: Basic strength :

— uncharged ion/species :

a) $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$

b) $HC\equiv C^{\ominus} < CH_2=\overset{\ominus}{C}H < CH_3-CH_2^{\ominus}$

c) $I^- < Br^- < Cl^- < F^-$ ⇒ Stability order in reverse order of basic strength order

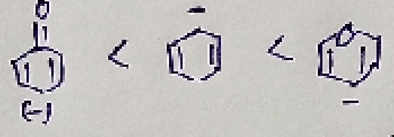
d) $TeH^- < SeH^- < SH^- < OH^-$

e) $Cl^- < CH_3-\overset{O}{\overset{\|}{C}}-O^- < OH^-$ ⇒ sp hybridised carbon is more en than N but less en than O.

f) $NH_3 < NH_2^- < NH^{2-}$

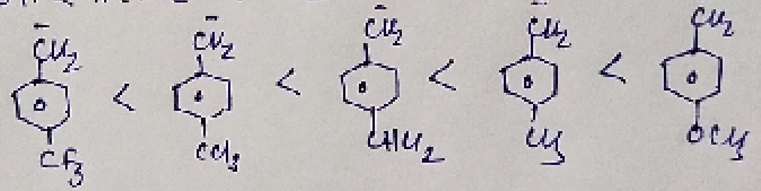
g) ~~O_2^{2+}~~ $H_2O < OH^- < O^{2-}$

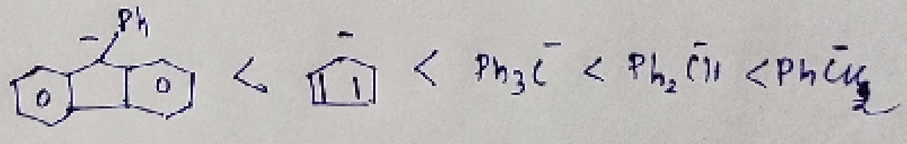
⇒ $R^{\ominus}$ is the strongest base

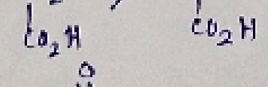
h)  ⇒ $F_3C-SO_3^-$ is the weakest organic base.

i) $HSO_4^- < H_2O < NH_3 < OH^-$

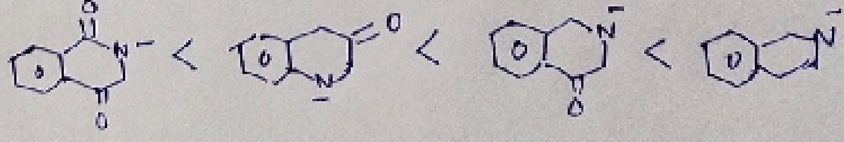
j) $OH^- < HC\equiv C^{(-)} < NH_2^- < CH_2=CH^- < CH_3-CH_2^-$

k) 

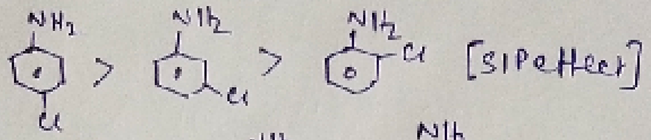
l) 

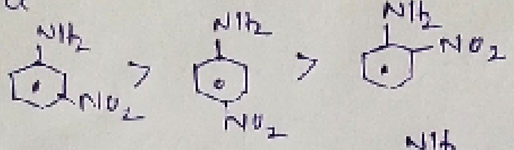
m) 

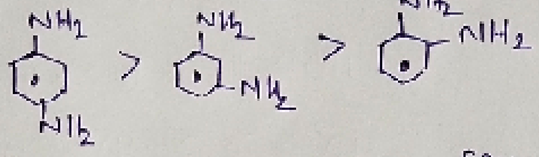
n) $H_3SO_3^- < CH_3CO_2^- < PhO^- < EtO^-$

o) 

: Aniline derivative : [Basic strength order]. 2

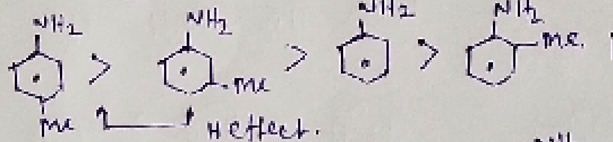
a)  [SIPeffect]

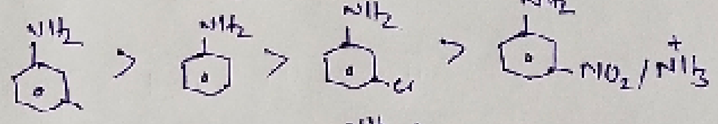
b) 

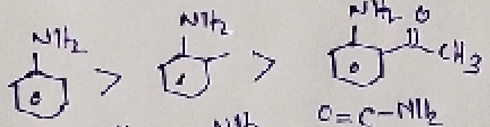
c) 

