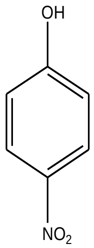
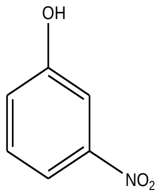
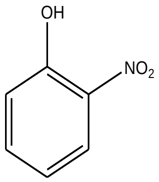
- **Compare the acidity of the following nitrophenol.**



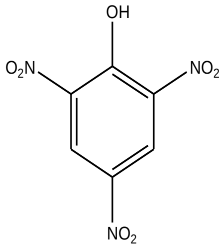
A



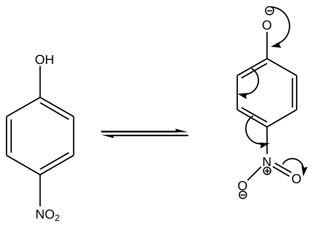
B



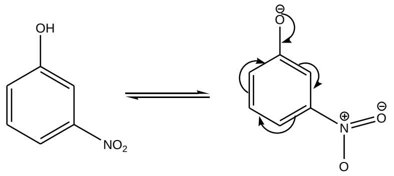
C



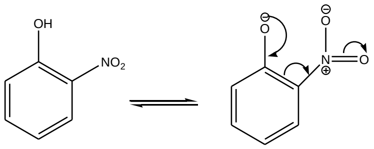
D



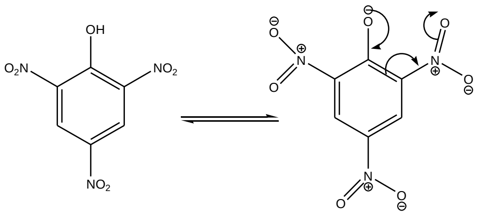
Here -ve charge over phenoxide ion is delocalized with benzene ring as well as with nitro group in p-position due to -R effect of $-NO_2$ group. -I effect of NO_2 group disperse the -ve charge also.



Here -ve charge over phenoxide ion is delocalized only with benzene ring but nitro group do not participate in resonance with phenoxide ion . Only -I effect of NO_2 group disperse the -ve charge .

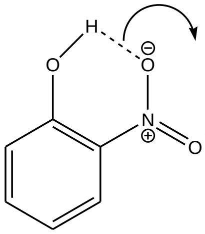


Here -ve charge over phenoxide ion is delocalized with benzene ring as well as nitro group in o- position. -I effect of NO_2 group disperse the -ve charge also.



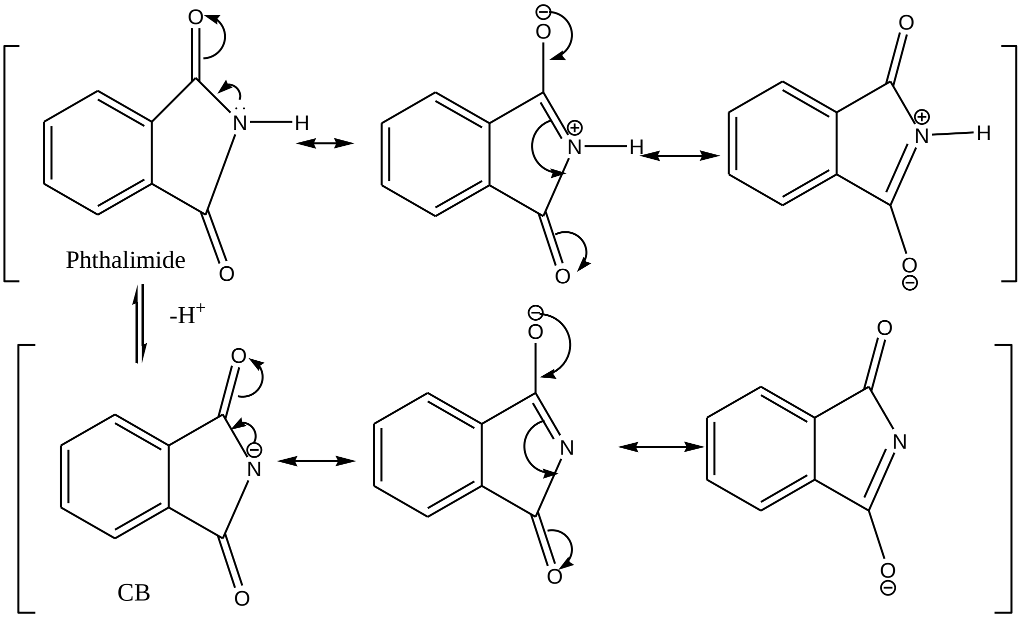
Here -ve charge over phenoxide ion is delocalized with benzene ring as well as 3 nitro group . -I effect of NO_2 group disperse the -ve charge also.

