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CSIR–NET

Chemical Science

Council of Scientific & Industrial Research (CSIR)

Volume - 2

Organic Chemistry - 1

SIERRA INNOVATIONS

INDEX

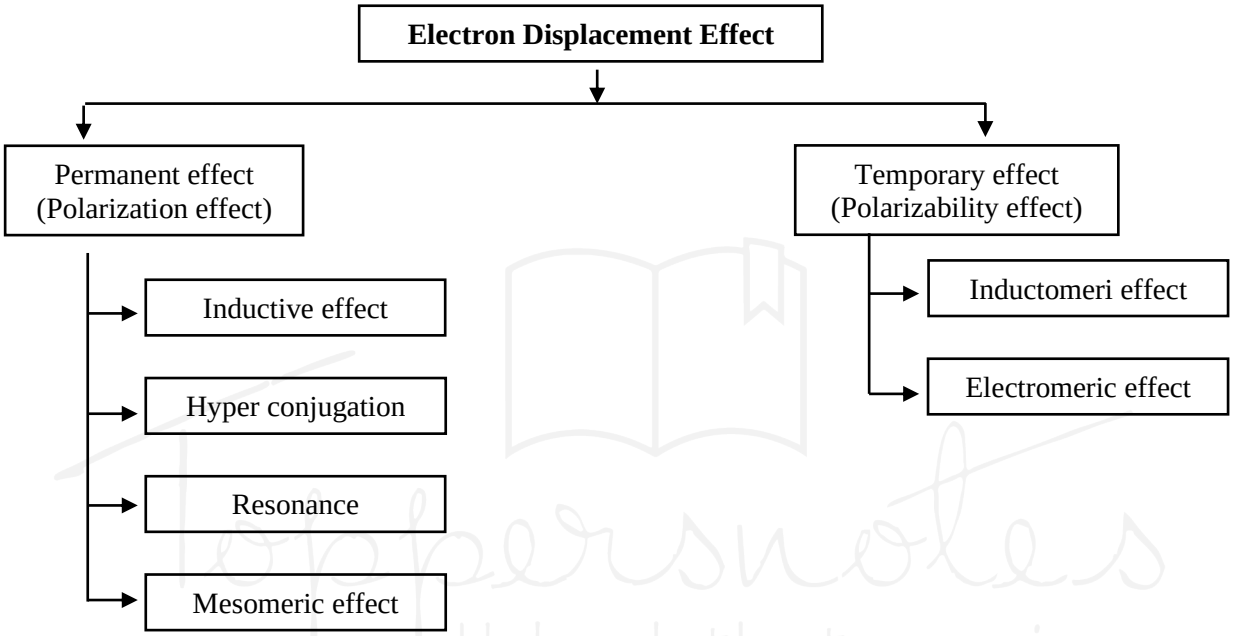
1 CHAPTER

GOC and Aromaticity

General Organic Chemistry

Electron Displacement Effects:

- Effect occuring due to displacement of electron in organic compound is called Electron Displacement Effect or Electron Delocalisation Effect.
- Electron displacement effect is of mainly two types.

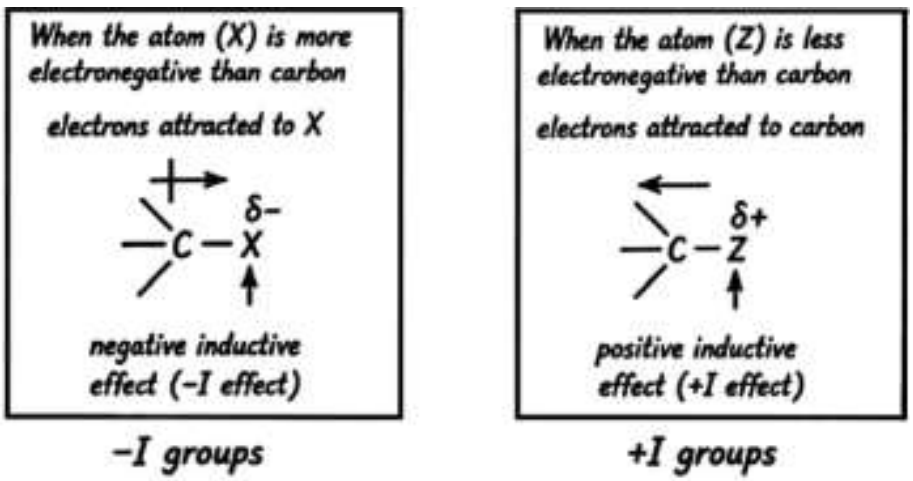


Other Effect:

(a) Steric inhibition of resonance (b) Ortho effect.

