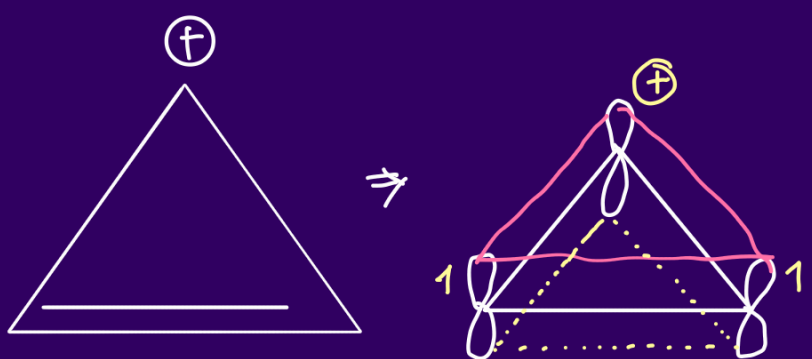
Aromaticity

5*

Resonance = ✓ min.* "3 p-orbitals"
✓ must be "continuous" p-orbitals
✓ they must be "parallel"



2πe⁻ conjugation
⇓
"Aromatic"

1] Hybridisation :-

> Hybridisation = σ-bonds + localised l.p.
> [fix l.p.]

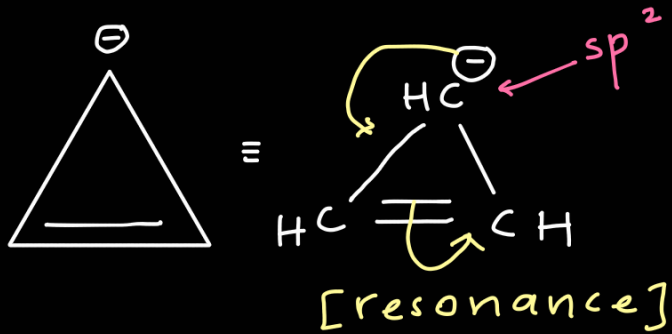
ex.

a> Carbocation [$C^{\oplus}$] → $H_3\overset{\oplus}{C} \equiv H_3C\overset{\oplus}{\otimes}$ ⇒ sp^2

b> Carbon free radicals [C·] → $H_3\dot{C} \equiv H_3C\overset{\cdot}{\otimes}$ ⇒ sp^2

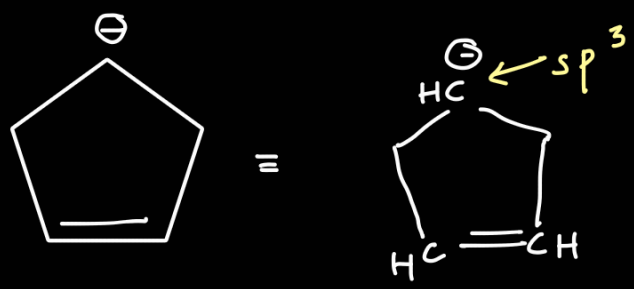
c> Carbanion [$C^{\ominus}$]

