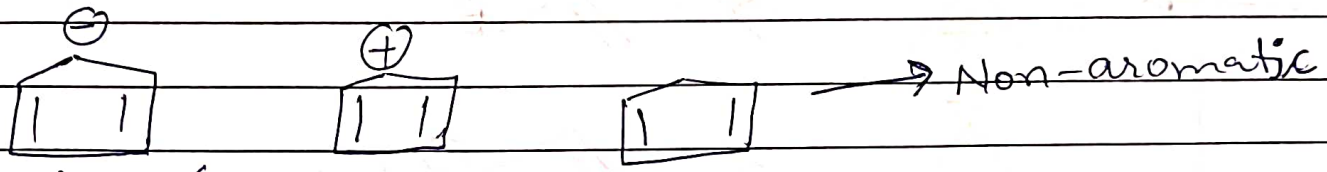
Aromaticity

Cyclic Resonance

- Extra stabilization ⇓ Aromatic ↓ → $(4n+2)\pi\ \bar{e}$, $n = 0, 1, 2, 3, \ldots$
- Extra destabilization ⇓ Anti-Aromatic ↓ $4n\ \pi\ \bar{e}$, $n = 0, 1, 2, \ldots$



$(4n+2)\pi = 6$

$n = 1$

↓ Aromatic

↓ Extra stabilised

$4n\pi = 4$

$n = 1$

↓ Antiaromatic

↓ Extra destablised

$4n+2 = 4$

$n = 1/2$ ✗

$4n = 4$

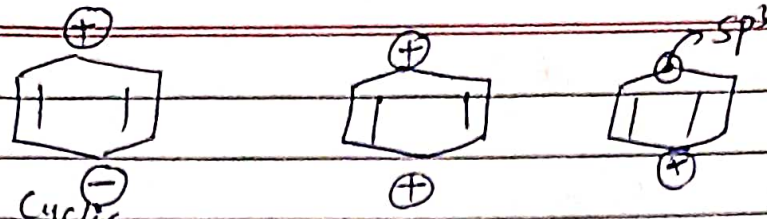
$n = 1$ ✗

Huckel's Rule

1. Cyclic system
2. Planar (sp^2 or sp)
3. Cyclic resonance
4.

- $(4n+2)\pi\ \bar{e}$ Aromatic
- $4n\pi\ \bar{e}$ Anti-aromatic

Q



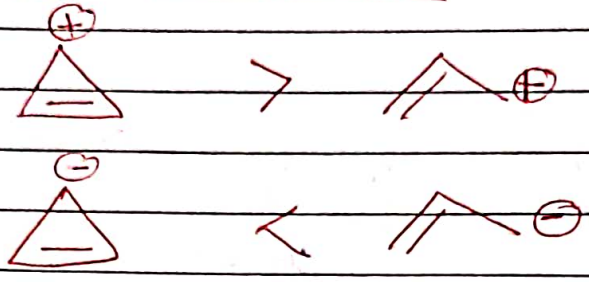
Cyclic Planar
$(4n+2)\pi\bar{e}$
↓
Aromatic