1. Inductive effects:

- ✓ In a covalent bond between two different atoms, the electrons in the σ-bond are not shared equally. The electrons are attracted towards the most electronegative atom. An arrow drawn above the line representing the covalently bonded electrons shifts toward the higher electronegative atom can show this. Electrons are pulled in the direction of the arrow.

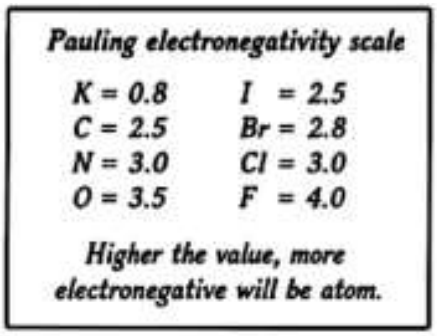


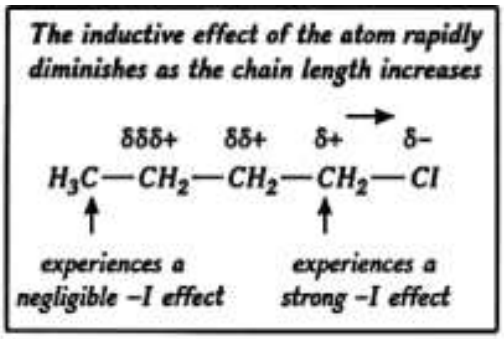
X=Br,Cl,NO_2,OH,OR,SH, SR,NH_2,NHR,NR_2 ,CN,CO_2H, CHO,COR

The more electronegative the atom (X), the stronger the $-I$ effect.

Z= (alkyl or aryl), metals (e.g. Li or Mg)

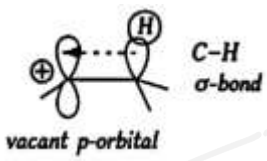
The more electronegative the atom (Z), the stronger the +I effect





- ✓ The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions, and this can be measured by the dipole moment (μ). Higher the dipole moment (measured in debyes (D)), more polar will be compound.

2. Hyperconjugation: $A\sigma$-bond can stabilise a neighbouring carbocation (or positively charged carbon) by donating electrons to the vacant p-orbital. The positive charge is delocalised or "spread out", and this stabilising effect is known as "no-bond resonance".



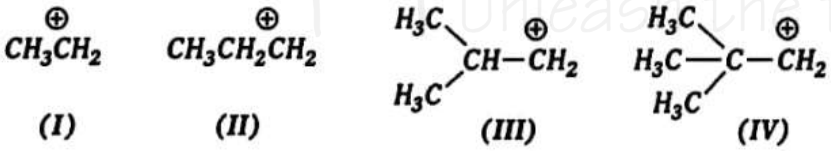
The electrons in the σ-bond σ-bond spend time in the vacant p-orbital

Points to Remember :

Number of α hydrogen α number of hyperconjugating structure α stability

$$\alpha \frac{1}{Heat\ of\ hydrogenation} \alpha\ Polarity\ \alpha\ dipole\ moment\ \alpha \frac{1}{bond\ length} \alpha$$

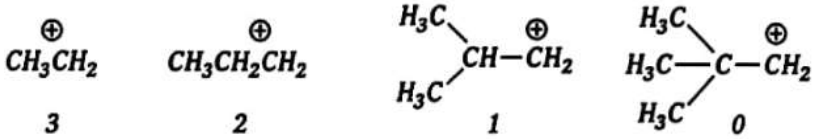
Problem : The correct order for the stability among following compound is



(a) I > II > III > IV (b) I > III > IV > II (c) IV > III > II > I (d) IV > III > I > II

Soln. Numberr of a hydrogen a stability

Thus

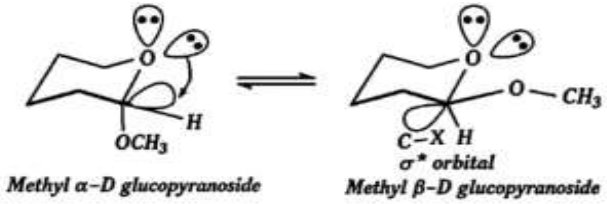


Number of a hydrogen 3 1 0

Stability, I > II > III > IV

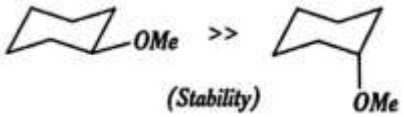
Hence, option (a) is corect

Problem : Which is more stable methyl $\alpha - D$ glucopyranoside or methyl $\beta - D$ glucopyranoside.