If ⊖ charge is in resonance ⇒ sp^2



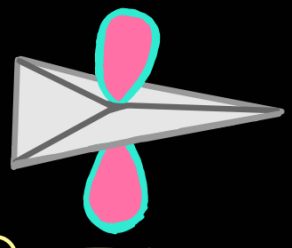
[resonance] ✓

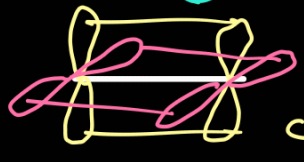
If ⊖ charge is not in resonance ⇒ sp^3



[no resonance] ✗

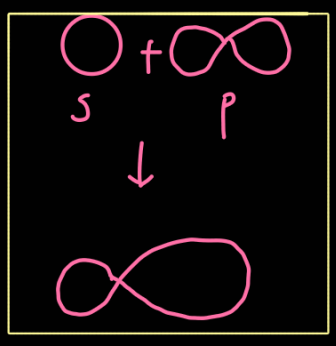
2] sp^3 → Tetrahedral  + Pure p = 0

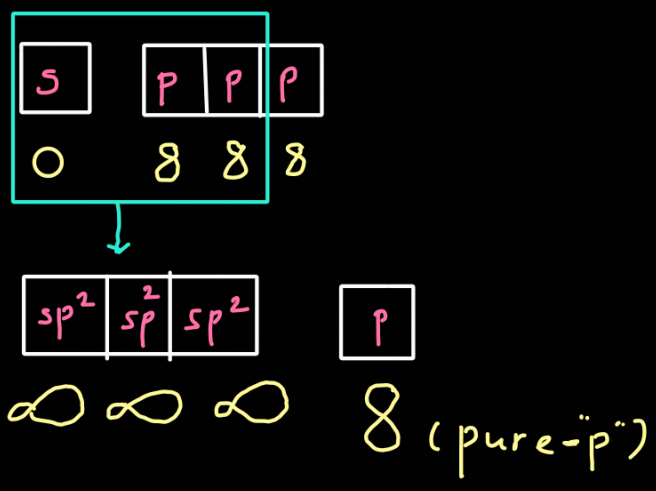
sp^2 → Trigonal planar  + 1

sp → Linear  + 2

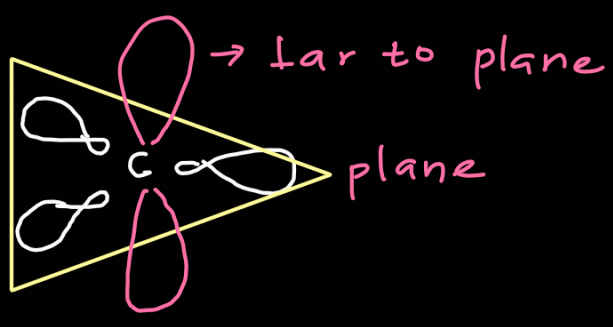
$CH \equiv CH$

* **Basic's :-** sp^2 → Trigonal planar

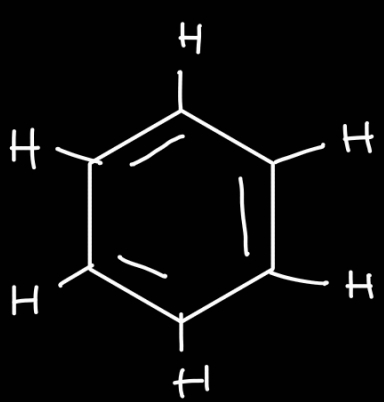




sp^2 ⇒



3] **Benzene [C_6H_6]**

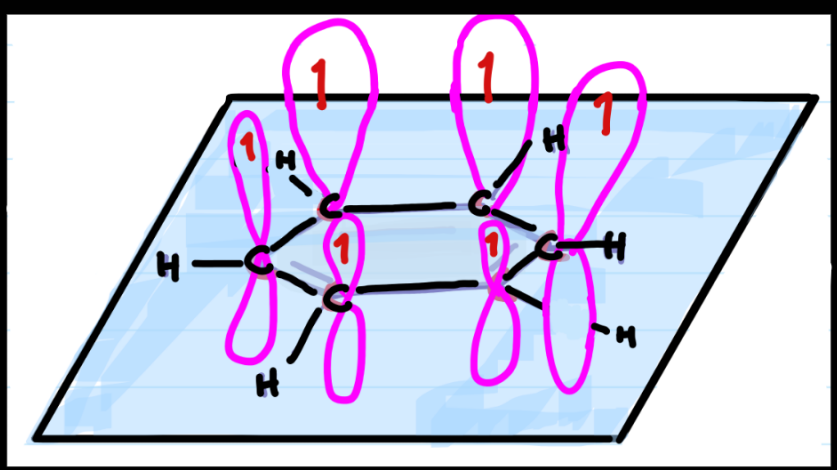


⇒

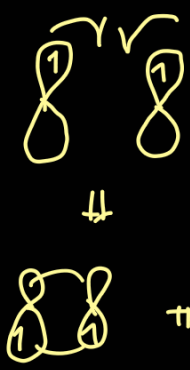
All "c" are sp^2 *

⇓

Mean's all "c" have "1-pure p-orbital".



* Note :-

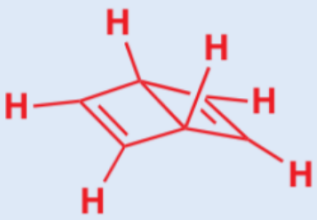


The two early proposals for the structure of benzene were wrong, but nonetheless are stable isomers of benzene (they are both C_6H_6) which have since been synthesized. For more on the Kekulé structure, see p. 24.