Cyclic Planar
$4n\pi\bar{e}$
↓
Anti-aromatic

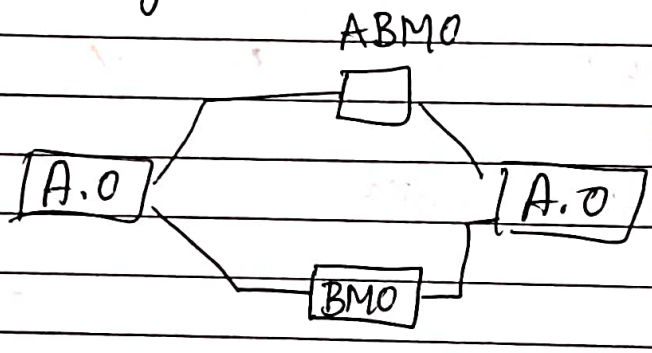
Cyclic Non-planar
↓
Non-aromatic

Cyclic Resonance Vs Acyclic resonance

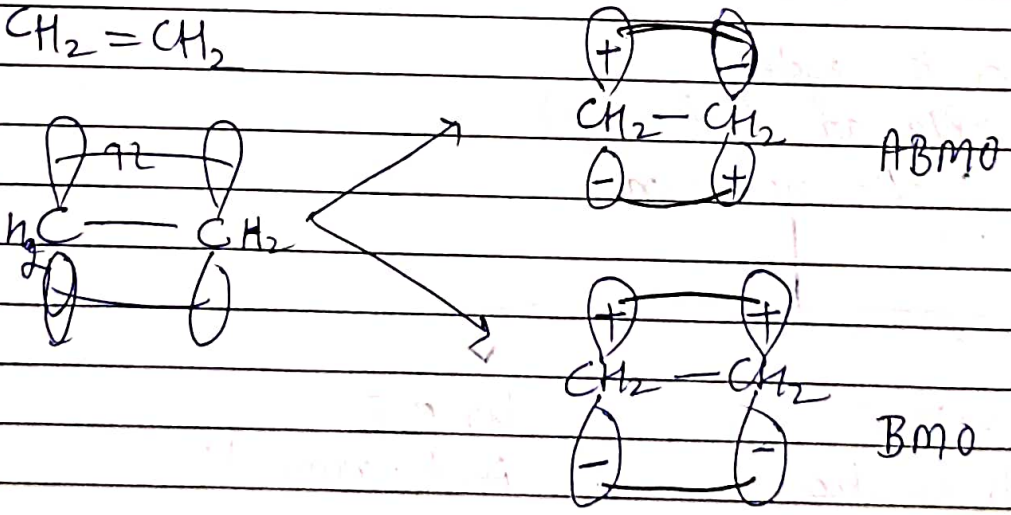
Stability



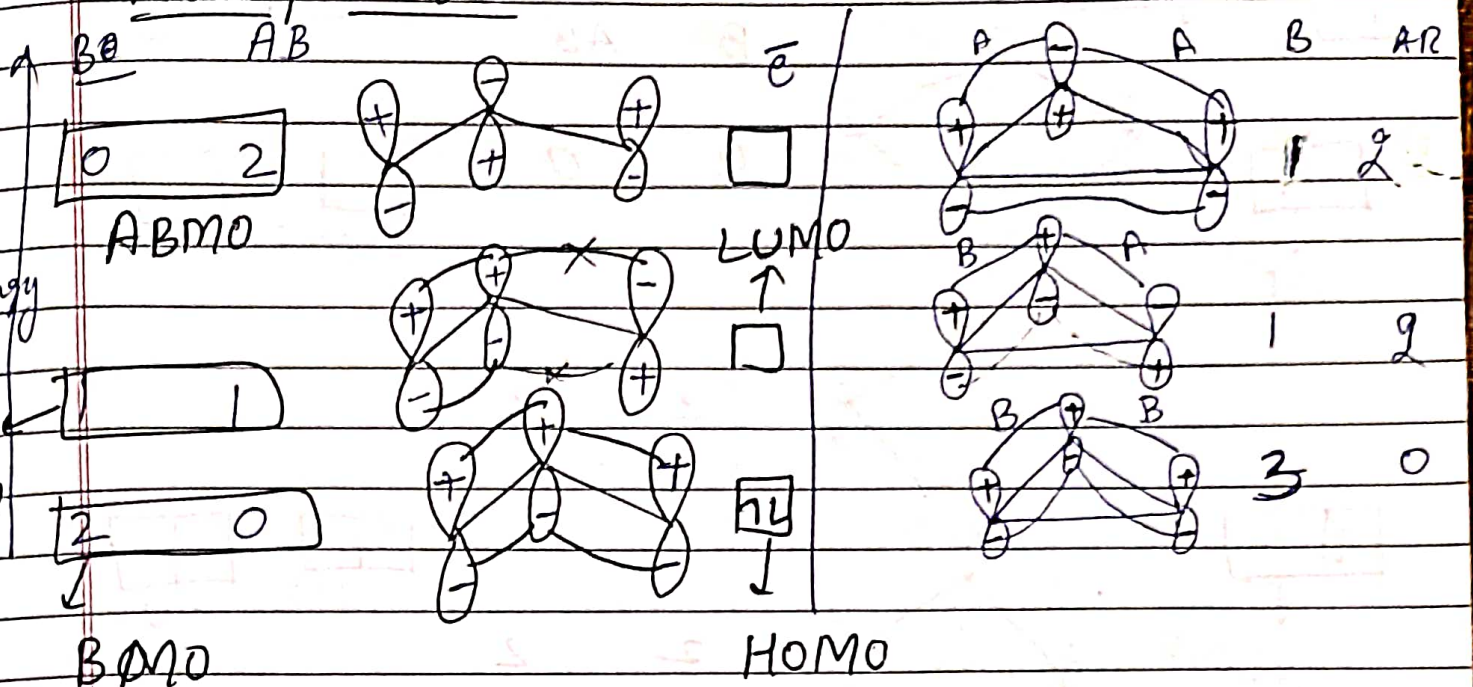
MO Diagram



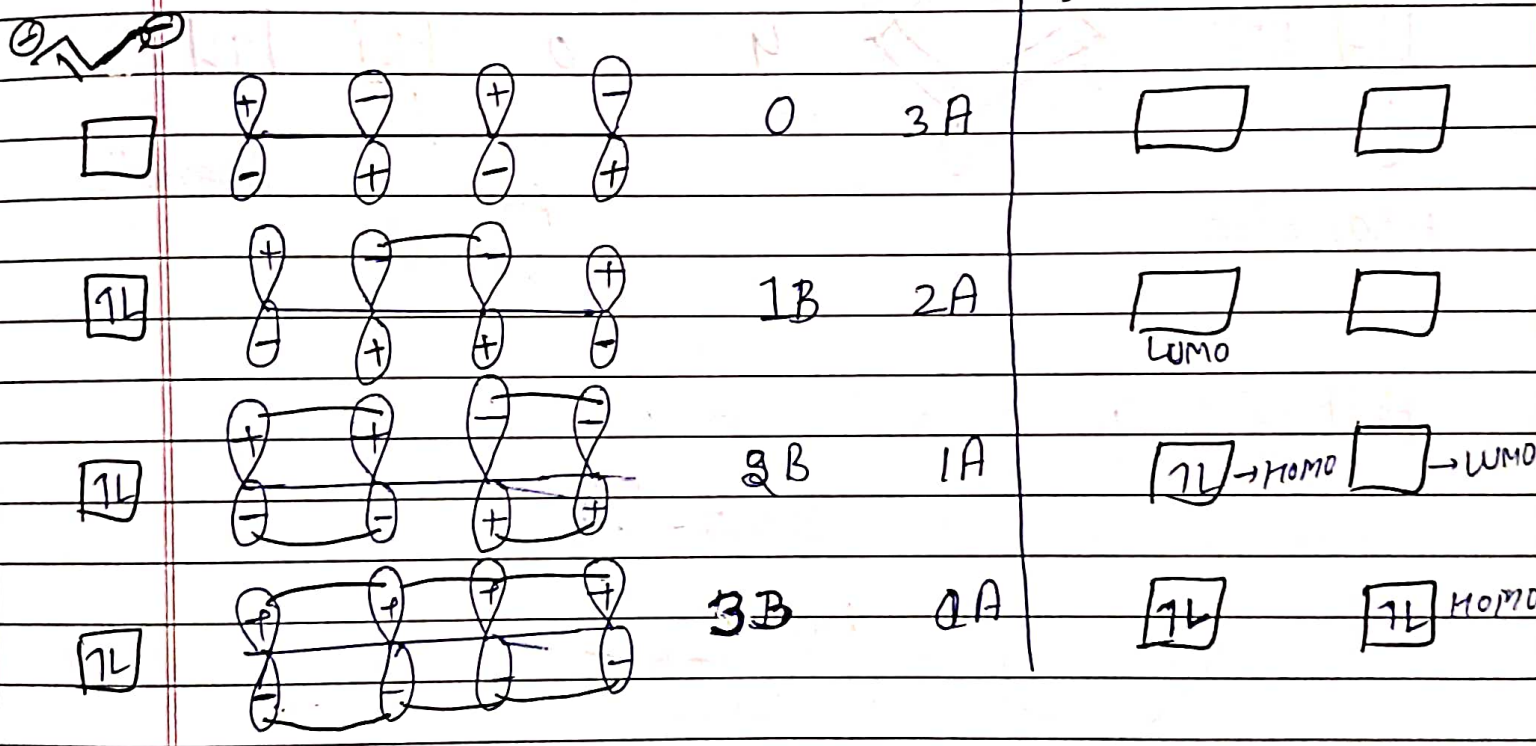
$CH_2 = CH_2$



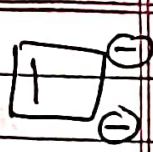
Three p-orbital :-

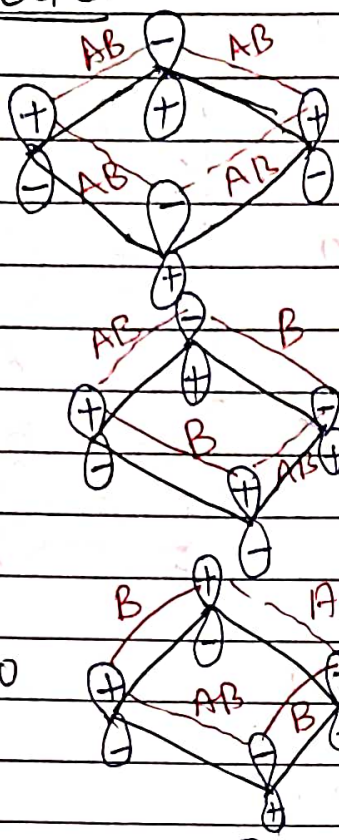


4-p-orbital



cyclic

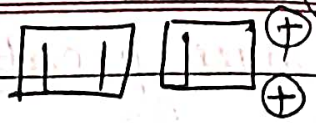




B0 AB

4 0

ABMO



LUMO

2 2

NBMO

HOMO LUMO

2 2

BMO

4 0

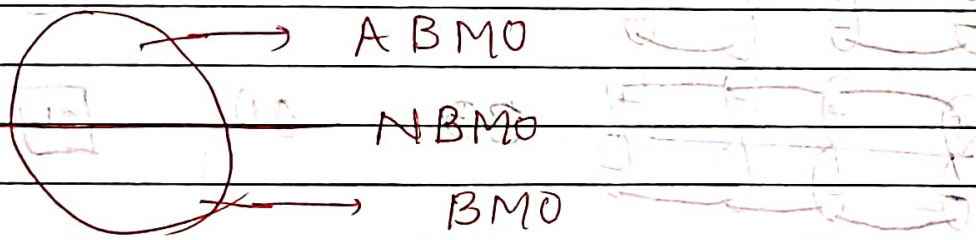
Aromatic

Anti aromatic

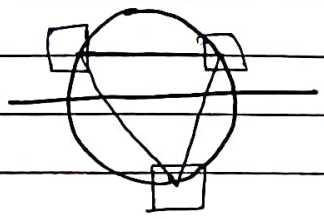
HOMO

Aromatic

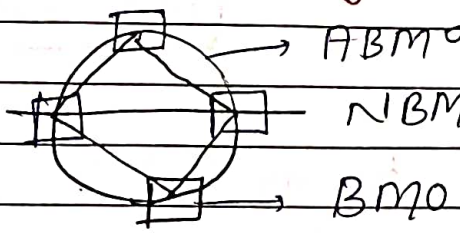
Frost cyclic Rule :-



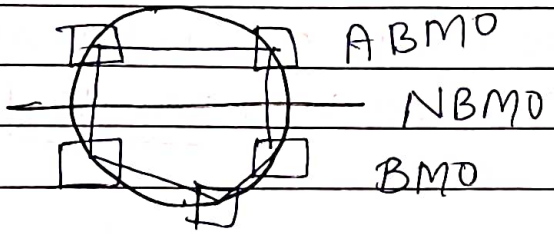
3-Membered ring



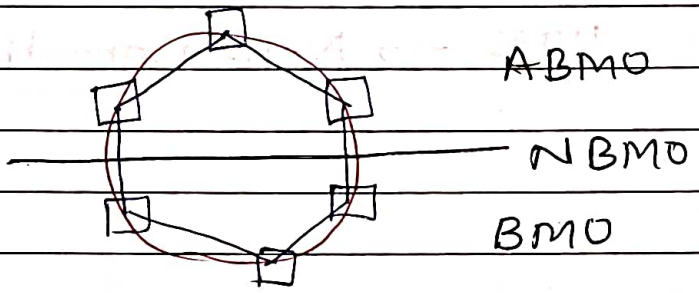
4-membered ring:-



5-membered ring:-



6-Membered ring:-

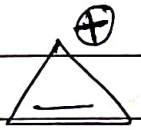


Type of Questions

1. Nomenclature (3 to 10)
2. Quasi Aromatic
3. Appⁿ of Aromaticity in Rxⁿ Mechanism
4. fused ring & Annulenes & Homo-aromatic

Nomenclature (3 to 10 Membered ring)

3-Membered ring :-

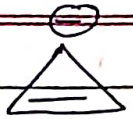


cyclic resonance
Planar

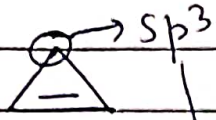
Aromatic

$4n+2 = 2$

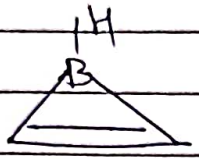
$n = 0$



cyclic resonance
planar
$4n\pi\bar{e}$
→ Anti-aromatic



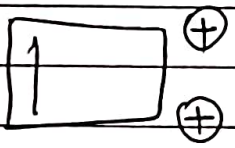
cyclic, planar
Resonance → X
→ Non-aromatic



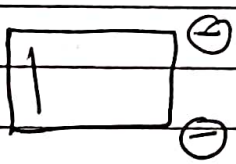
Cyclic resonance, planar (sp^2)
$2\pi\bar{e}$ → Aromatic

Cyclic resonance
$4\pi\bar{e}$ → Anti-aromatic

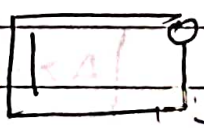
4-membered ring



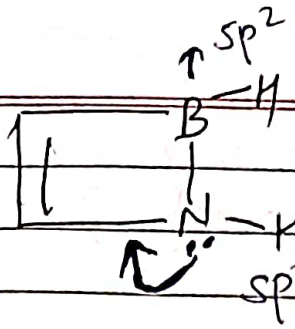
Cyclic, planar, resonance
$2\pi\bar{e}$ → Aromatic



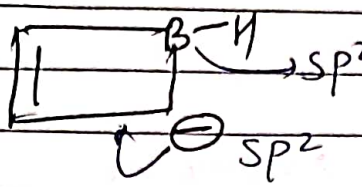
Cyclic, planar, resonance
$6\pi\bar{e}$ → Aromatic



→ sp^3 → Non-aromatic

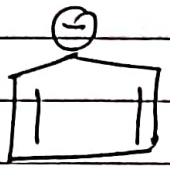


cyclic, planar, resonance
4π e⁻ → Anti-aromatic



cyclic, planar, resonance
4π e⁻ → Anti-aromatic

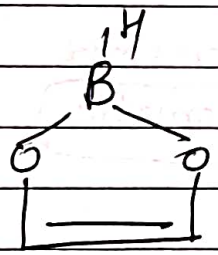
5-membered ring



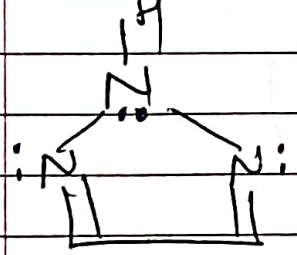
cyclic, planar; resonance
6π e⁻ → Aromatic

cyclic, planar, resonance
4π e⁻ → Anti-aromatic

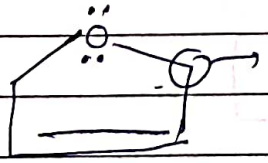
sp³ → Non-aromatic



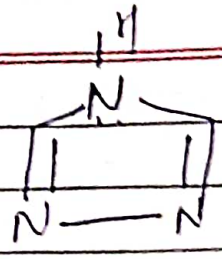
cyclic, planar, resonance
6π e⁻
↓ Aromatic



cyclic, planar, resonance
6π e⁻ → Aromatic

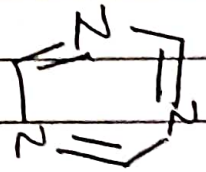


sp³ → Non-aromatic

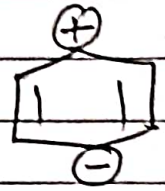


cyclic, planar, resonance
$6\pi\bar{e}$ → Aromatic

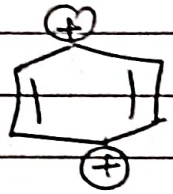
6-Membered ring



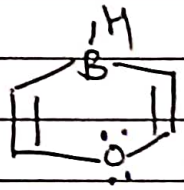
cyclic, planar, resonance
$6\pi\bar{e}$ → Aromatic



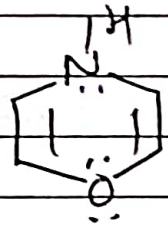
cyclic, planar, resonance
$6\pi\bar{e}$ → Aromatic



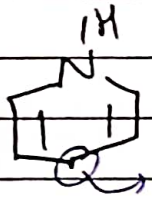
cyclic, planar, resonance
$4\pi\bar{e}$ → Anti-Aromatic