There is stabilising interaction i.e. hyperconjugation between the unshared pair on the hetero atom and σ^* orbital for the axial $C-X$ bond in the case of α anomer. thus it is more stable as compared to its β analogen in which there is no such interaction.

Note : If oxygen is replaced by carbon, there is no such stability interaction as like as above. Thus, stability can only be decided on steric ground. Thus stability order for such species will be



3. Mesomeric effects:

✓ Whilst inductive effects pull electrons through the σ-bond framework, electrons can also move through the π-bond network. A π-bond can stabilise a negative charge, a positive charge, a lone pair of electrons or an adjacent bond by resonance (i.e. delocalisation or 'spreading out' of the electrons). Curly arrows are used to represent the movement of π or non-bonding electrons to give different resonance forms. It is only the electrons, not the nuclei, that move in the resonance forms and a double-headed arrow is used to show their relationship.

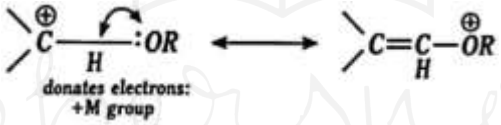
(a) Positive mesomeric effect:

- When a π-system donates electrons, the π-system has a positive mesomeric effect ($+M$ effect).

donates electrons:

+M group

- When a lone pair of electrons is donated, the group donating the electrons has a positive mesomeric effect.



(b) Negative mesomeric effect:

- When a π-system accepts electrons, the π-system has a negative mesomeric effect (-M effect).

Accept electrons:

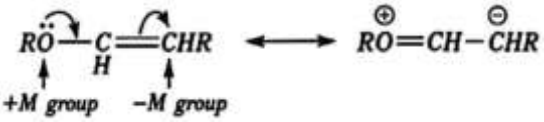
-M group

➢ The actual structures of the cations or anions lie somewhere between the two resonance forms. All resomanc forms must have the same overall charge and obey the same rules of valency.

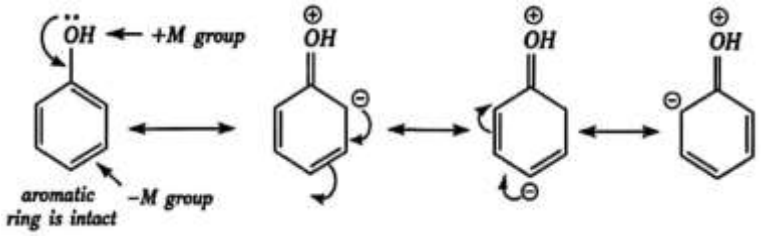
M groups generally contain an electronegative atom (s) and/or a π-bond (s) : $CHO, C(O)R, CO_2H, CO_2Me, NO_2$, aromatics groups, alkenes etc. $+M$ groups generally contain atleast a lone pair of electrons or a π-bond (s) : : $Cl, : Br, : OH, : OR, : SH, NH_2, NHR, NR_2$, aromatics, alkenes etc. Aromatic (or aryl) groups and alkenes can be both $+M$ or $-M$ effect.

➢ In neutral compounds, there will always be $a+M$ and $-M$ groups(s):

➢ One group donates ($+M$) the electrons and the other group(s) accepts the electrons($-M$).



➢ All resonance forms are not of the same energy. In phenol, for example, the resonance form which the intact aromatic benzene ring is expected to predominate.



- As a rule of thumb, the more resonance structures an anion, cation or neutral π - system can have, the more stable it is.

Inductive versus mesomeric effects:

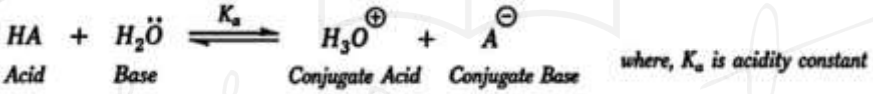
- Mesomeric effects are generally stronger than inductive effects. A + M group is likely to stabilise an anion more effectively than $a + I$ group.
- Mesomeric effects can be effective over much longer distances than inductive effects, provided that conjugation is present (i.e. alternating single and double bonds). Whereas inductive effects are determined by distance, mesomeric effects are determined by the relative positions of $+M$ and $-M$ groups in a molecule.

Application of inductive effect, hyperconjugation and mesomeric effect:

Acidity and basicity:

Acids: An acid is a substance that donates a proton (Bronsted-Lowry). Acidic compounds have low pK_a values and are good proton donors, as the anions (or conjugate bases), formed on the deprotonation, are relatively stable.