So dispersion of negative charge and hence stability of CB of D (**picric acid**) is maximum and B is minimum and acidity order is D > A > C > B, Here o- is less acidic than p- because there is intramolecular hydrogen bonding in o-nitrophenol which decrease the tendency to lose proton from o-nitrophenol.



Intramolecular
H-bonding
So lose of the -O-H
proton is difficult, so acidity
decreases

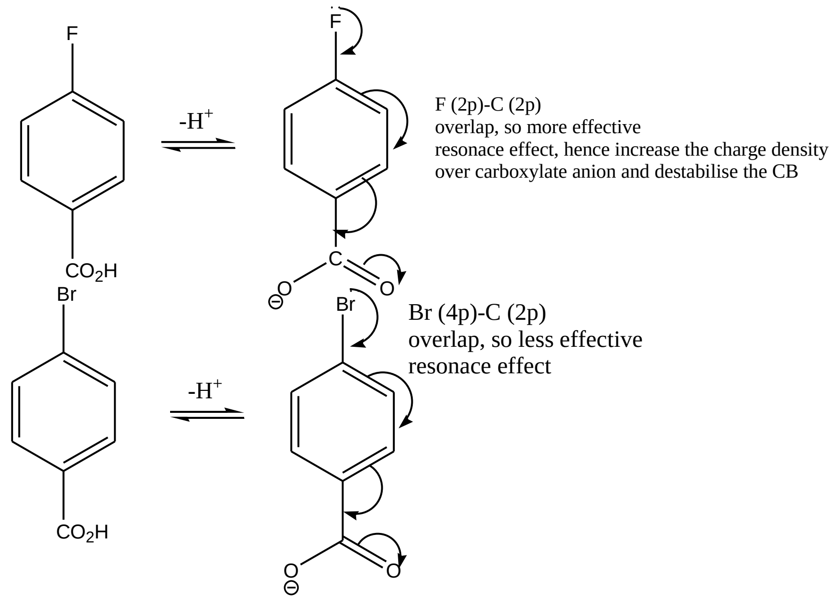
Q. Imides (phthalimide) are sufficiently acidic and dissolve in alkaline metal hydroxide solution to form salt-explain.



In case of the imide, N-H group have two adjacent carbonyl groups, so both phthalimide and its CB are resonace stabilized because both have three resonating structures. But the resonance stabilization is greater in CB than neutral molecule because in the former case there occurs no charge separation. As the CB is more stabilized, therefore ionization is more favourable i.e., the compound show considerable acidity.

Q. Although F is more electronegative than Br but p-fluorobenzoic acid is less acidic than p-bromobenzoic acid- explain.

F more electronegative than Br i.e., -I effect of F is greater than that of Br which decreases the charge density of benzene ring, But +R effect of F (use 2p orbital) is much greater than Br (use 4p orbital). In fact +R effect and –I effect are counterbalanced but +R effect of Br is much weaker than –I effect. Therefore although both halogen atom tend to decrease the charge density of the ring , but the lowering is much effective in bromo acid. So the charge density of CB of p-fluorobenzoic acid is greater than that of p-bromobenzoic acid. Hence p-fluoro acid is weaker than p-bromo acid.