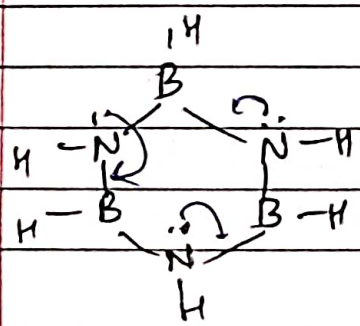
cyclic, planar, resonance
$6\pi\bar{e}$ → Aromatic



cyclic, planar, resonance
$8\pi\bar{e}$ → Anti-Aromatic



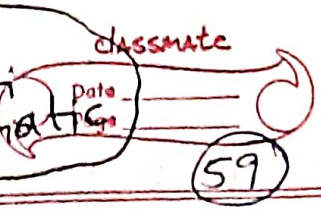
sp^3 → Non-aromatic

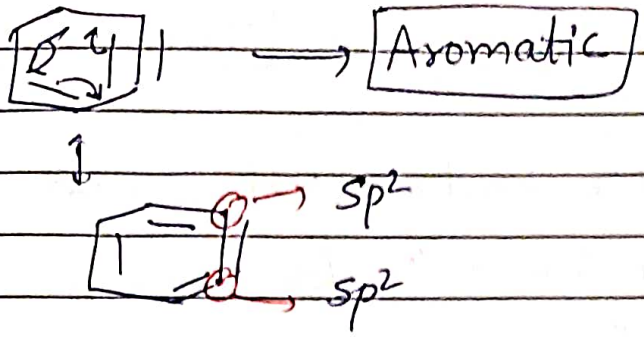


Aromatic

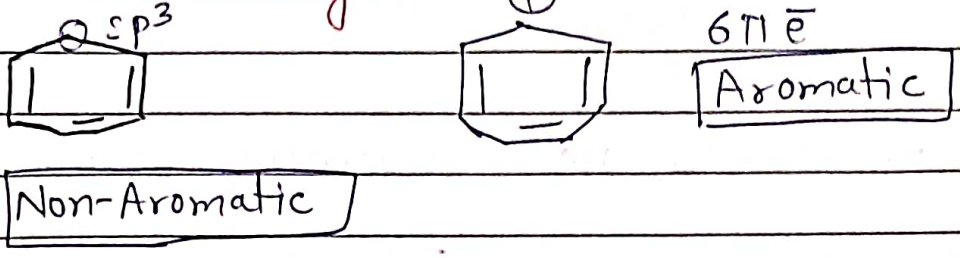
Stability order

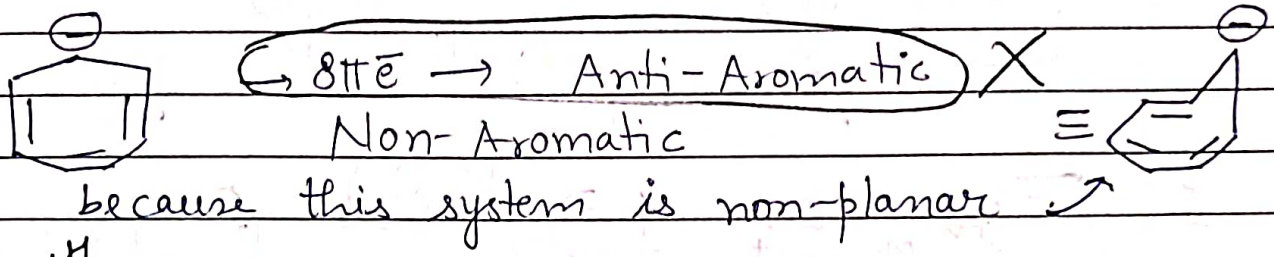
Aromatic > Non-Aromatic > Anti Aromatic

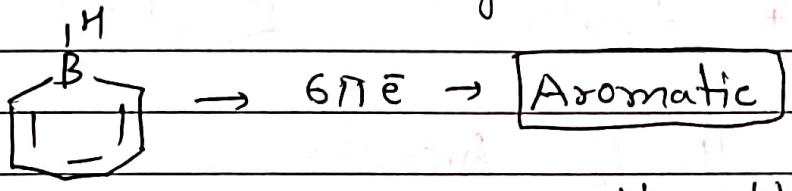


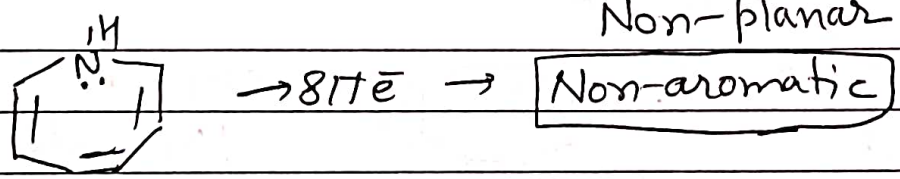


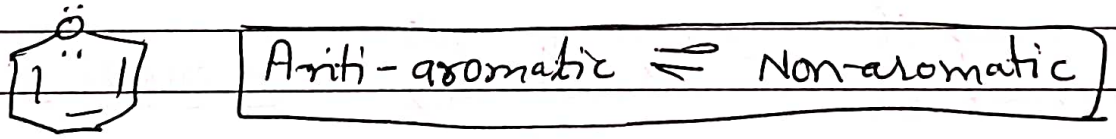
7 member ring



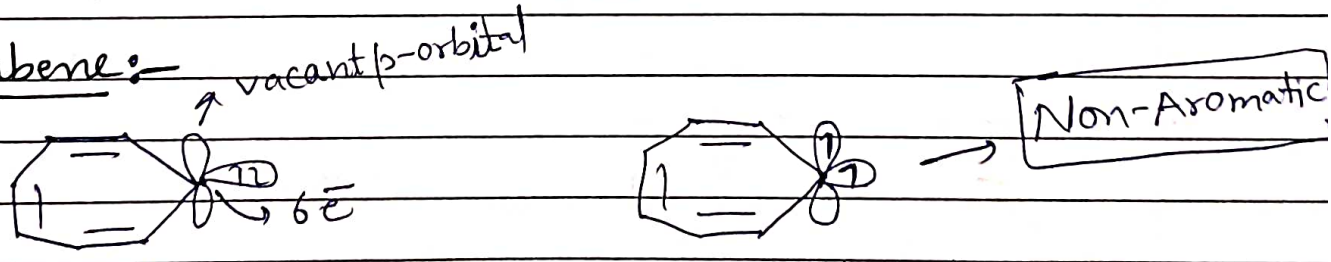








Carbene:-



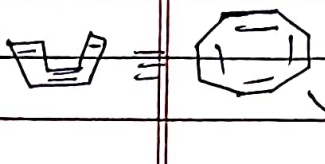
Singlet carbene

6π e̅ → Aromatic

Triplet carbene

Does not exist

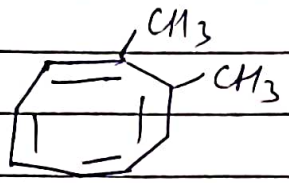
8-member ring :-



Non-planar system ⇒ Non-Aromatic

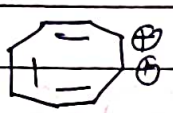
→ COT

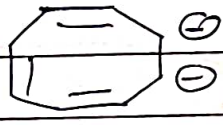
Here single & double bond are not in resonance & thus have unequal bond length

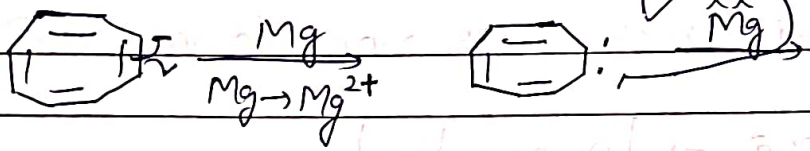
Q 

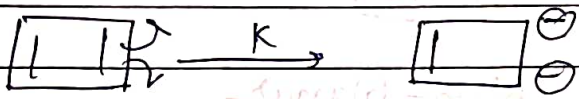
(a) (b)

a & b are isomers not resonating structure.

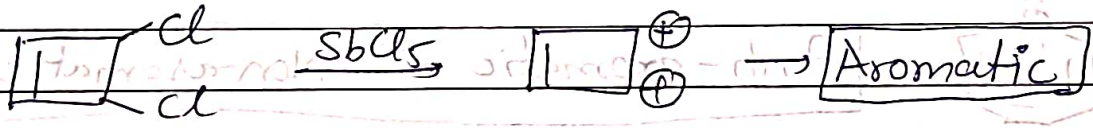
→  $6\pi\bar{e}$ → Aromatic

 $10\pi\bar{e}$ → Aromatic

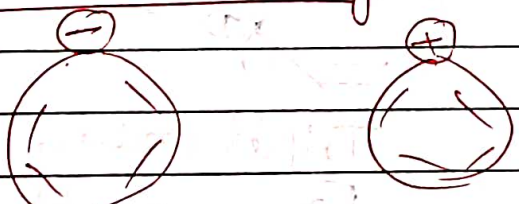
Q  Aromatic

Q  Aromatic

Q  $6\pi\bar{e}$ → Aromatic

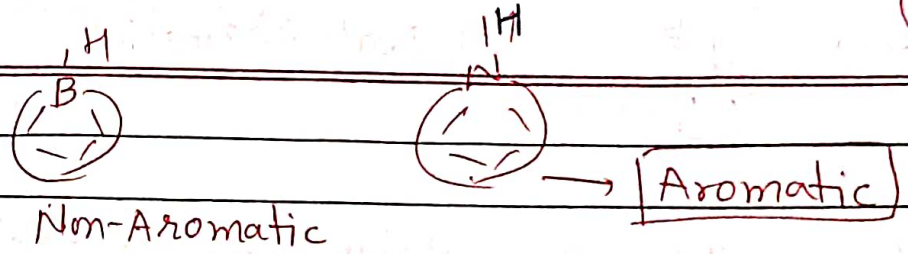
Q  → Aromatic

9-member ring :-



$10\pi\bar{e}$ → Aromatic

 → $8\pi\bar{e}$ → Non-aromatic

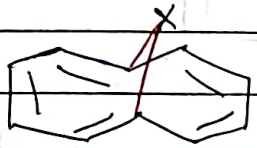


10-member ring

$10\pi\bar{e}$

Non-planar → Non-Aromatic

Steric repl^{n} → Non-planar



$10\pi\bar{e}$ & no repl^{n}

Aromatic

X = C, N, O

Quasi-Aromatic :-

$A = B \longrightarrow \overset{\oplus}{A}-\overset{\ominus}{B}$ or $\overset{\ominus}{A}-\overset{\oplus}{B}$