In water:



- The more stable the conjugate base the stronger the acid

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

As H_2O si in excess

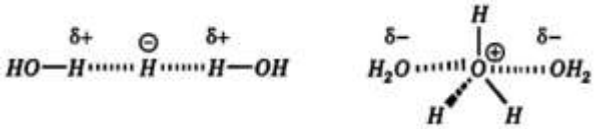
$$pK_a = -log_{10}\ K_a$$

The higher the value of K_a, the lower the pK_a value and the more acidic is HA

- The pK_a-value equals the pH of the acid when it is half dissociated. At pH above the pK_a the acid exists predominantly as the conjugate base in water. At pH below the pK_a, it exists predominantly as HA.

$$pH = 0\ (strongly\ acidic)$$
$$pH = 7\ (neutral)$$
$$pH = 14\ (strongly\ basic)$$

- The pK_a-values are influenced by the solvent. Polar solvents will stabilise cations and/or anions by solvation, in which the charge is delocalised over the solvent (e.g. by hydrogen-bonding in water).



- The more electronegative the atom bearing the negative charge, the more stable the conjugate base (which is negatively charged).

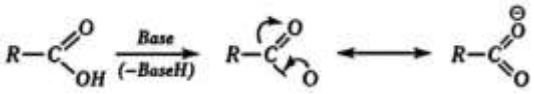
pK	3		16		33		48
Most acidic	HF	>	H_2O	>	NH_3	>	CH_4
			increasing electronegativity				

- Therefore, F^- is more stable than $CH_3{}^-$.
- The conjugate base can also be stabilised by $-I$ and $-M$ groups which can delocalise the negative charge. (The more spread out the negative charge, the more stable it is)

$$-I \text{ and } -M \text{ groups therefore lower the } pK_a, \text{while}$$
$$+I \text{ and } +M \text{ groups raise the } pK_a$$

(a) Inductive effects and carboxylic acids:

- ✓ The carboxylate anion is formed on deprotonation of carboxylic acids. The anion is stabilised by resonance (i.e. the charge is spread over both oxygen atoms) but can also be stabilised by the R group if this has $a - I$ effect.



The greater the $-I$ effect, the more stable the carboxylate anion and the more acidic is carboxylic acid.

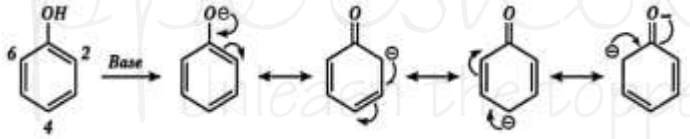
	$\overset{-I}{F-CH_2-CO_2H}$	$\overset{-I}{Br-CH_2-CO_2H}$	$\overset{-I}{CH_3-CO_2H}$
$p\,K_a$	2.7	2.9	4.8
	Most acidic as F is more electronegative than Br and hence has a greater -I effect		Least acidic as the CH_3 group is $a + I$ group

(b) Inductive and mesomeric effects and phenols:

- ✓ Mesomeric effects can also stabilise positive and negative charges.

The negative charge needs to be on adjacent carbon atom for $a - M$ group to estabilise it The positive charge needs to be on adjacent carbon atom for $a + M$ group to stabilise it

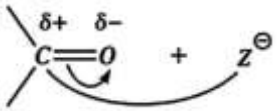
- ✓ On deprotonation of phenol the phenoxide anion is formed. This stabilised by delocalisation of the negative charge at the 2-, 4-and 6-positions of the benzene ring.



Temporary Effect :

1. Electromeric Effect :

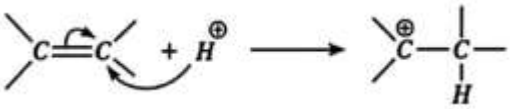
- ✓ Temporary effect.
- ✓ Takes place between two atoms joined by a multiple bond
- ✓ Occurs at requirement of attacking reagent.



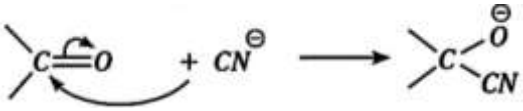
Instantaneous shift of electron pair of carbonyl group towards oxygen.

It is of two types.

(a) $+E$ effect : Transition of electron towards the attacking reagent.



(b) $-E$ effect : Transition of electron away from attacking reagent.



2. Inductomeric Effect ;

- ✓ Temporary effect.
- ✓ Takes place in sigma bonded system
- ✓ In presence of attacking reagent, transition of a electron cloud takes place more readily.
- ✓ **Example:**

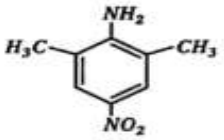
$$R - O \leftarrow H + B^{\ominus} \longrightarrow$$

In presence of base B, movement of sigma electron takes place faster.