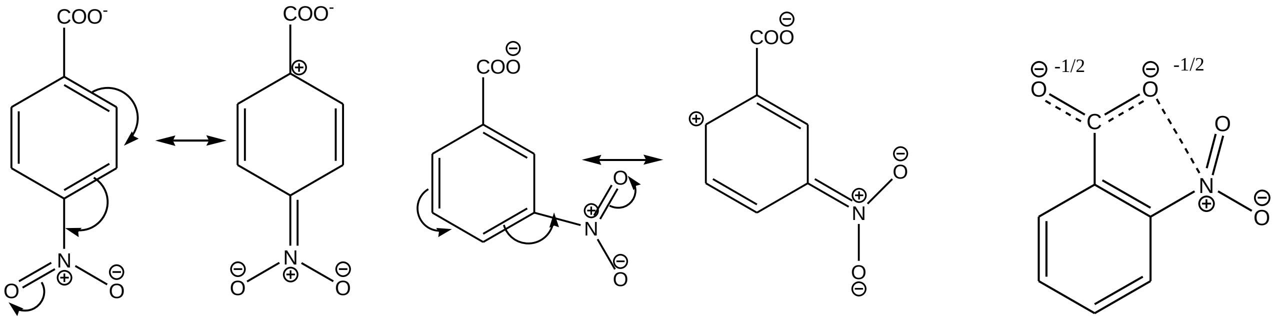


F (2p)-C (2p) overlap, so more effective resonace effect, hence increase the charge density over carboxylate anion and destabilise the CB

Br (4p)-C (2p) overlap, so less effective resonace effect

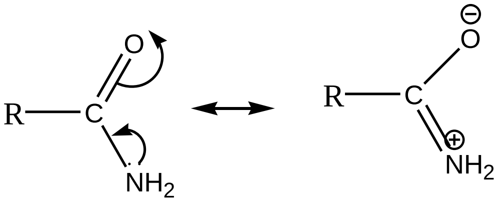
Q. **p-Nitrobenzoic acid is stronger than its m- isomer but much weaker than o-isomer- explain.**

In case of CB of o- and p- isomers, -R effect of –NO_2 group decrease the charge density of carbon attached with the –COO^- group. So dispersion of negative chage of -COO^- is greater but in case of m-isomer, only –I effect of –NO_2 group is effective but –R effect cannot decrease the carge density of C attached to –COO^- group. So here –ve charge of –COO^- is not dispersed effectively. So CB of o- and p-isomer is more stable than that of m-isomer. Hence o- and p-nitrobenzoic acid are stronger than m-isomer. Again o- isomer is more acidic than p-isomer because the CB of o-isomer is further stabilized by electrostatic interaction between carboxyl and nitro group as well as NO_2 group exerts more -I effect because of very short distance.



- **Amides are less basic than amine-explain.**

The basicity of a base depends on the availability of lone pare. Higher the availability, higher will the basicity. Because of –I effect and –R effects of C=O group, the unshared electron pair of amide nitrogen is less available for coordinating with proton. In case of amine +I effect of alkyl group attached with N push electron density towards N atom and increases the charge density over N. So make the lone pair more available for sharing. Hence amides are less basic than amines



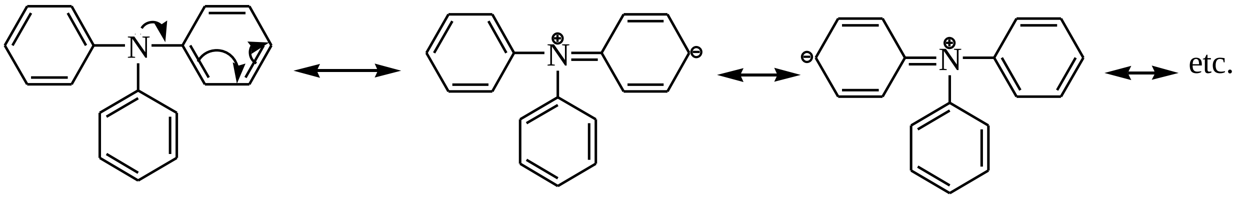
$R-CH_2-\ddot{N}H_2$

Amine

This lone pair is engaged in resonance
with C=O group, so less available for sharing.

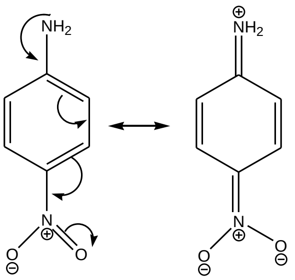
- **Triphenylamine (Ph_3N) is not at all basic-explain.**

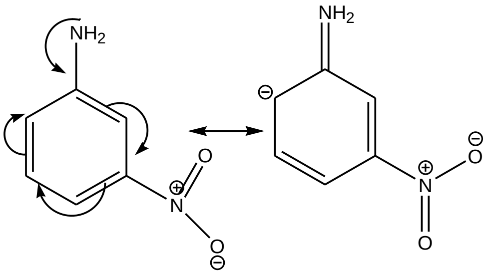
Because N lone pair is highly delocalized over three benzene rings so N it is not available for sharing. So the compound has no basic strength.



