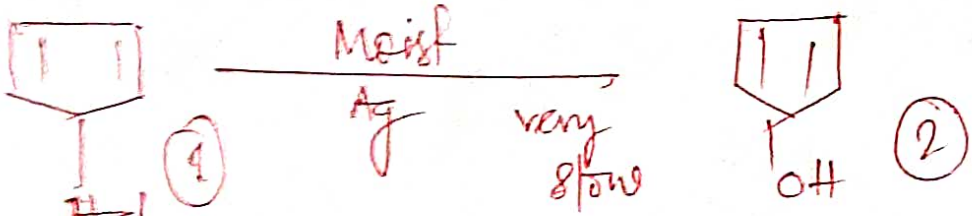


Here the charged species is not very much stable as the $-R$ effect of two $-NO_2$ groups in its p-positions destabilize the carboration. As a result dipolemoment becomes less.

* 

(heat of formation) ΔH of the reaction is +31 kCal/mole. What conclusion?

Since ΔH is (+)ve it implies that cyclopropenium cation (A) is much more stable than ally cation (B). This is because the aromatic character of cyclopropenium cation is lost in course of the reaction

* 

Hydrolysis of cyclopentadienyl halide is extremely slow

(1) to (2) gives the reverse formation of  , which is antiaromatic