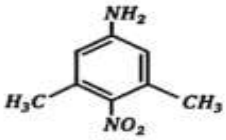
3. Other Effect :

(a) Effect of inertia/steric inhibition of resonance:

- Resonance ability of an atom is lost if it loses planarity with the other part of the system due to steric crowding by bulky group in adjacent positions.

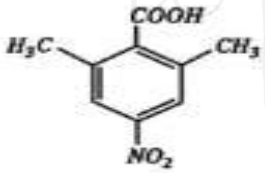


(A)

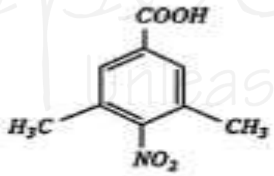


(B)

- The above two compounds A and B have everything identical except position of the two methyl group. It is expected that A should be stronger base than B due to closeness of two electron donating methyl group to $-NH_2$. The fact is opposile to this. In compound $B - NO_2$ is surrounded by two bulky methyl group and they sterically repel the $-NO_2$ group. In order to minimize the steric repulsion by the two adjacent methyl group, the nitro group loses planarity with the benzene ring. So , now $-NO_2$ due to lack of planarity weigh ring, not able to resonate. This is known as steric inhibition of resonance. Thus in $B, -NO_2$ is not decreasing basic strength by resonance. In $A - NO_2$ lies in the plane of the ring, it is in resonance with the ring, decreases basic strength of $-NH_2$ by resonance, hence weaker base.
- Similarly we can explain the acidic strength of C and D



(C)

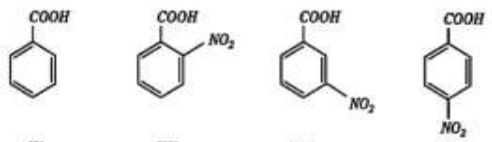


(D)

- C is stronger acid inspite of closeness of two electron donating methyl group to -COOH .

(b) Ortho effect:

- If any group present on ortho position of the benzoic acid. It always increases acidic nature of acid because this group decreases outer resonance of the ring toward acidic nature. Similarly if any group present on ortho position of aniline, it decreases basic nature. This effect is known as ortho effect.
- **Problem :** The correct order of acidity among the following compound I-IV is



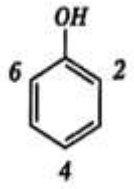
(I) (II) (III) (IV)

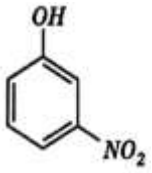
(a) II > III > IV > I (b) IV > II > III > I (c) II > IV > III > I (d) IV > III > II > I

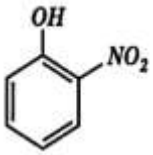
- **Soln.** Because of ortho effect o-nitro benzoic acid is most acidic followed by para and meta. Thus order will be II $> IV > III > I$.
  Hence, option (c) is correct.

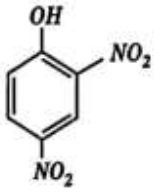
- ✓ If $-M$ groups are introduced at $2-$,4 - and/or 6 -positions, the anion can be further stabilised by delocalisation through the π-system , as the negative charge can be spread onto the $-M$ group. We can use double-headed curly arrows to show this process.
- ✓ If -M groups are introduced at the 3- and/or 5-positions, the anion cannot be stabilised by delocalisation, as the negative charge cannot be spread onto the $-M$ group. There is no way of using curly arrows to delocalise the charge onto the $-M$ groups.
- ✓ If -I groups are introduced on the benzene ring, the effect will depend on their distance from the negative charge. The closer the $-I$ group is to the negative charge, the greater the stabilising effect will be. The order of $-I$ stabilisation is therefore $2-$ position $> 3-$ position $>$ 4-position.
- ✓ The $-M$ effects are much stronger than $-I$ effects.

Example : The NO_2 group is strongly electron-withdrawing; -I and -M.

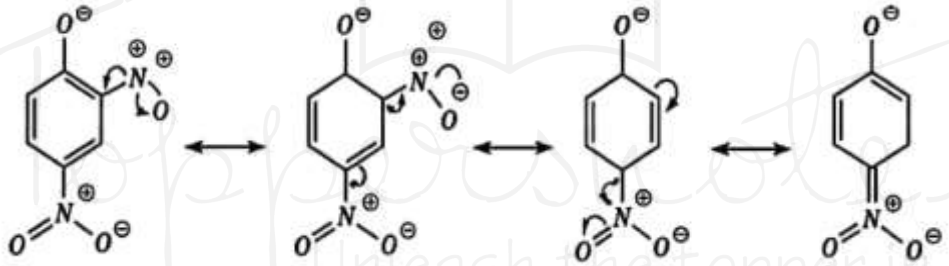






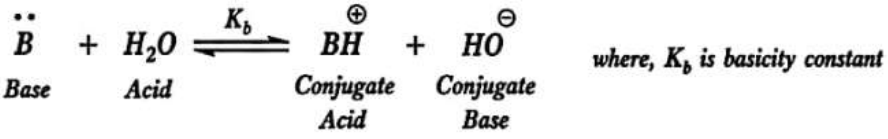


pK_a	**9.9**	**8.4**	**7.2**	**4.0**
	Least acidic as no -I or -M groups on the ring by resonance	The NO_2 can only stabilise the anion inductively inductively and by resonance	The NO_2 can only stabilise the anion inductively and	Most acidic as both NO_2 groups can stabilise the anion