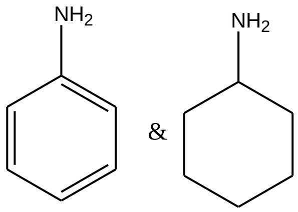
- **P-Nitroaniline is less basic than m-nitroaniline-explain.**

Nitro group in the p- position withdraw the unshared electron pair on N of NH_2 group by –R aand –I effect and thereby makes the lone pair less available. On the other hand nitro group in m-position cannot enter into resonance with NH_2 group because it is not in proper conjugation with unshared pair of electron on N. Only a weak inductive effect (-I effect) operates. So availability of lone pair is better in case of m-isomer hence m-nitroaniline is more basic.

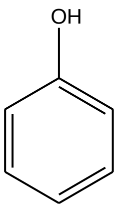




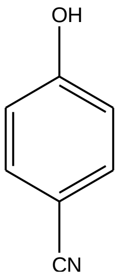
Q. Compare the basicity of



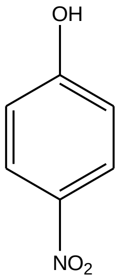
Q. Compare the basicity of



I



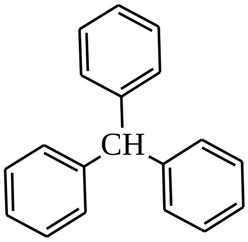
II



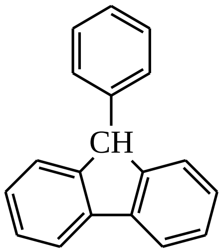
III

Ans: As CN and NO_2 group have –R effect so these groups helps to disperse the negative charge over phenoxide ion and stabilize the corresponding CB and increases the acidity of corresponding acid. Now as the –R effect of NO_2 group is greater than CN group so NO_2 group disperse the negative charge of CB more than CN group. Therefore the acidity order is III > II > I.

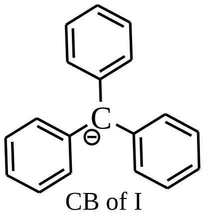
- **Explain the acidity of**



pKa 31.5

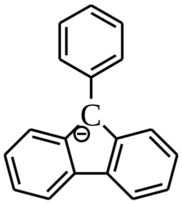


18.5



CB of I

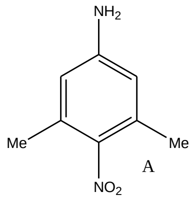
This -ve charge is not fully delocalised
because three Ph ring are not coplanner
due to steric effect of ortho Hs of adjacent ring
so stability of this CB is less and acidity
of corresponding acid is lower.



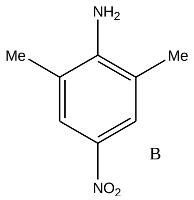
CB of II

This -ve charge is fully delocalised
because two Ph rings are tied together
by removing ortho hydrogens and
ensures coplanarity.
so stability of this CB is higher and acidity
of corresponding acid is greater.