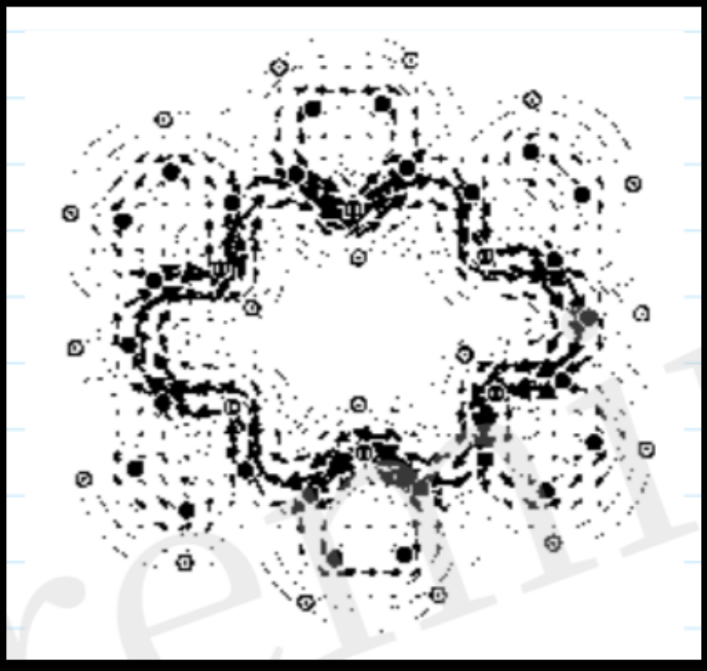
=

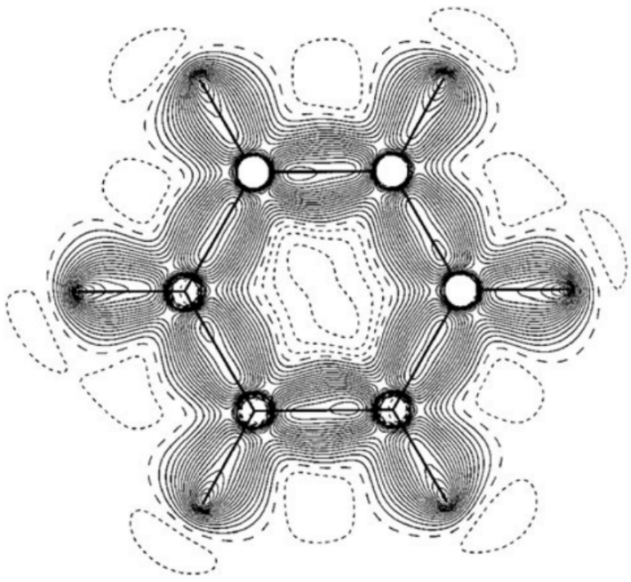
prismane
synthesized
1973

=

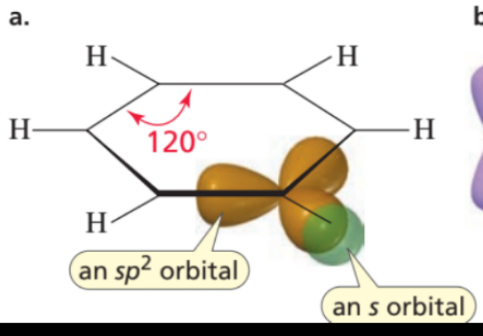


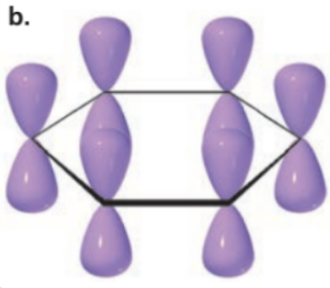
Dewar
benzene
synthesized
1963

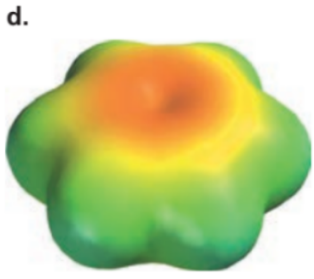


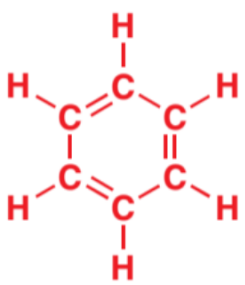


Electron diffraction image of a molecule of benzene

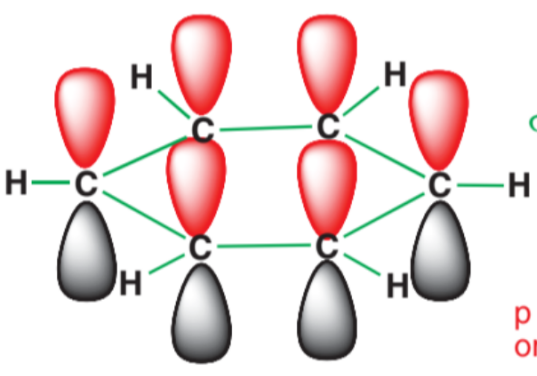








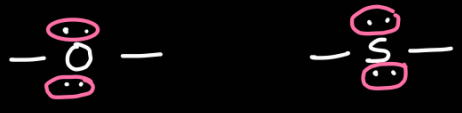
Kekulé's structure for benzene



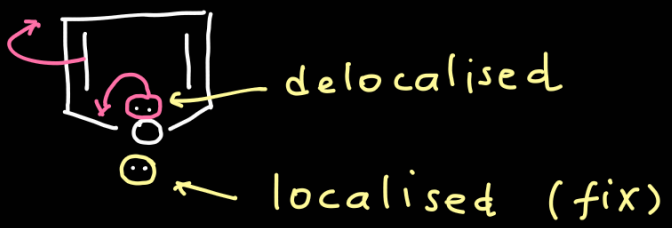
σ bonds shown in green

p orbitals shown with
one phase red, one phase black

4] If atom has more than one lone pair then only one lone pair get involved in the resonance.