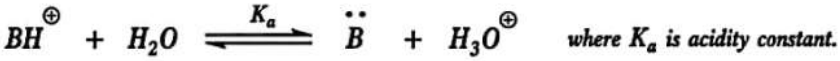
Bases: A base is a substance that accepts a proton (Bronsted-Lowry). Basic compounds have high pK_a values and are good proton acceptors, as the cations (or conjugate acids), formed on protonation, are relatively stable.

In water:



where, K_b is basicity constant

The strength of bases are usually described by the K_b-and pK_a-values of the conjugate acid.



where K_a is acidity constant.

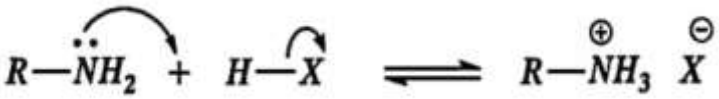
$$K_a = \frac{[B][H_3O^+]}{[^+BH]}$$ *[As H_2O is in excess]*

- ✓ If B is a strong base, then BH^+will be relatively stable and not easily deprotonated. BH^+will therefore have a high pK_a-value
- ✓ If B is a weak base, then BH^+will be relatively unstable and easily deprotonated. BH^+will therefore have a low pK_a-value.

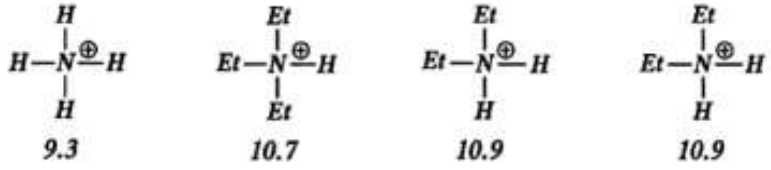
The cation can be stabilised by $+I$ and $+M$ groups, which can delocalise the positive charge.
(The more 'spread out' the positive charge, the more stable it is).

(c) Inductive effects and aliphatic (or alkyl) amines:

- On protonation of amines, ammonium salts are formed.



The greater the $+I$ effect of the R group, the greater the electron density at nitrogen and the more basic th amine. The greater the $+I$ effect, the more stable the ammonium cation and the more basic the amine.



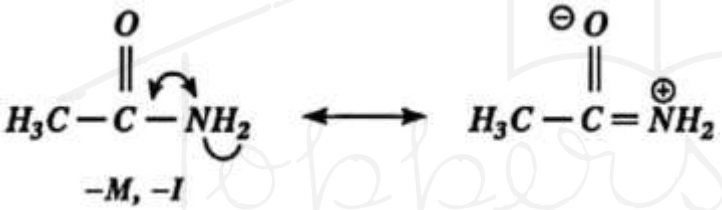
The pK_a-values should increase steadily as more $+I$ alkyl groups are introduced on nitrogen. However, the pK_a-values are determined in water, and the more hydrogen atoms on the positively charged nitrogen, the greater the extent of hydrogen-bonding between water and the cation. This solvation leads to the stabilisation of the cations containing $N-H$ bonds.

In organic solvents (which can not solvate the cation), the order of pK_a is expected to be as follows:

$$R_3\,N_{most\ basic} > R_2NH > RNH_2 > NH_{3\ least\ basic}\ (R = +I\ alkyl\ group)$$

The presence of $-I$ and/or $-M$ groups on nitrogen reduces the basicity, and hence, for example, amides are poor bases.

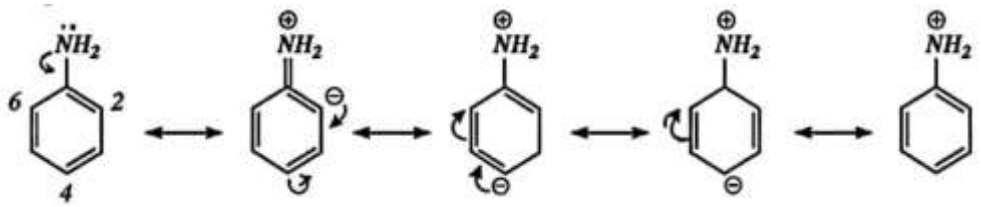
Ethamamide has a pK_a of -0.5 .