Q. Explain the basicity order :



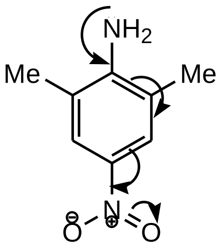
A

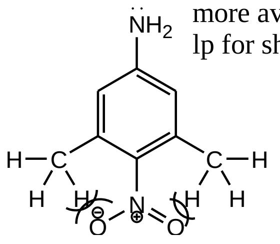


B

Pka 2.49 0.95

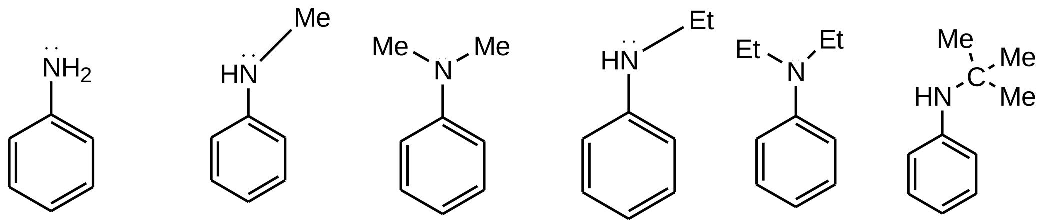
From the data it is found that A is more basic than B. In case of A, N lone pair of amine is not involved in conjugation with NO_2 group because NO_2 group are not coplanar with benzene ring due to bulk effect of (Steric interaction) two ortho methyl groups (This is called steric inhibition of resonance). So Lone pair of amine group is more available for sharing and basicity is higher. But in case of B, steric inhibition of resonance is not happen because hydrogens of the amine group are small in size than O of nitro group and so steric interaction between amine groups and two ortho methyl groups is not possible. Therefore this lone pair is engaged in resonance with nitro group at p-position and less available for sharing.Thus A is more basic Than B.





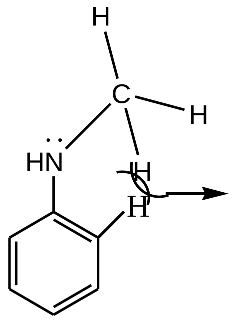
more available
lp for sharing

- N-alkylated anilines are strong base than anilines. This is due to steric inhibition of resonance which arises from the steric interaction between N-alkyl groups and o-hydrogens. Thus we can see the following acidity order. With increasing bulkiness of N-alkyl gr. Or with introducing second alkyl group basicity will increases.

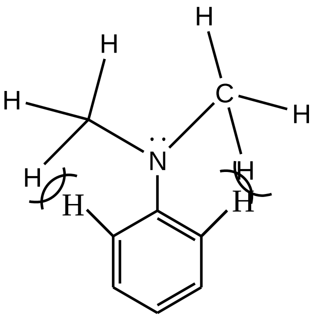


Pka 4.58 4.85 5.06 5.11 5.56 7.11

Basicity increases

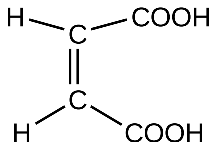


Steric interaction between
N-alkyl gr. and o-H

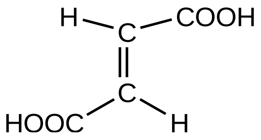


Hydrogen bonding effect

Consider the acidity of maleic acid and fumaric acid.