Non-polar form — Polar form — Polar form

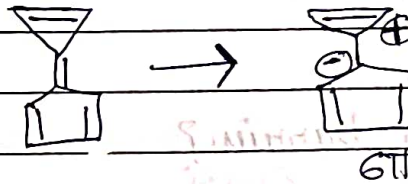
Aromatic

Quasi-Aromatic

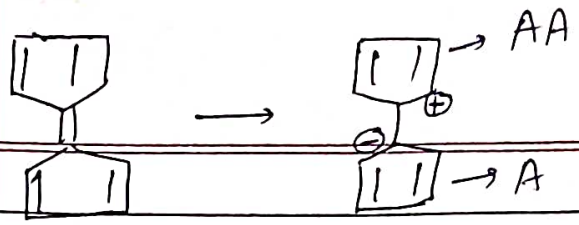
Quasi Aromatic

- Cyclic Hydrocarbon
- Cyclic ketone
- Azulene

(1) Cyclic hydrocarbon :-



⇒ Quasi-Aromatic

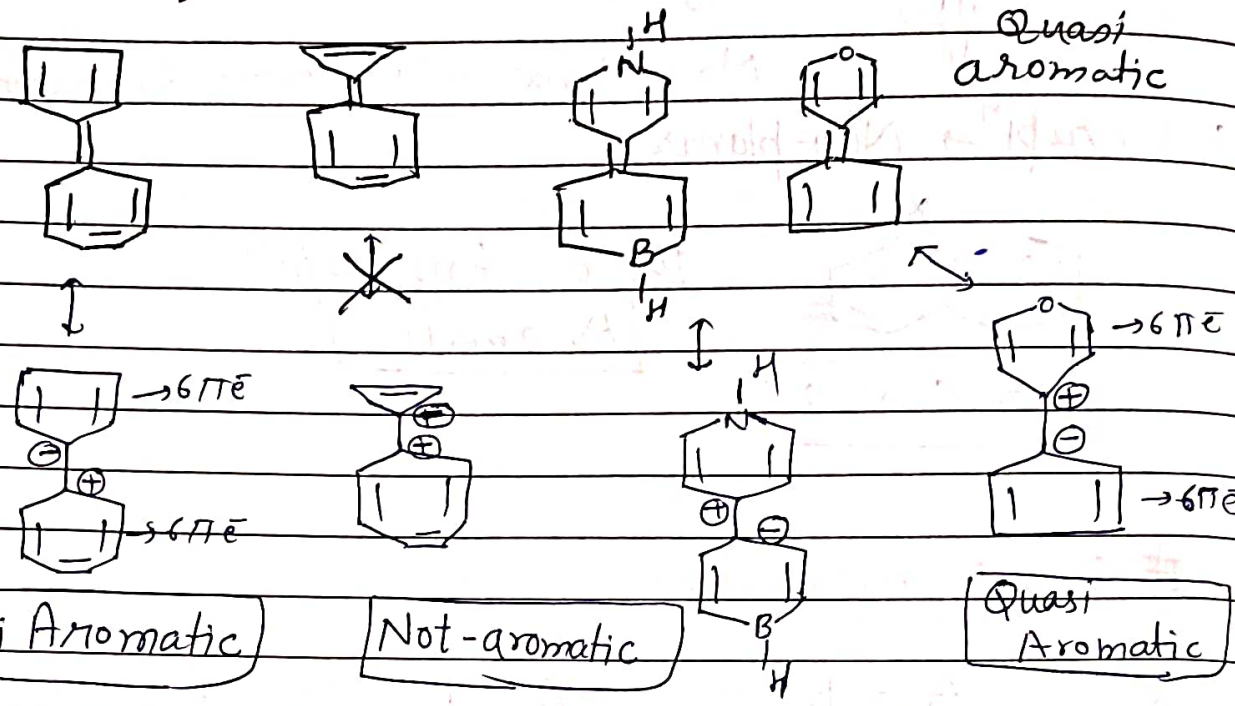


⇒ Not-Aromatic

Quasi Aromatic

- Polar forms are more stable than non-polar form
- High dipole moment
- High solubility in water
- We require low bond rotation Barrier

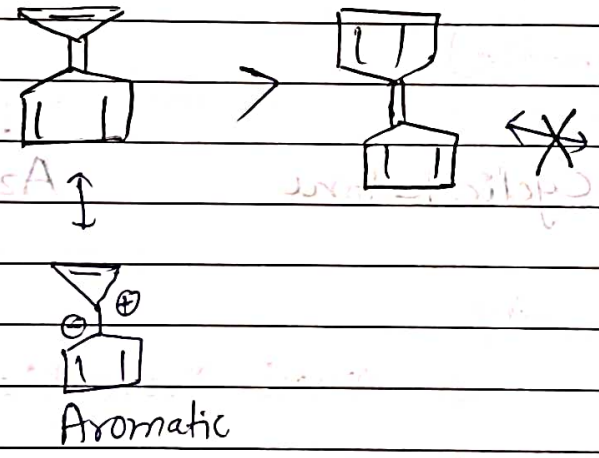
Que



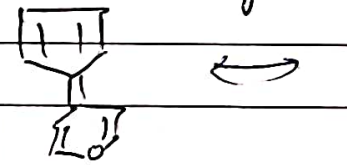
Quasi Aromatic | Not-aromatic | Quasi Aromatic

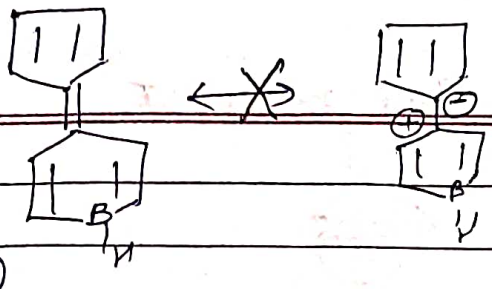
Quasi- Aromatic

Q Which compd has high dipole moment?



Q Which has high bond rotation barrier?

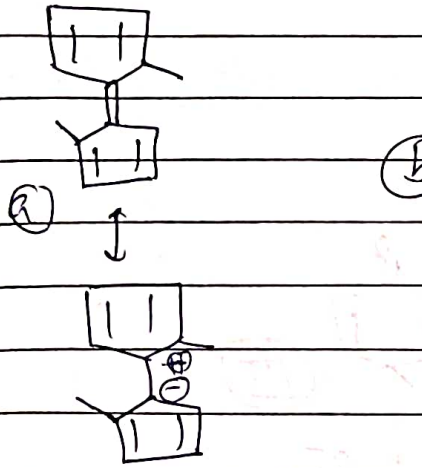




(b)

(b) has high bond rotation barrier than (a)

Q Which compd can convert in cis ↔ trans?

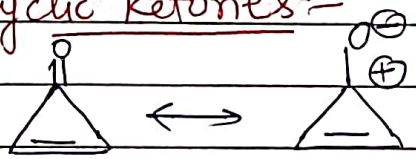


(b) is interconvertable from trans ↔ cis

Not-aromatic

Aromatic

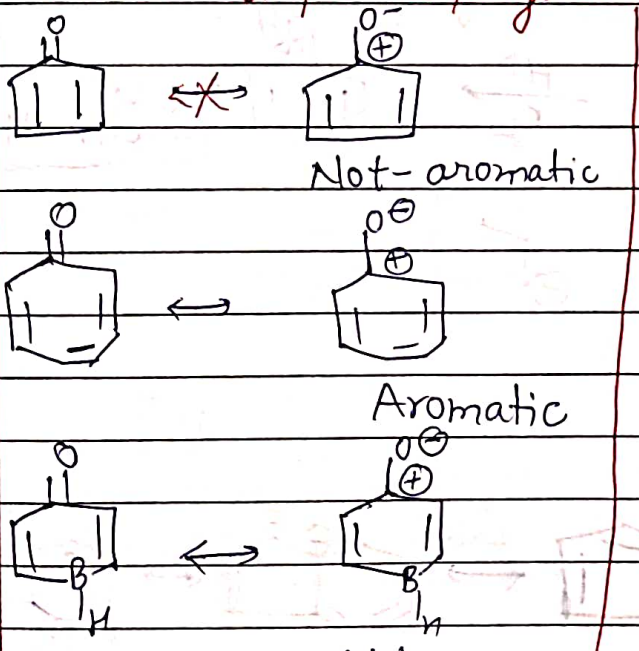
(2) Cyclic ketones:-



Quasi-Aromatic

$2\pi\bar{e}$

Q Which compd is/are aromatic?



Not-aromatic

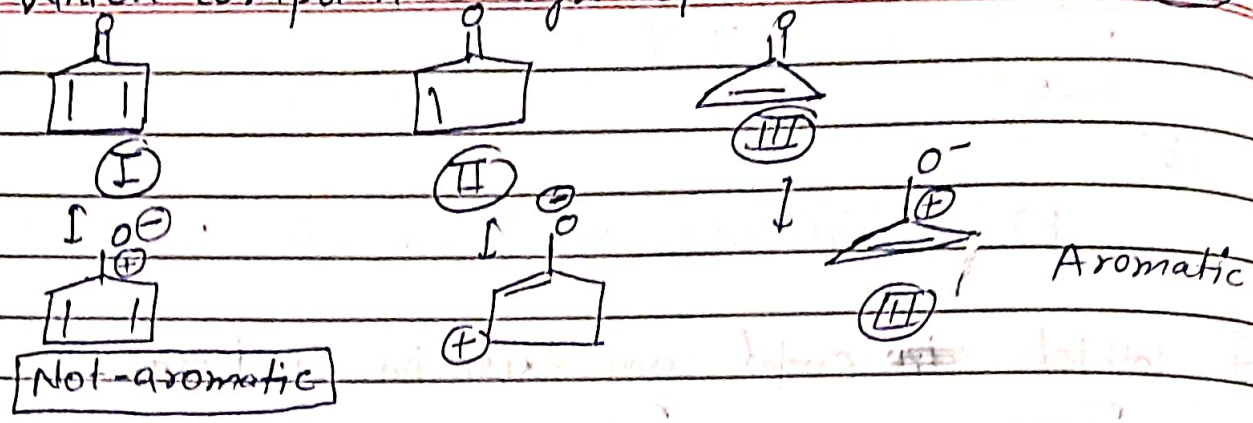
Aromatic

Aromatic

Aromatic

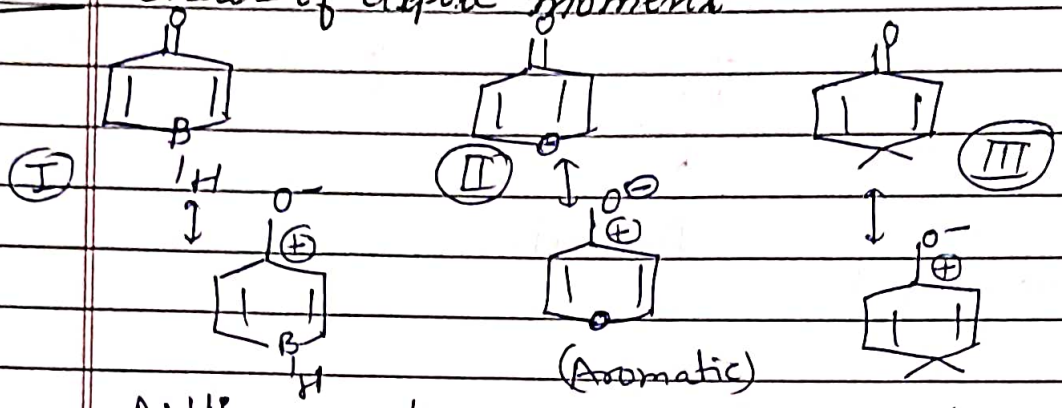
Not aromatic

Q Which compd has high dipole moment?