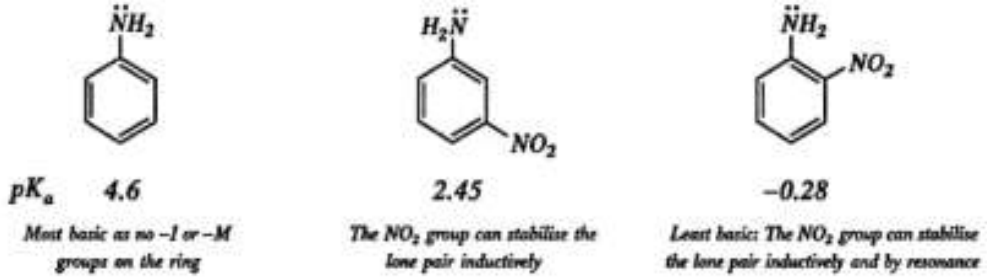
The $C=O$ group stabilises the lone pair on nitrogen by resonance. This reduces the electron density on nitrogen

(d) Mesomeric effects and aryl (or aromatic) amines:

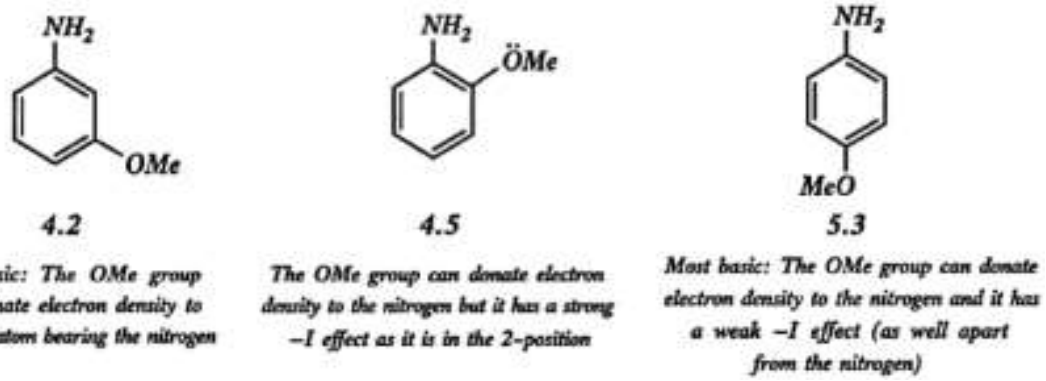
The lone pair of electrons on the nitrogen atom of aminobenzene (or aniline) can be stabilised by the delocalisation of the electrons onto the 2-, 4-and 6-positions of the benzene ring. Aromatic amines are therefore less basic than aliphatic amines.



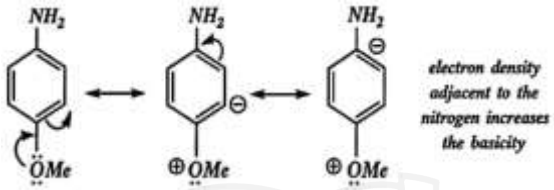
- If - M groups are introduced at the 2-, 4-and/or 6-positions (but not at the 3- or 5-position), the anion can be further stabilised by delocalisation, as the negative charge can be spread onto the $-M$ group. This reduces the basicity of the amine.
- If $-I$ groups are introduced on the benzene ring, the order of $-I$ stabilisation is 2-position $>$ 3-position $>$ 4 position. This reduces the basicity of the amine.



- If $+M$ group (e.g. OMe) are introduced at the 2-, 4- or 6-position of aminobenzene, then the basicity is increased. This is because the $+M$ group donates electron density to the carbon atom bearing the amine group.

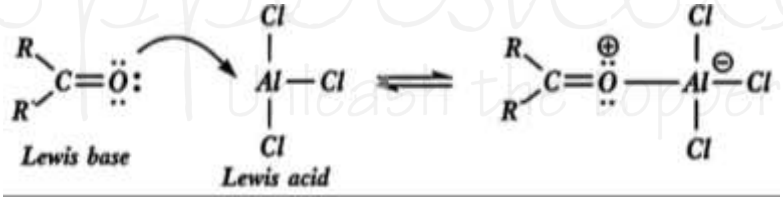


- Curly arrows can be used to show the delocalisation of electrons onto the carbon atom bearing the nitrogen.