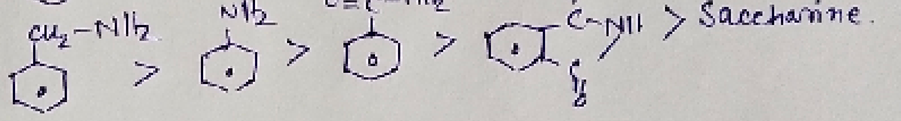
d) $PhNH_2 > Ph_2NH > Ph_3N$. [Resonance delocalisation].

e) $PhNMe_2 > PhNHMe > PhNH_2$ [+I effect].

f) 

g) 

h) 

i) 

Aliphatic Amine :

$Et_3N > Et_2NH > Et-NH_2$ (gas phase) / (Chlorobenzene medium)

321 $Me_3N > Me_2NH > MeNH_2$ (gas phase)

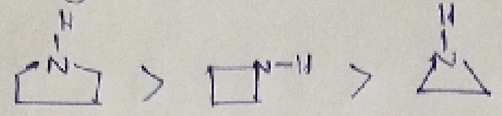
231 $Et_2NH > Et_3N > Et-NH_2$ [In aqueous medium]

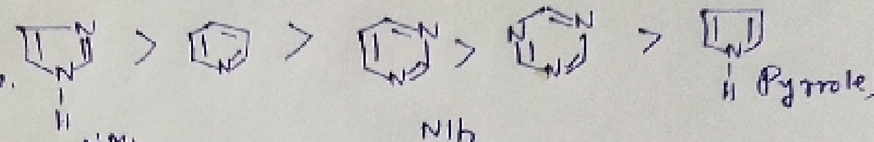
213 $Me_2NH > MeNH_2 > Me_3N$ [aq. medium]. / K_b.

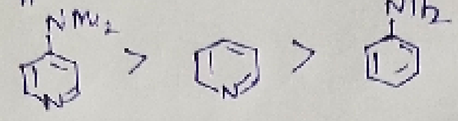
$R_4\overset{+}{N}\overset{-}{OH} > R_2NH > RNH_2 > R_3N$ (R = Me)

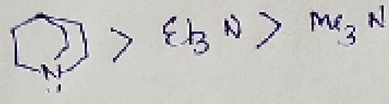
NH_3 is least basic w.r.t all in all medium

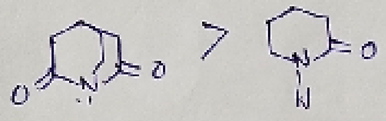
: Heteroaycylic base :

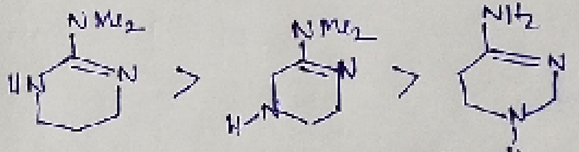
c)  ring size reduced
basic strength reduced.

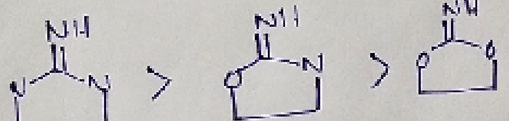
b) 
Imidazole. (Pyrrole)

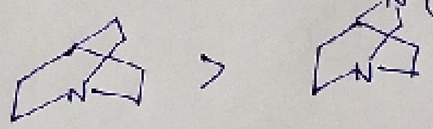
e) 

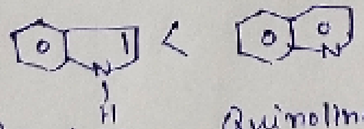
d)  9n cpd 1 (Quinuclidine) flipping does not take place.

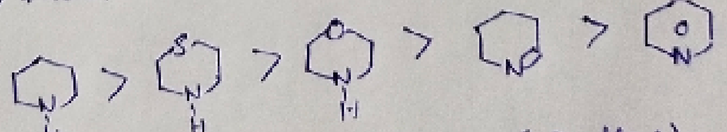
e)  9n cpd 1, N lone pair is not delocalised.

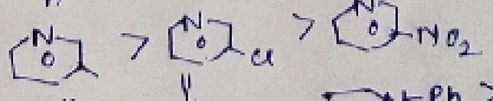
f) 

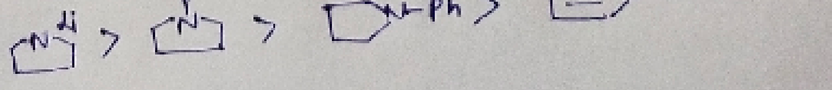
g)  +R effect N > O.

h)  (-I effect)

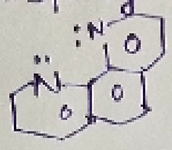
i) 
(delocalised) Indole Quinoline (localised lone pair)

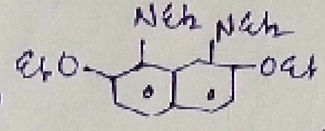
j) 

k)  (-I effect).

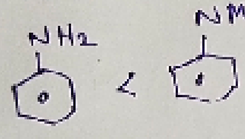
l) 

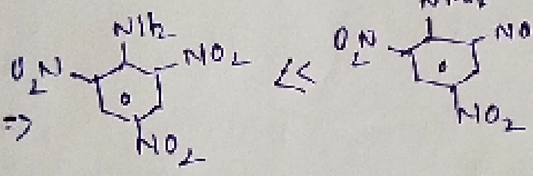
=> The following nitrogeneous bases are called proton sponge.