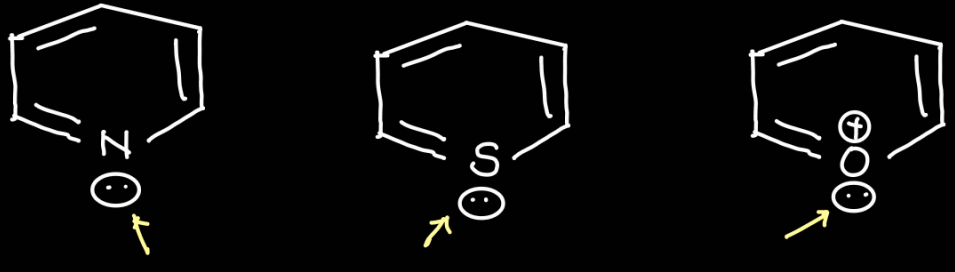
ex.



5]

← fix / localised l.p. / does not get involved in resonance

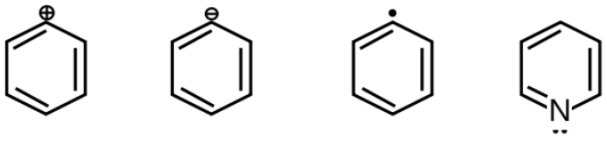
ex.

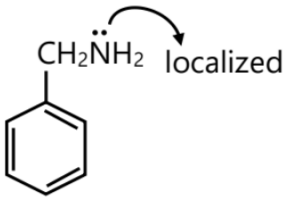


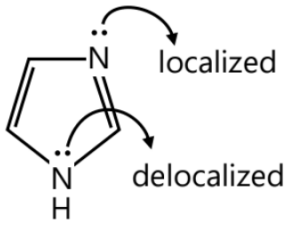
does not get involved in resonance

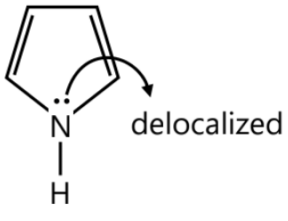
6]

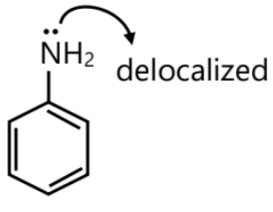
–ve/+ve/free radical/lone pair on double bonded atom in ring, does not take part in resonance. They are said to be localized.











1] Aromatic

- ✓ cyclic
- ✓ planar (all atom's sp^2/sp)
- ✓ complete cyclic resonance [complete closed loop]
- ✓ Follow Huckel's rule $[4n+2]\pi\ e^-$

ex.

$n=0 \rightarrow 2\pi e^-$

$n=1 \rightarrow 6\pi e^-$

$n=2 \rightarrow 10\pi e^-$

$n=3 \rightarrow 14\pi e^-$

2, 6, 10, 14 delocalised πe^-

⇓

- ✓ cyclic
- ✓ all atom's sp^2 (Planar)
- ✓ complete resonance
- ✓ $6\pi e^-$

⇓

Aromatic

* posses "diamagnetic ring current."

Anti-aromatic

- ✓ cyclic
- ✓ Planar (all atom's sp^2/sp)
- ✓ complete cyclic resonance [complete closed loop]
- ✓ must follow $[4n]\pi\ e^-$ system.

ex.

$n=0 \rightarrow 0\pi e^-$ (not possible for resonance)

$n=1 \rightarrow 4\pi e^-$

$n=2 \rightarrow 8\pi e^-$

$n=3 \rightarrow 12\pi e^-$

$n=4 \rightarrow 16\pi e^-$

4, 8, 12, 16 delocalised πe^-

⇓

I

- ✓ cyclic
- ✓ all atom's sp^2
- ✓ complete resonance
- ✓ $4\pi e^-$

⇓

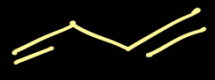
Anti-aromatic

* "paramagnetic ring current."

Non-aromatic

- ✓ Compound's which are neither (A) nor (AA); are called "NA".
- ✓ All alicyclic compound's are "NA"

ex.



Not cyclic

$4\pi e^-$ (NA)

⇓

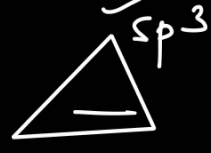
$6\pi e^-$

(NA)

⇓

$8\pi e^-$

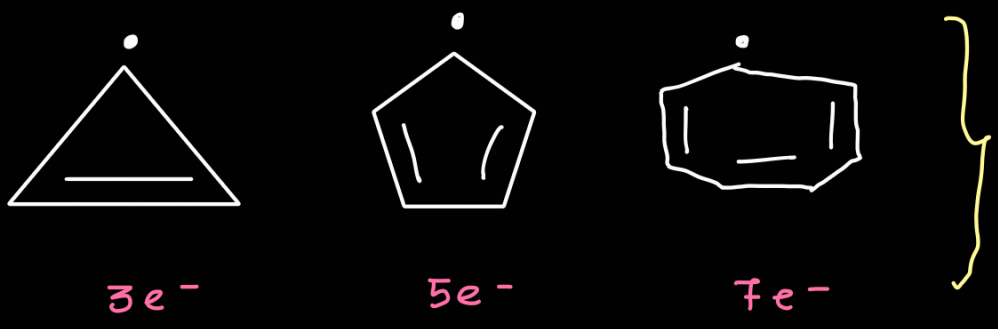
(NA)