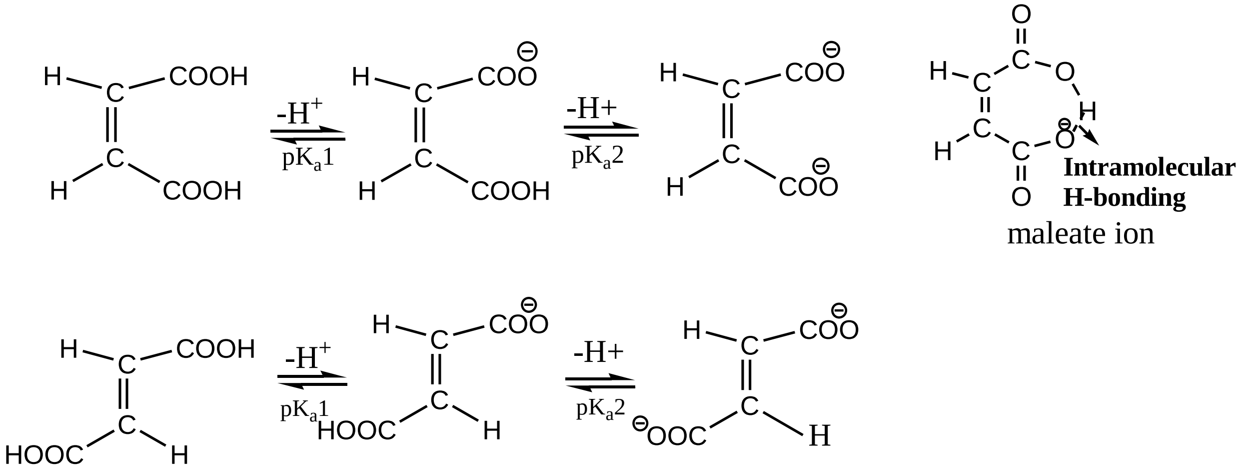


Maleic acid



fumaric acid

	Maleic acid	fumaric acid
Pk_a^1	1.92	3.02
Pk_a^2	6.23	4.38



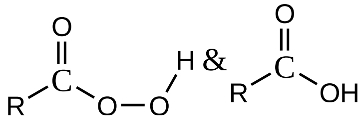
From the data it is observed that release of first proton is easier for maleic acid than fumaric acid ($Pk_a^1 < Pk_a^2$), but release of 2nd proton is easier for fumaric acid than maleic acid.

After losing first proton, the carboxxyalte ion is stabilized by forming intramolecular hydrogen bonding in case of Maleic acid or cis- butenedioic acid. But such Stabilization factor is absent in case of CB of fumaric acid. So release of first proton is easier for maleic acid than fumaric acid.

After the departure of first proton in both acids, we have a carboxylate anion, which exerts +I effect and makes the release of second proton difficult for both case.

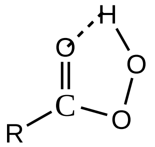
But after release of 1st proton, the carboxylate ion of maleic acid (i.e., maleate ion) gets stability therefore it has lower tendency to release the 2nd proton and therefore it has higher Pk_a^2 than that of fumaric acid.

- Compare the acidity of



As the peroxyacid R-COOOH is stabilized through intramolecular hydrogen bonding so release of proton from this acid is more difficult. No such intramolecular hydrogen bonding is not possible in case of simple carboxylic acid.

Again the negative charge of carboxylic acid i.e., carboxylate ion is more dispersed through resonace with two equivalent resonance but the CB of peroxyacid lack any dispersion of negative charge.



Similar trends:

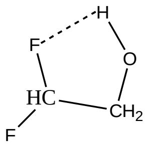
CH_3CH_2OH (Ethanol) & CH_3CH_2OOH (Hydroperoxyethane)

pKa 15.9 11.8

H_2O (Water) & H-O-O-H (Hydrogen peroxide)

pKa 15.74 11.6

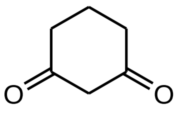
CHF_2CH_2OH



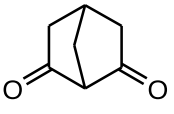
& CH_3CF_2OH

Bridge head carbon and acidity

Compare the acidity of

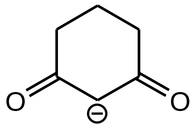


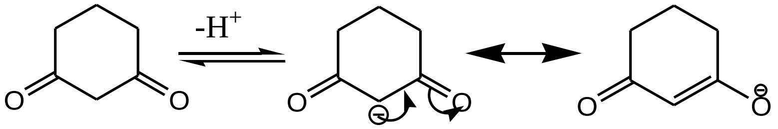
&



A B

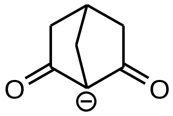
In case of A the conjugate base is Here the –ve is dispersed through conjugation with two carbonyl groups.

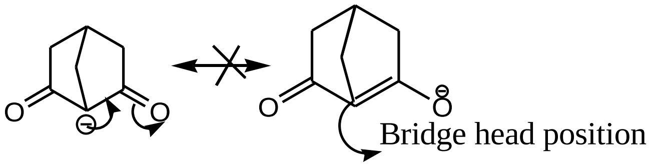




Thus methylene protons, flanked by two carbonyls are very acidic.

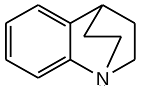
But in case of B the conjugate base is Here above type of dispersion of -ve charge is not possible because it will introduce double bond to bridge head position which is not possible according to Bredt’s rule.



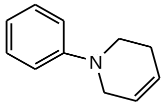


Thus bridge head protons are not acidic at all.

- **Compare the basicity of**



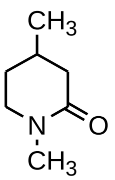
A

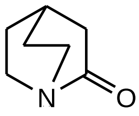


B

Here A is more basic than B because lone pair of electrons on N of A is not involved in resonance with neighboring benzene ring as it is in bridge head position. So more available for sharing and therefore more basic. But the said lone pair of B is engaged in resonance with neighboring benzene ring and thus less available for sharing and less basic.