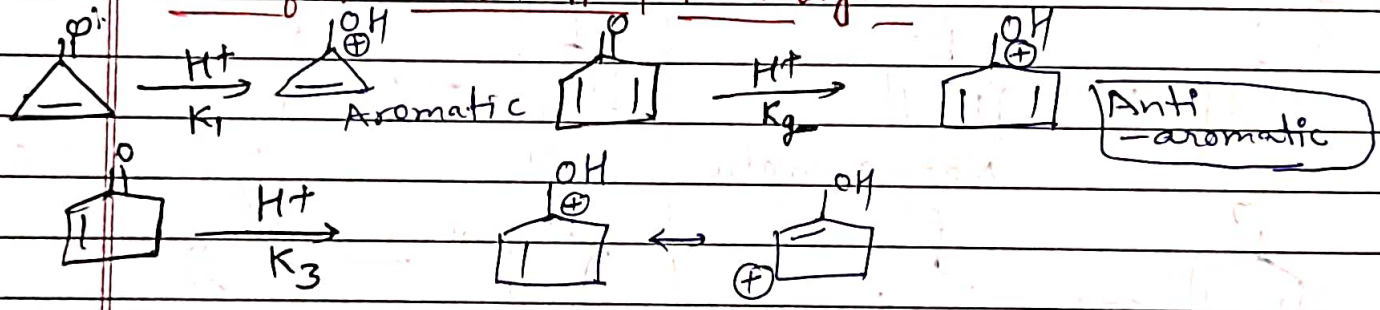
(III) > (II) > (I)

Que Order of dipole moment



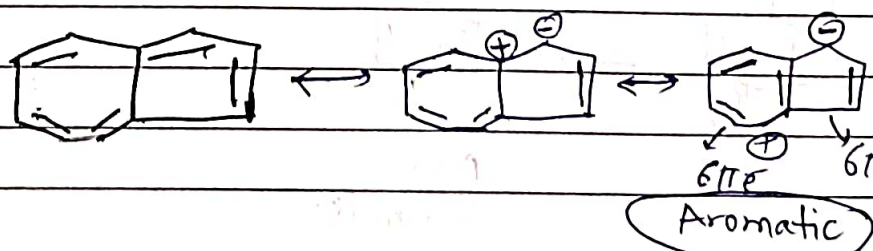
(II) > (III) > (I)

Rate of Protonation / Basicity :-



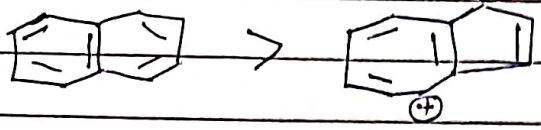
$K_1 > K_3 > K_2$

③ Azulene



↳ Polar form more stable than non-polar.
↳ High dipole moment
↳ Highly soluble in Water
↳ Azulene is less stable than napthalene

Q Which one is more stable?

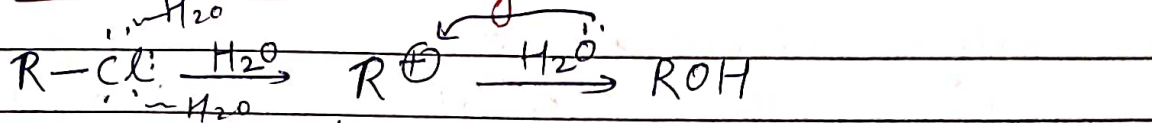


③ App^{n} of Aromaticity in Rx^{n} mechanism :-

R ⟶ [I] ⟶ (P)

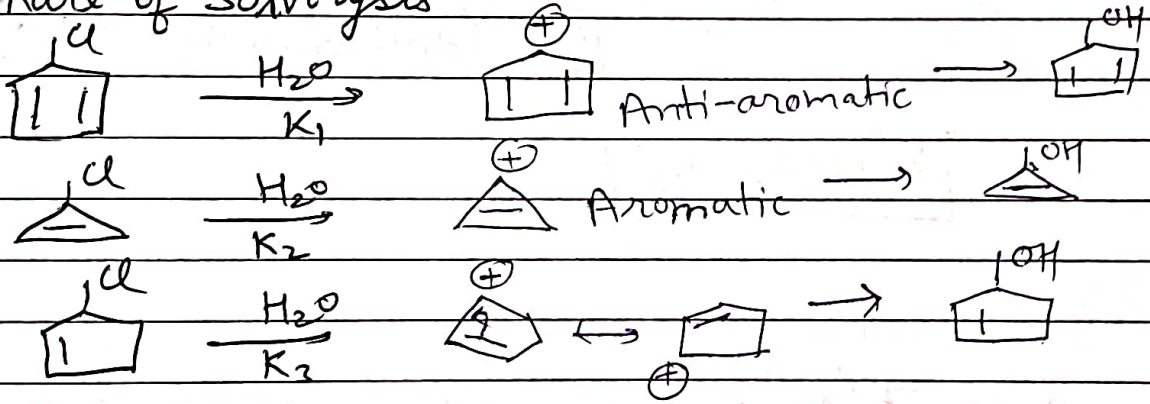
↳ Aromatic ⟶ Rx^{n} occur
↳ Anti-aromatic → Not occur

(i) In S_N1 rx^{n} (Solvolysis) :-



↳ Aromatic ⟶ Fast
↳ Non-aromatic → Moderate
↳ Anti-aromatic → slow

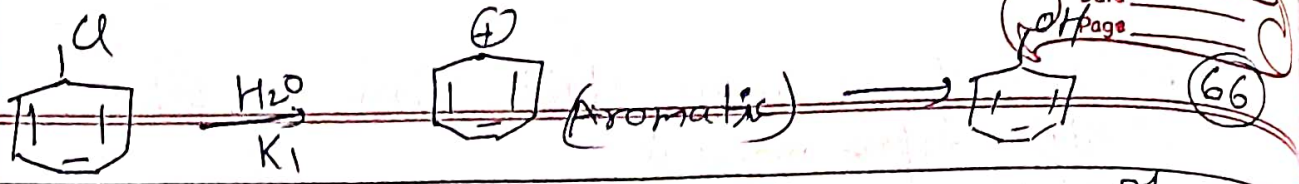
Q Rate of Solvolysis

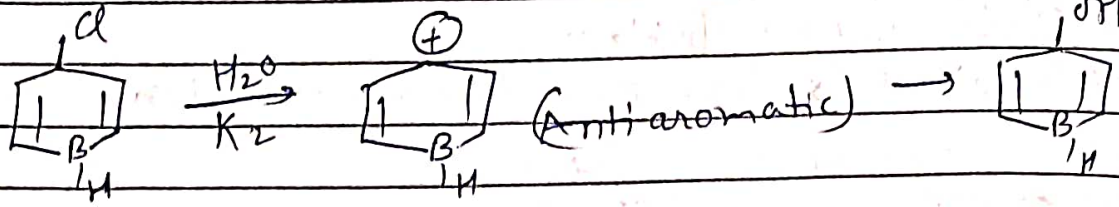


$K_2 > K_3 > K_1$

Rate of solvolysis ∝ (stability of carbocation)

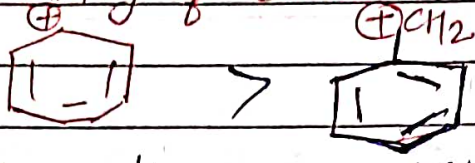
(b)





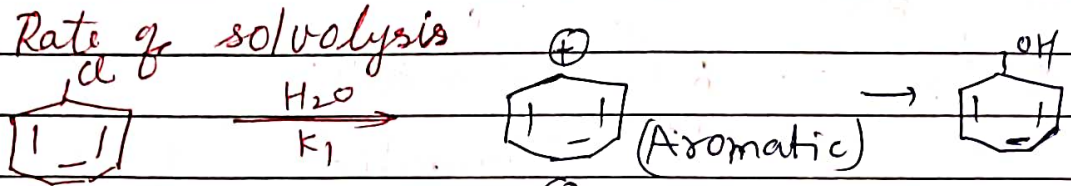
$K_1 > K_2$

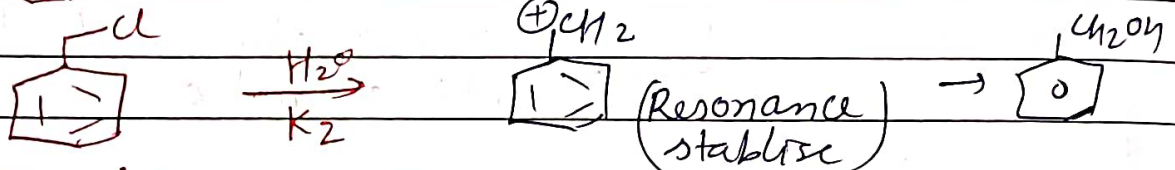
Q Stability of Carbocation

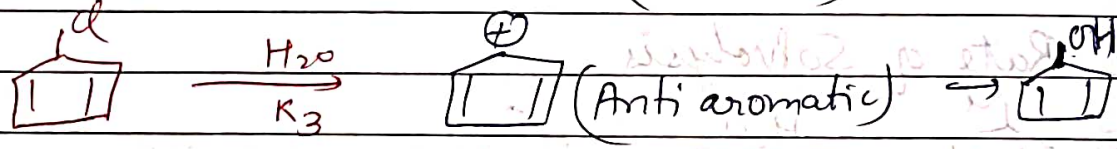


2018 I AM

Q Rate of solvolysis

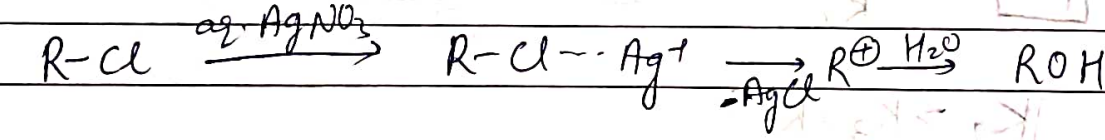




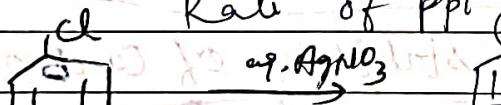


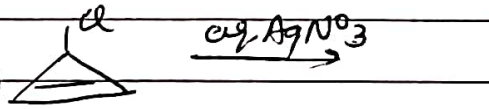
$K_1 > K_2 > K_3$

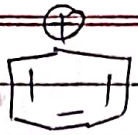
(ii) Rate of Ppt :-



Ques Rate of ppt

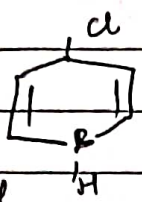
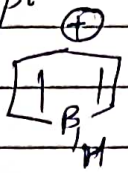
(a) 

(b) 

(c)  $\xrightarrow{aq\ AgNO_3}$  (Aromatic)

$c > b > a$

Que Rate of ppt.