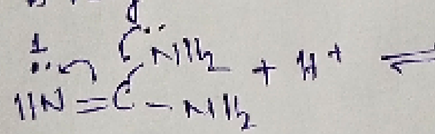


conjugate acid is stabilised through chelation. Compound itself has lone pair - lone pair repulsion (localised lone pair) which makes it very much basic.

=>  pK_b difference 0.53. (+I effect only)

 pK_b difference = 4.06. [SIR effect in 2nd cpd].

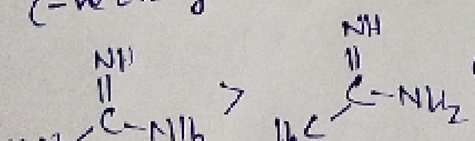
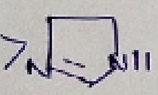
=> Compounds having guanidine type linkage is very much basic.

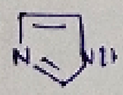


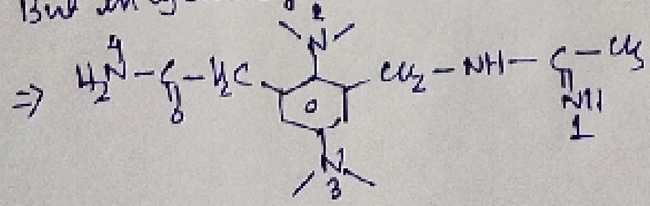
(Guanidine)

Conjugate acid. (3 identical R.S).

$\ddot{N}$ localised lone pair (-ve charge on N) ⟶ makes it very much basic.

 (ethane amidine) > 

But in cyclic system this effect is reduced. > 

=> 

Basic strength:

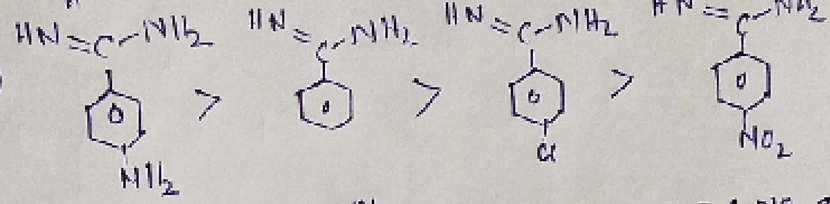
$N^4 > N^2 > N^3 > N^1$.

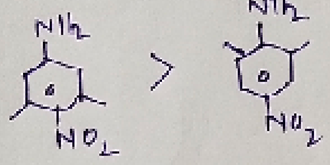
Other examples of basic strength:

i) $CH_3-CH_2-NH_2 > CH_3-CH=NH > CH_3-C\equiv N$

ii)  $> CH_2=CH-CH_2-CH_2-NH_2 > CH_3-CH-CH_2-CH=NH$

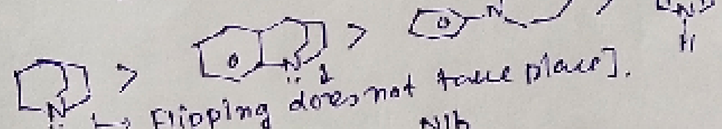
$> CH_2=CH-CH=CH-NH_2$

iii) 

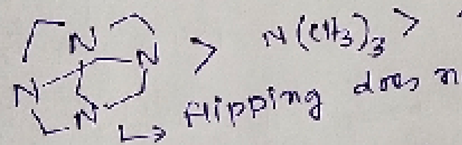
iv) 

In Ist cpd SIR ($-NO_2$ only $-I$)

In 2nd cpd SIP.

v) 

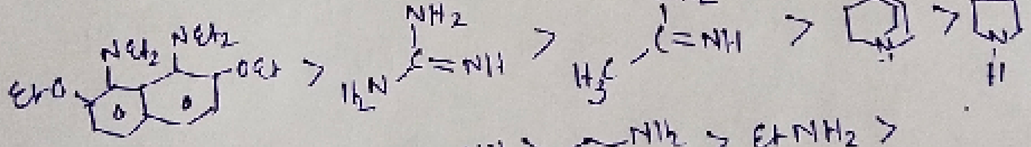
↳ Flipping does not take place].

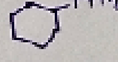
vi) 

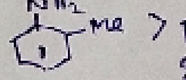
↳ Flipping does not take H place.

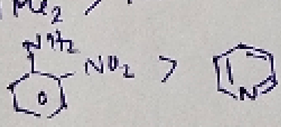
General order of basic strength (Nitrogeneous).

pKa order ≡ Basic strength order.



$> Et_2NH > Et_3N > Me_2NH >$  $> EtNH_2 >$

$> PhNMe_2 > PhNHMe > PhNH_2 >$ 

$>$ 

$>$  $> MeC\equiv N.$

⇒ Conjugate acid of Pyrrole is non aromatic.