2]

* Relative stability = A > NA > AA
* Relative P. E. = AA > NA > A
* Relative Resonance E. = A > NA > A

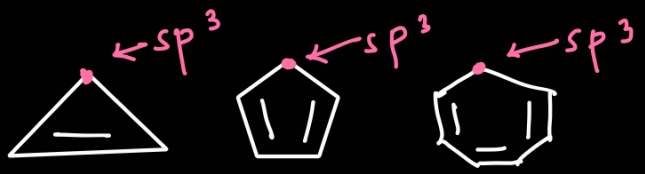
3] Planar cyclic compounds having **odd** no. of delocalised $e^{\ominus}$ are also non-aromatic in nature.



4] Compounds which are cyclic in nature and possess $(4n+2\pi)\ e^{\ominus}$. But if delocalisation of e^{-} is absent → then also compound is non-aromatic in nature.

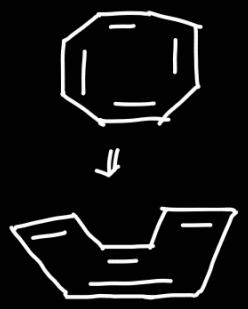
Delocalisation of $\pi e^{\ominus}$'s stop because of two reason

a) Insertion of sp^3 c-atom



b) If compound is Non-planar

ex. COT



→ Non-planar
→ Non-aromatic

* Calculation of delocalised $\pi e^{\ominus}$:-

1] $=$ → 2 π e-

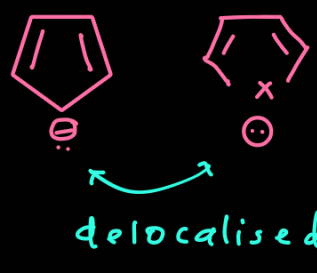
2] $\equiv$ → 2 π e-

3] $\oplus$ve → 0 π e-

4] $\ominus$ → Localised → 0 π e-
Delocalised → 2 π e-

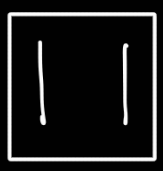
5] Lone pair → Localised → 0 π e-
Delocalised → 2 π e-

Localised



delocalised

* **Cyclobutadiene** (CBD)



$4\pi e^-$

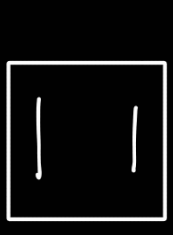
AA *

✓ It's absolute answer is "Non-aromatic".

✓ But for exam always's tick "Anti-aromatic".

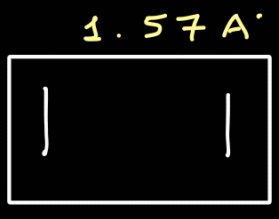
Reason :-

It can't be anti-aromatic as it's bond lengths are different i.e., it exist as rectangular structure ; not square structure.



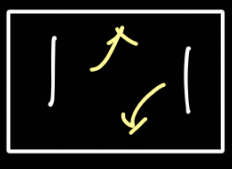
square xx

1.57 A°



1.35 A°

rectangle ✓



wrong

It exist's as "dimer." ⇒ Since, cyclobutadiene is antiaromatic in nature. so, it is highly unstable and it has the tendency to undergoes dimerisation.

+

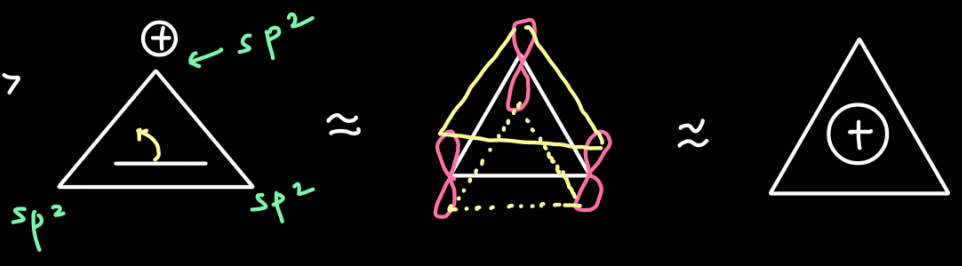
Dimerisation →

↑ sp^3

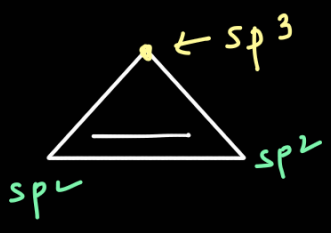
NA

* Type's of system :-

A] 3-membered ring's

1> 

2π e⁻
"Aromatic"