 $\xrightarrow[k_1]{aq.\ AgNO_3}$  Anti-aromatic

 $\xrightarrow[k_2]{aq.\ AgNO_3}$  Aromatic

$k_2 > k_1$

(III) Effect of protonation :-

$\rangle\!-\ddot{N}H_2 + H^{\oplus} \longrightarrow \rangle\!-\overset{\oplus}{N}H_3$

sp^3 (localised lone pair) sp^3

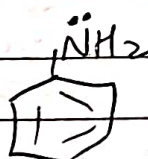
$\rangle\!=\ddot{N}H + H^{\oplus} \longrightarrow \rangle\!=\overset{\oplus}{N}H_2$

(localised lone pair) sp^2 sp^2

$\rangle\!=CH-\ddot{N}H_2 + H^{\oplus} \longrightarrow \rangle\!=CH-\overset{\oplus}{N}H_3$

(delocalised lone pair) sp^3

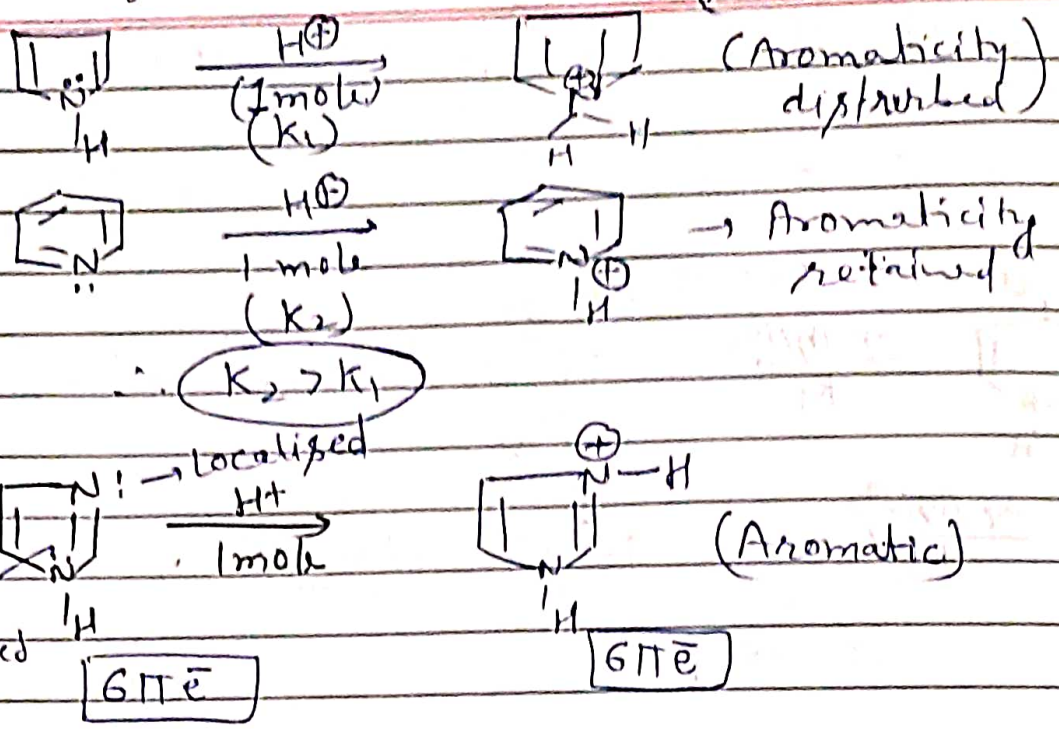
$sp^2 \rightarrow (2\pi\bar{e})$ $(2\pi\bar{e})$

Que  $\xrightarrow{H^{\oplus}}$  $(6\pi\bar{e})$

(delocalised lone pair) $N \rightarrow sp^3$

$N \rightarrow sp^2$

Q Rate of Protonation



Q

(iv) Acidic strength comparison :-

$$AH \underset{}{\overset{K_a}{\rightleftharpoons}} A^{\ominus} + H^{\oplus}$$

$$K_a = \frac{[A^-][H^+]}{[AH]} \Rightarrow K_a \propto [A^-]$$

Acidic strength $\propto K_a$

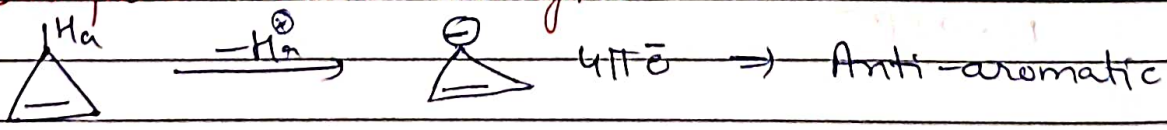
$\propto \frac{1}{pK_a}$

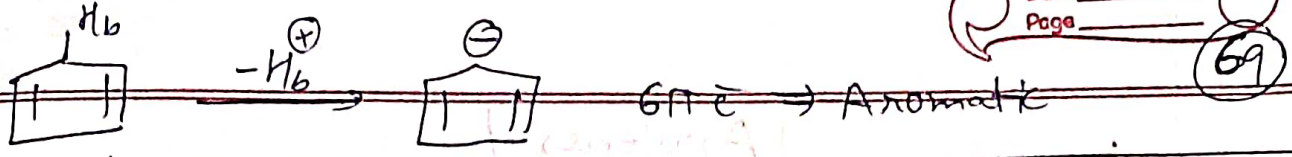
(Acidic strength) $\propto$ (Stability of anion)

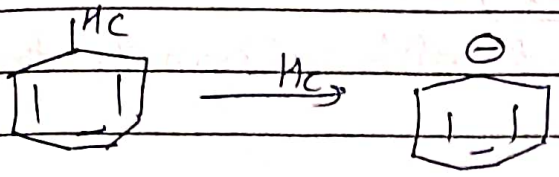
Carbanion

Aromatic	Non-aromatic	Anti-aromatic
⇓	⇓	⇓
Strongest Acid	Moderate Acid	Weak acid

Q Compare acidic strength

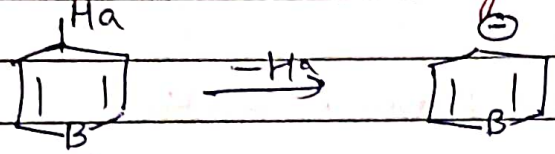


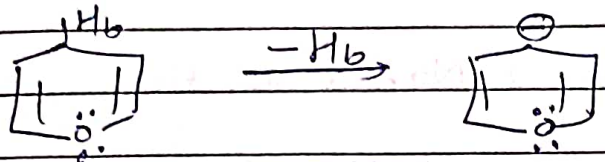




$H_b > H_c > H_a$

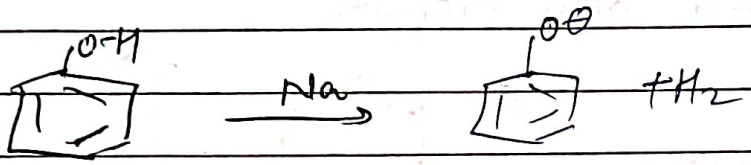
Q Compare acidic strength

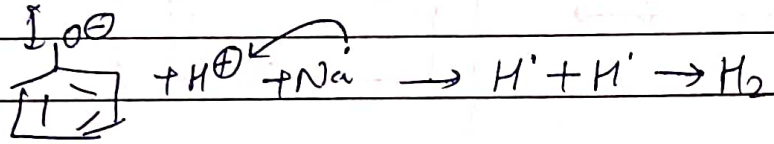




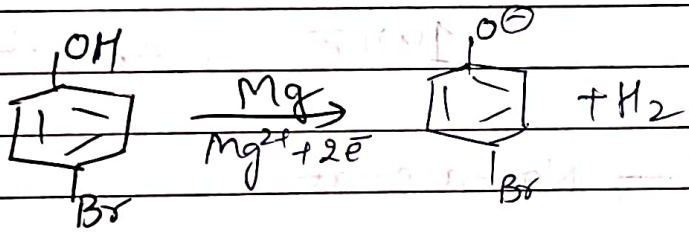
$H_a > H_b$

Que

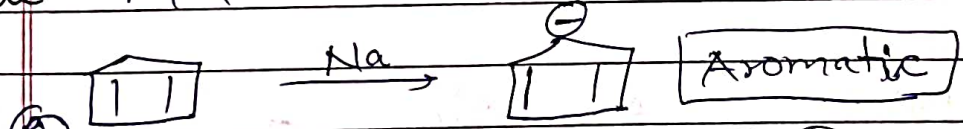




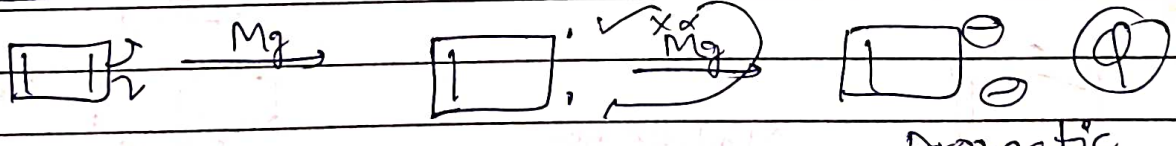
2020 JAM Que



JAM'19 Que P & Q are



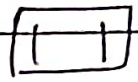
(A)



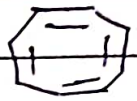
(B)