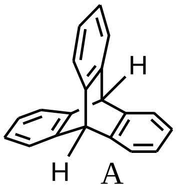
- Compare the basicity of





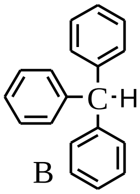
Compare the acidity of

Here CB of B is more stable because here -ve charge is partially delocalised but in case of CB of A -ve charge cannot be delocalised with neighboring three Ph ring as it is in bridge head position. so B is more acidic than A.

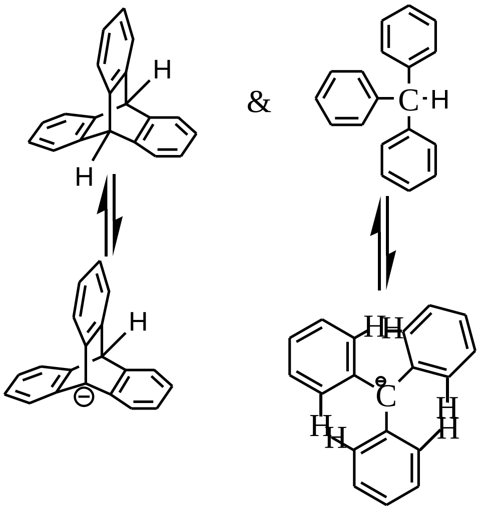


A

&



B



Solvation effects:

Solvation plays an important role in the strength of acid and bases. In the absence of solvent, i.e., in the gas phase most acids are far weaker than they are in aqueous solution.In the gas phase acetic acid has pKa value 130 where as in aq. solution pKa value is 4.76. This means in aq. solution acidity increases many folds. Because in the aq. Solution both acetate ion and H_3O^+ ions are highly solvated in comparison to acetic acid itself. But no such possibility arises in gas phase. Thus in aq. solution equilibrium will be favouring the dissociation of acetic acid much more in comparison to that in the gas phase. Thus we have the above acidity order.

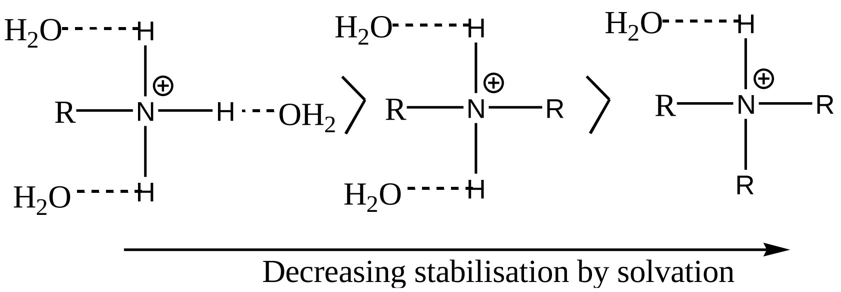
Let us consider the basicity of ammonia and three types of aliphatic amines i.e., NH3, RNH_2, R_2NH, R_3N.

If we consider the increasing +I effect of the alkyl group then the basicity order will be

$NH_3 > RNH_2 > R_2NH > R_3N$. Because with increasing alkyl group , +I effect increases which increases the availability of lone pair of N.As a result of this basicity increases.**This order is in gas phase.**

But in polar protic medium such as H_2O, the actual basicity order will be $NH_3 > R_3N > RNH_2 > R_2NH$.

Basic strength of an amine in water is determined not only by electron availability on the nitrogen atom but also by the extent to which the CA can undergo salvation and get stability. The more hydrogen atom attached to the N atom in CA the greater the possibility of powerful salvation via hydrogen bonding between the CA and water. The CA of ammonia and amines are NH_4^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+ and the extent of hydrogen bonding are shown below:



Thus on going from $NH_3 \rightarrow RNH_2 \rightarrow R_2NH \rightarrow R_3N$

The inductive effect will tend to increase the basicity, but less sovation of CA will tend to decrease the basicity. As the two effects are acting in opposite direction so the net order will be $NH_3 > R_3N > RNH_2 > R_2NH$.