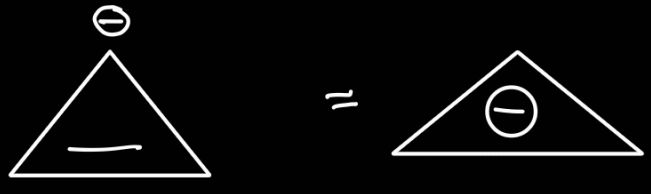
2> 

Non-aromatic

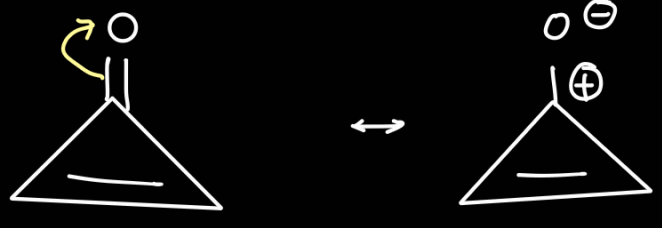
3> 

Free radical

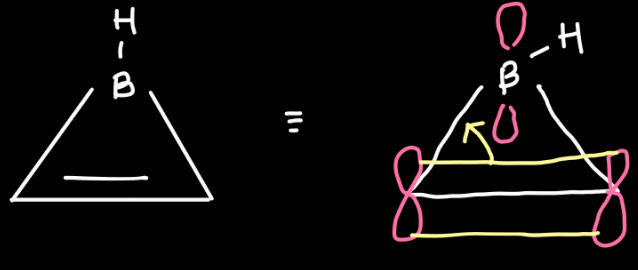
3 π e⁻
Non-aromatic
(odd e⁻)

4> 

4π e⁻
"Antiaromatic"

5> 

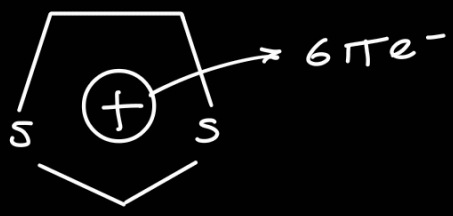
2π e⁻ "Aromatic"
[Quasi aromatic]

6> 

2π e⁻ ring current
"Aromatic"

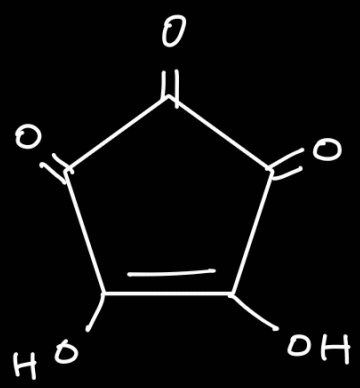
15>

≡

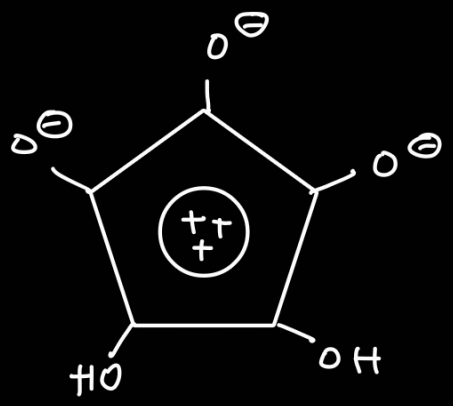


Aromatic

16>



≡



2πe-

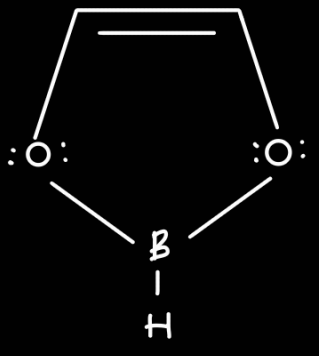
Aromatic

"Croconic acid"

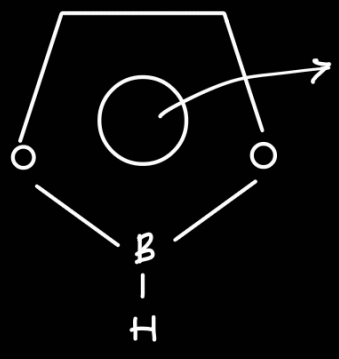
⇓

[as strong as H_2SO_4]