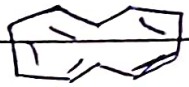
Anulenes

↳ Monocyclic compound with alternate double bond
↳ Even C-atom

 [4] Annulene ⇒ Anti-aromatic

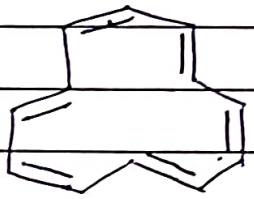
 [6] Annulene ⇒ Aromatic

 [8] Annulene ⇒ Non-aromatic

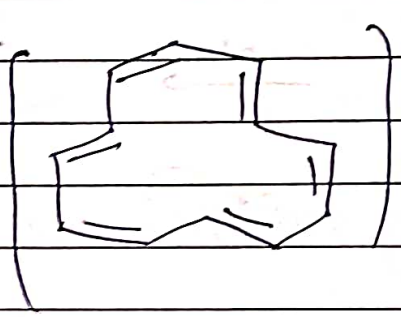
 [10] Annulene ⇒ Non-aromatic

→ [12]-Annulene

$12\pi\bar{e}$ ⟶ Non-aromatic

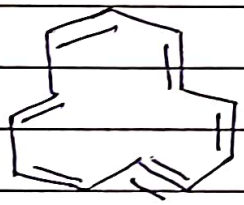


Mg



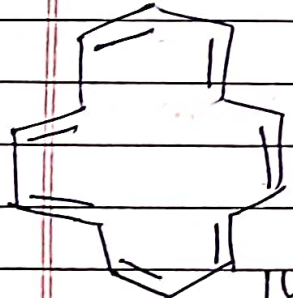
Non-aromatic

$14\pi\bar{e}$ ⇒ Aromatic

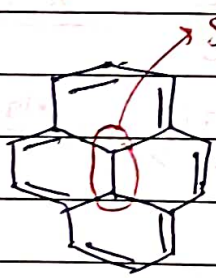
 ⇒ $12\pi\bar{e}$ ⟶ Non-aromatic

→ [14]-Annulene :-

$14\pi\bar{e}$ ⇒ Aromatic

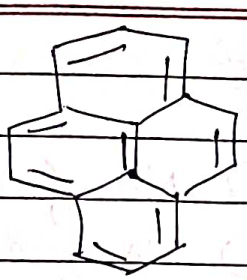


Modification



sp^3

$14\pi\bar{e}$
Aromatic

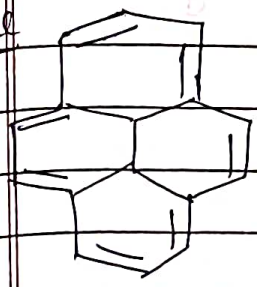


$14\pi\bar{e} \Rightarrow$ Aromatic

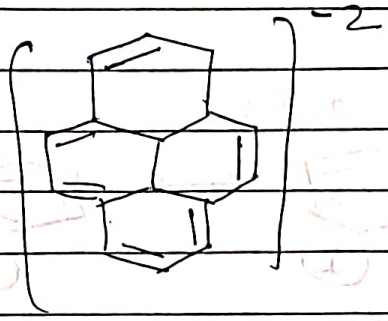
$4n+2 = 14$

$\boxed{n=3}$

Que



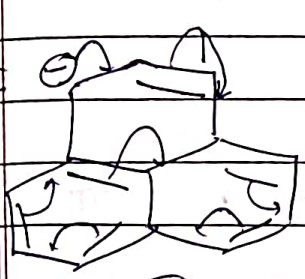
$\xrightarrow{Mg}$

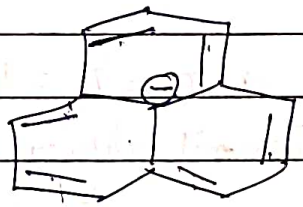


$16\pi\bar{e}$

Anti-Aromatic

Que





$n=3$

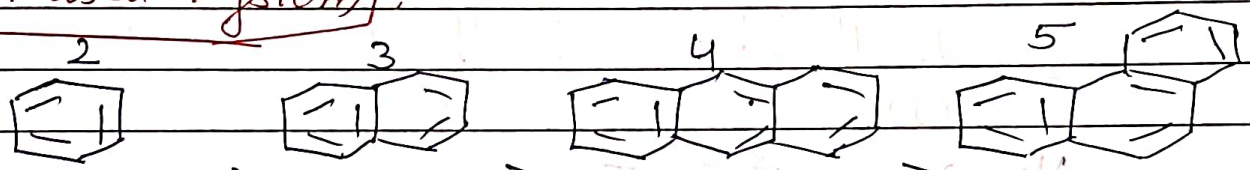
(P)

Aromatic

Aromatic

Fused System :-

No. of Rs



Aromatic Behaviour $>$ $>$ $>$

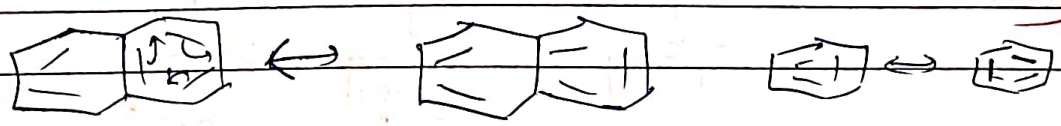
Que ① No. of Resonating structure (RS)

② Aromatic Behaviour

No. of Resonating structure

Linearly ring attached $= (n+1)$ (n = no. of ring)

non-linearly " " $= (n+2)$

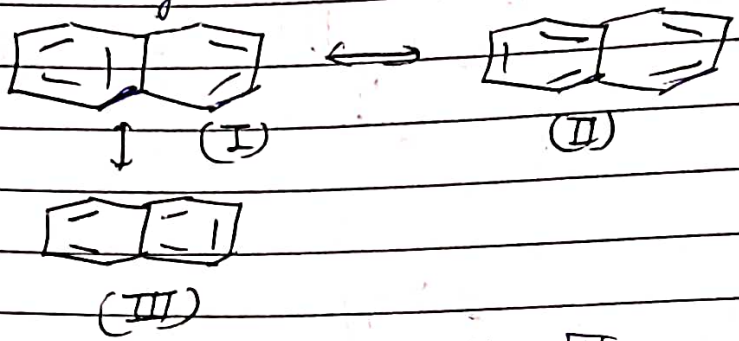


Stability of Resonating structure:-

In fused ring

Stability of R.S. $\propto$ ① No. of ring
② No. of Benzenoid ring

Que Stability order

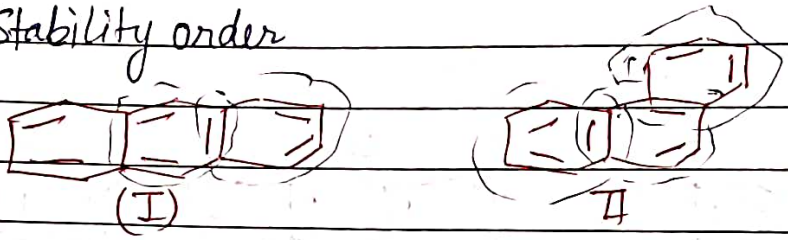


Ans No. of ring → I = II = III

No. of Benzenoid ring → I = 2 , II = 1 , III = 1

∴ Stability order **I > II = III**

Que Stability order

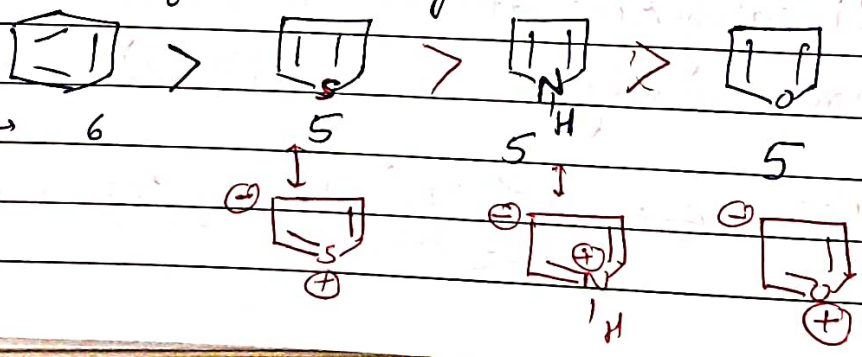


No. of ring → I = II

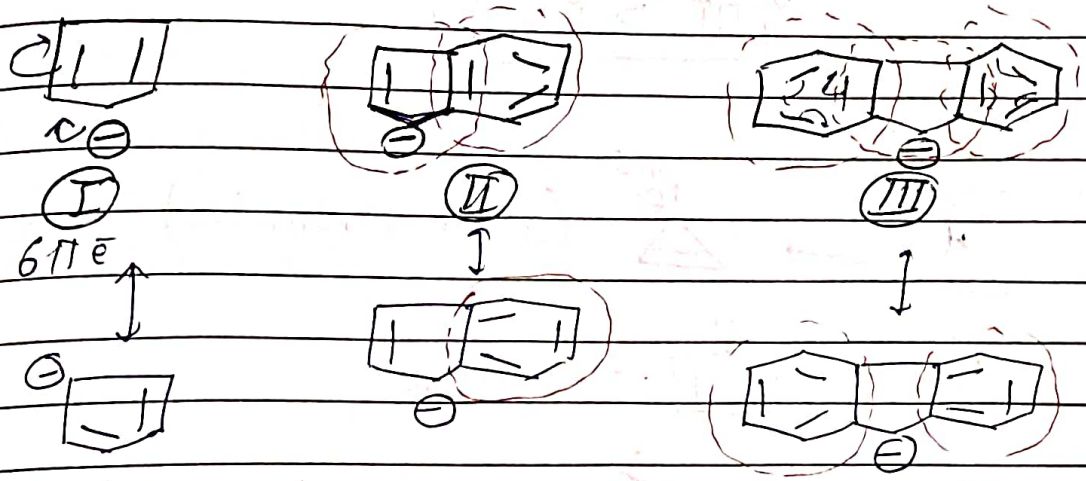
No. of Benzenoid ring → I = 2 , II = 3

∴ Stability Order **II > I**

Que Order of Aromaticity



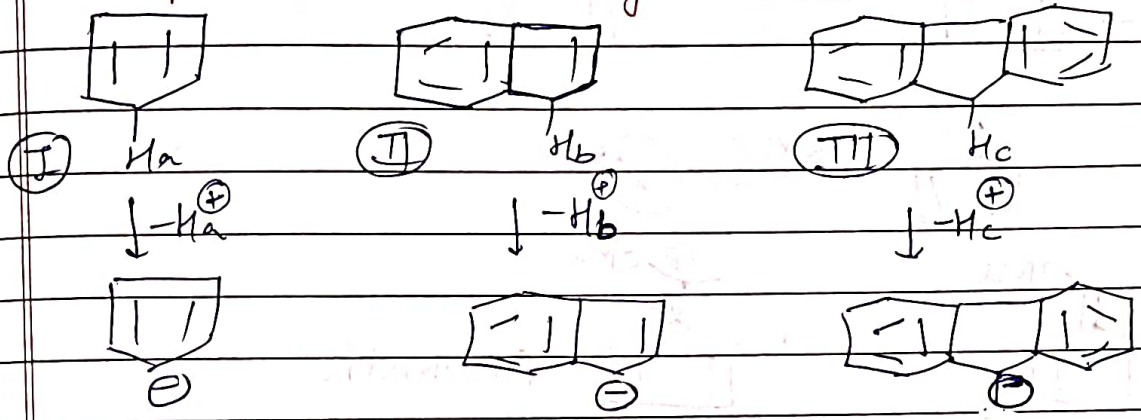
Annelation Effect :-



Stability order

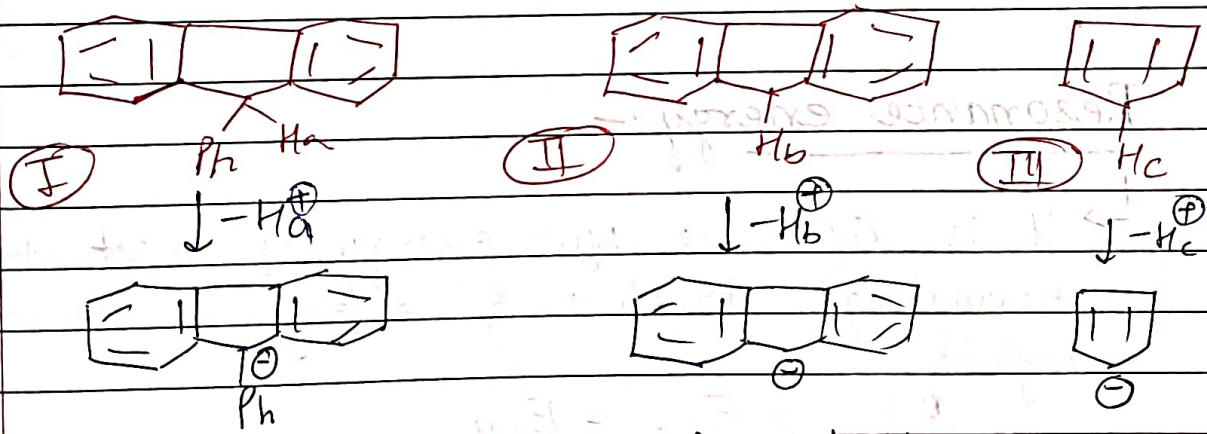
I > II > III

Que Compare acidic strength



I > II > III

Que Compare Acidic strength



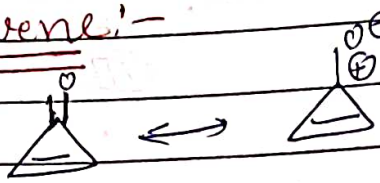
Aromaticity + Resonance

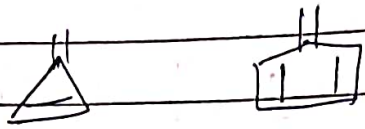
Aromaticity

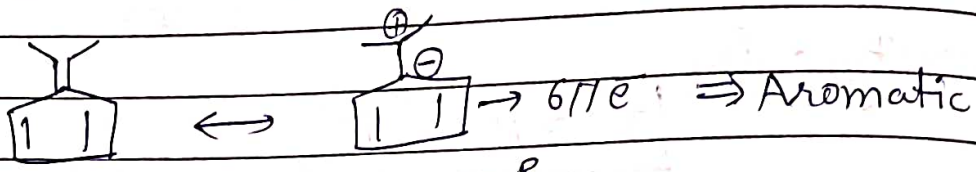
Acidic strength

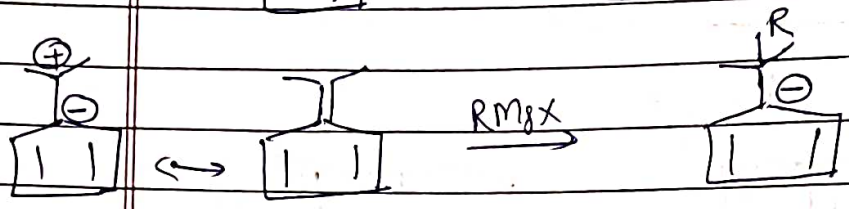
III > I > II

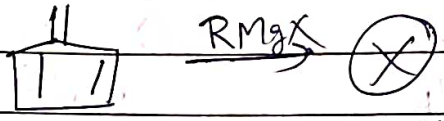
Fulvene :-

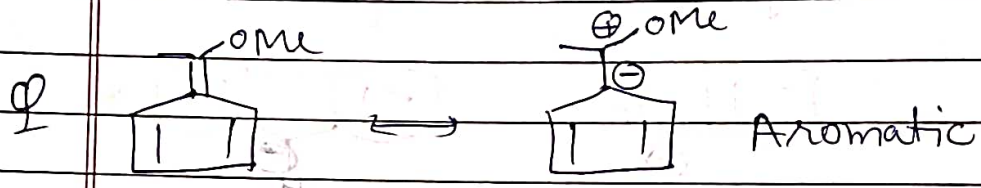












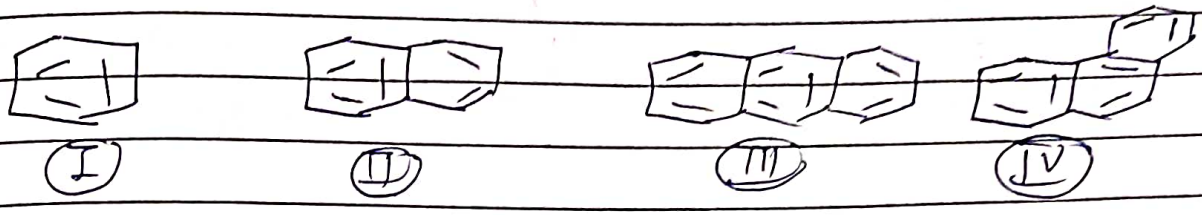
Resonance energy :-

↳ It is difference b/w energy of most stable resonating structure & energy of resonance hybrid

$$R.E. = E_{R.S} - E_{R.H}$$

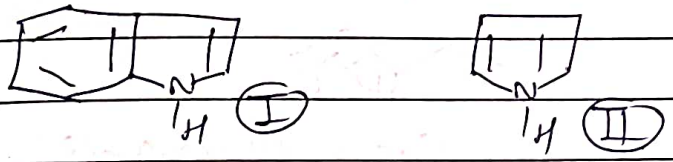
Comparison of Resonance Energy :-

Check
(1) No. of ring
(2) No. of benzenoid ring
(3) Resonance
(4) Aromaticity

Q 

Resonance energy order

Ans $\boxed{I < II < III < IV}$

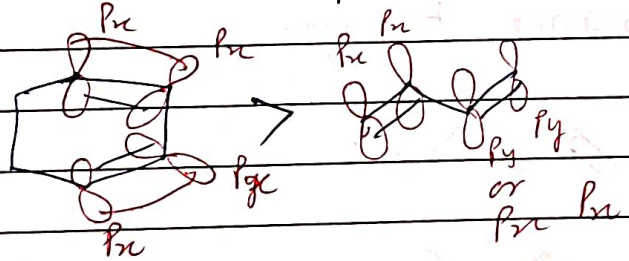
Q 

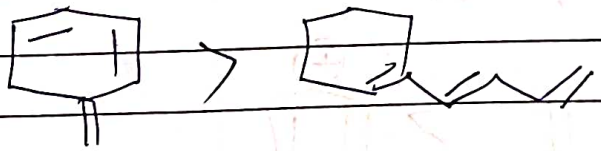
order of R.E

Ans I > II

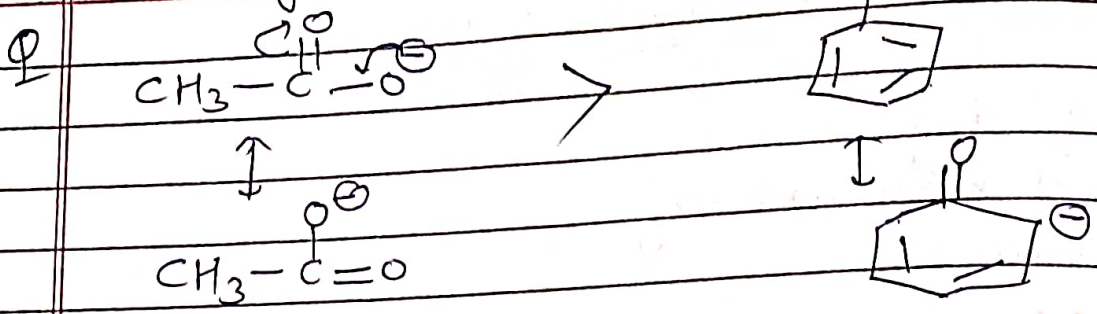
(3) Resonance :-

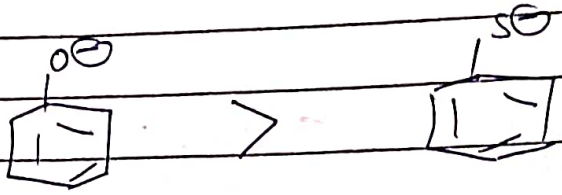
(i) Effective Resonance
(ii) Quality of Resonance
(iii) Extended / Cross Resonance



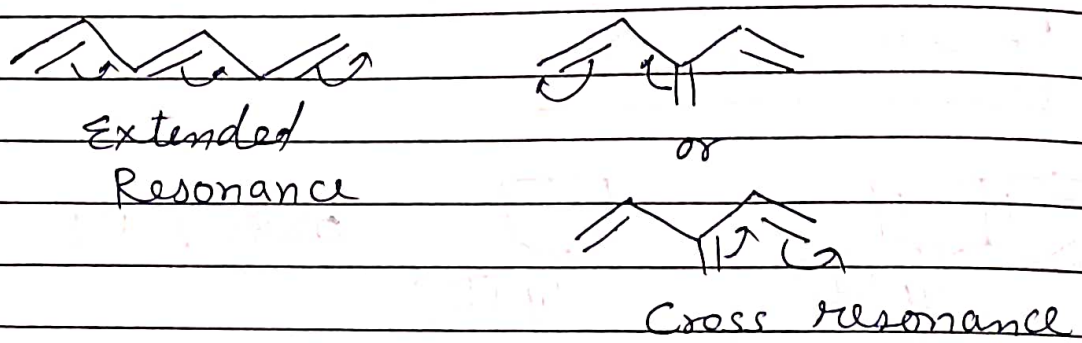
Q 

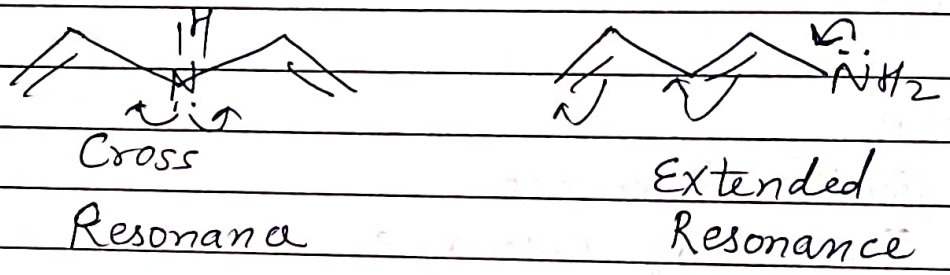
Quality of resonance

Q 

Q 

Extended / cross resonance

Q 

Q 

Q Order of Resonance Energy