17>

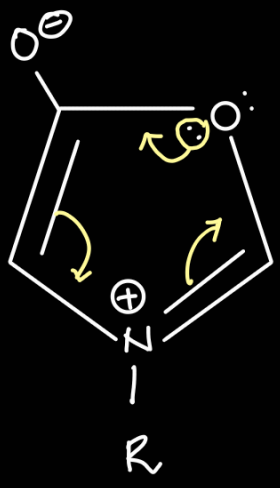


≡



Aromatic

18>



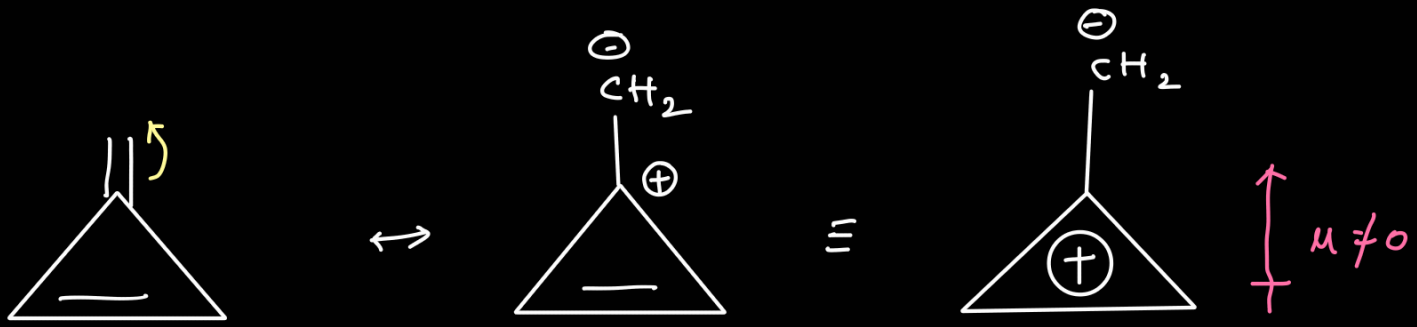
6πe- Aromatic

Sydnone (Internal salt)

* Chameleon aromaticity

"In non-polar state; Non-aromatic & in dipolar state shows aromaticity." This is called chameleon aromaticity.

1>



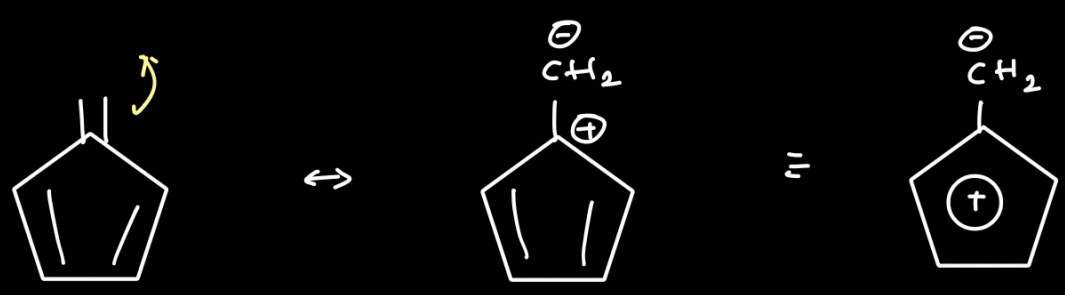
Methylene cyclopropene or Trifulvene

5*
2πe⁻ Aromatic

R.H.

μ = 1.9 D

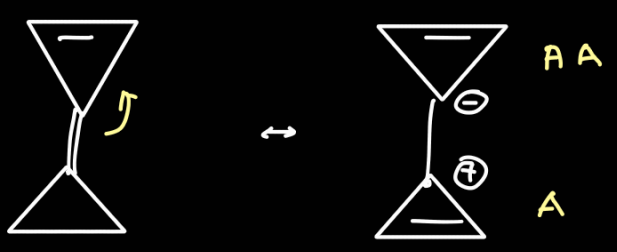
2>



5*
4πe⁻ Anti-aromatic

μ = 1.5 D

3>



5* Overall it is Non-aromatic

* A] **Annulene's** :-

(H/C)

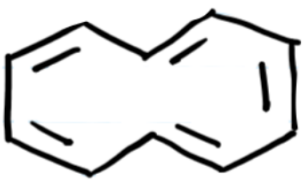
" Monocyclic hydrocarbon containing alternative single bond and double bond."

↷  not annulene

[4]-Annulene

[6]-Annulene

[8]-Annulene

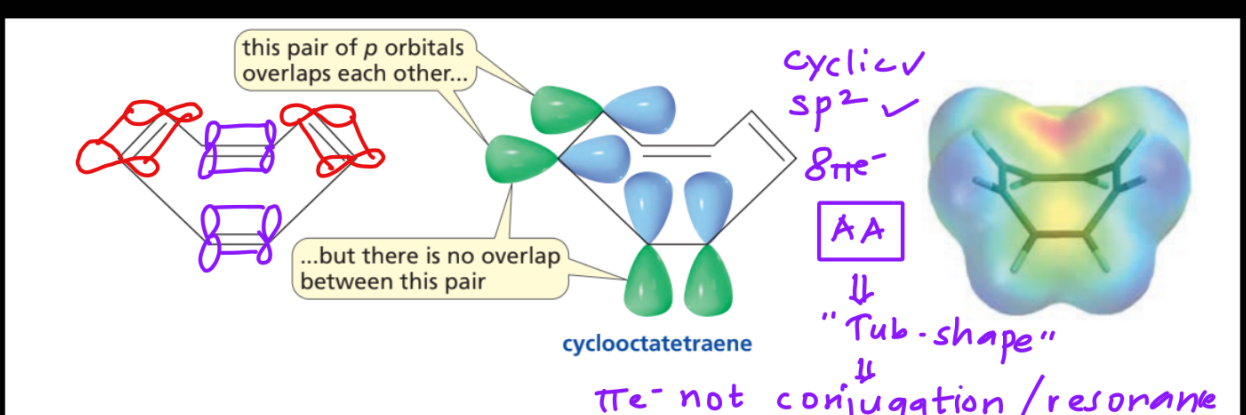


[10]-Annulene

1] [8]-Annulene / cyclooctatetraene [COT]

 ≈ 

exist's in "Tub-shape"



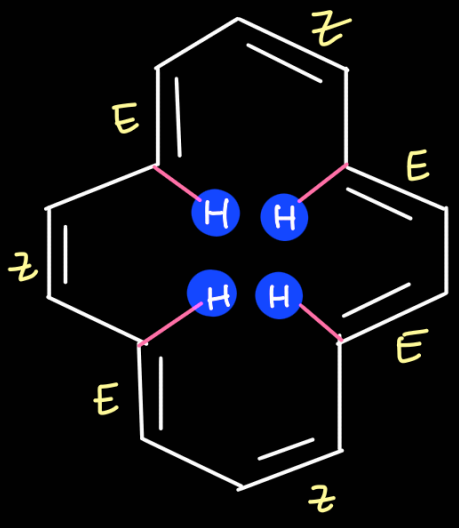
cyclic ✓
sp^2 ✓
$8\pi e^-$
AA
⇓
"Tub-shape"
⇓
πe^- not conjugation / resonance
⇓
⇓ because (3p) min. parallel absent ∴

COT: Non-planar ⇒ **Non-aromatic**

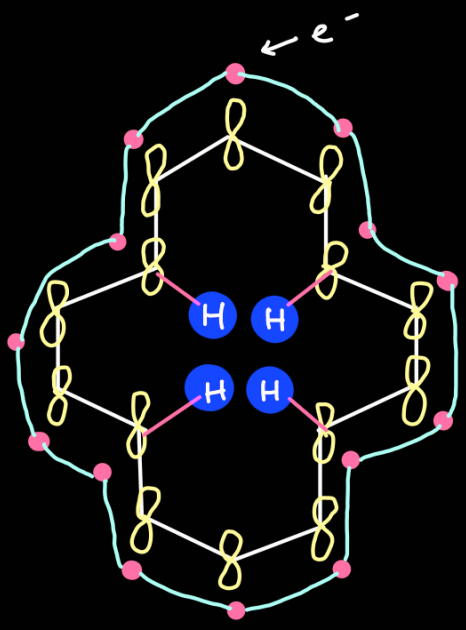
Q. Why 8-annulene is not aromatic though all carbon are sp2 hybridized and having 8 pi electrons ?

Ans: Because it exists in Tub-shape in nature it lost its planarity , which resists it from doing conjugation/resonance.

77 **14- Annulene**



ZEZEEZE



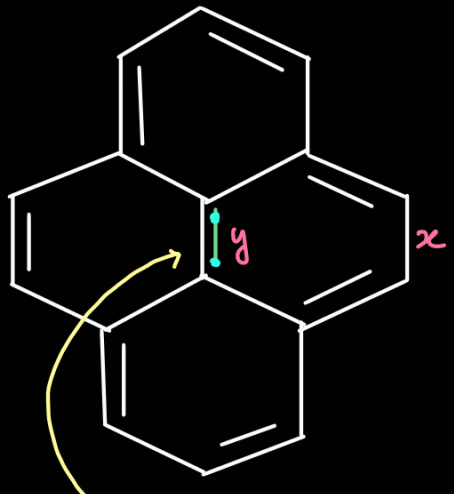
"14e⁻ closed loop"

⇓

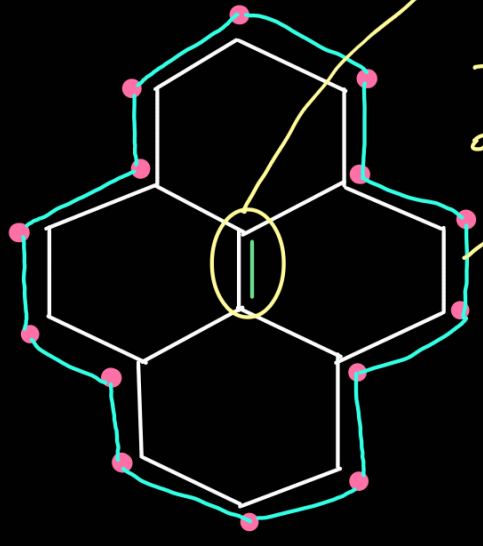
Aromatic

"Trans-annular H-atom's repulsion is less due to larger cavity size."

* If we bridge transannular H-atom's by using carbon atom we get new compound.



localised π-e⁻/π-bond



"Non-huckel double bond"

⇓

This π-bond gives olefinic test.

"14e⁻ closed loop"

⇓

Aromatic

(14 πe⁻ ring current)

Polycyclic peripheral/circumference resonance

Bond length = $x > y$