(e) Lewis acids and base:

- A Lewis acid is any substance that accepts an electron pair in forming a coordinate bond. Examples include $H^+, BF_3, AlCl_3, TiCl_4, ZnCl_2$ and $SnCl_4$. They have unfilled valence shells and hence can accept electron pairs.
- A Lewis base is any substance that donates an electron pair in forming a coordinate bond. Examples include $H_2O, ROH, RCHO, R_2CO, R_3N$ and R_2S. They all have a lone pair(s) of electrons on the hetero atom (O, N or S)



(f) Basicity and hybridisation:

- The greater the ' s ' character of an orbital, the lower is energy the electrons and the more tightly the electrons are held to the nucleus. The electrons in an sp-orbital are therefore less available for protonation than those in an sp^2 - or sp^3-hybrid orbital and hence the compounds are less basic.

most basic:	$R_3N >$	$R_2C = N^{\cdot\cdot}H >$	$RC \equiv N^{\cdot\cdot}$	least basic
most basic:	$R_3C^{\ominus} >$	$R_2C = CH^{\ominus} >$	$RC \equiv C^{\ominus}$	least basic
	sp^3	sp^2	sp	
	$(25\%s)$	$(33\%s)$	$(50\%s)$	

Aromaticity :

Introduction : Aromaticity is a chemical property of organic compound, aromatic compound have following characteristics:

(i) It has high degree of stability

(ii) It shows electrophilic substitution reaction rather than electrophilic addition reaction. It means it does not decolourise bromine water solution.

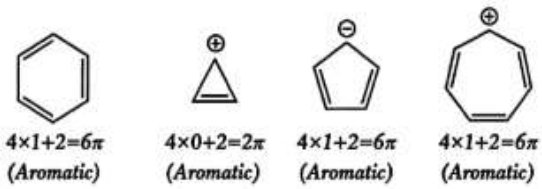
(iii) Aromatic compound follow Hückel rule. According to which A cyclic planar conjugated species having $(4n+2)\pi$ electrons (where $n = 0,1,2,3, \ldots \ldots$) is aromatic in nature.

(iv) There is a diamagnetic ring current.

(v) Each carbon must be sp^2-hybridized or sp-hybridized.

(vi) It has high degree stability due to filled bonding molecular orbital.

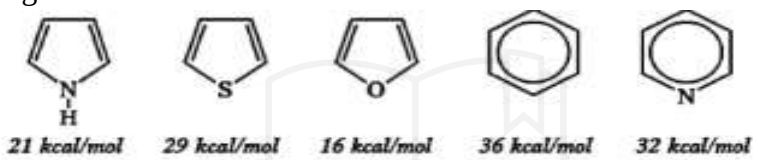
For example:



1. **High Degree of stability:** High degree of stability is associated with resonance energy. The compound which have more resonance energy is more stable. The compound which have more potential energy is least stable.

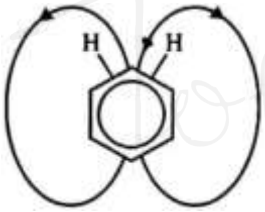
   Aromaticity $\propto$ Resonance energy $(R.E) \propto$ Stability $\propto \frac{1}{Potential\ Energy\ (P.E.)}$

2. Greater the resonance energy higher will be the stability of compound. Resonance energy of some aromatic system are given below as



3. **Presence of diamagnetic ring current:**

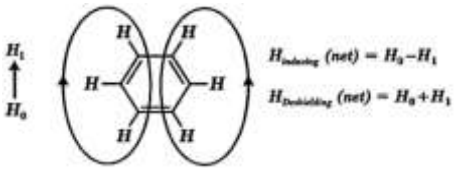
   ✓ Aromatic compounds show diamagnetic ring current due to paired electron.



Two equal and opposite ring currents are set up above and below the plane of the ring, producing a net diamagnetic effect.

(clockwise) (anticlockwise)

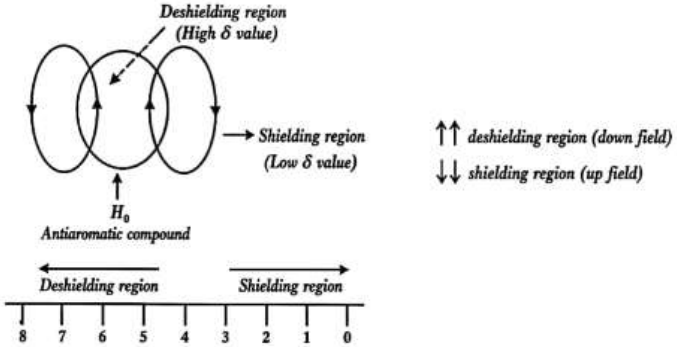
   ✓ Aromatic compounds show diamagnetic ring current due to paired electron.



where, H_0 = external magnetic field

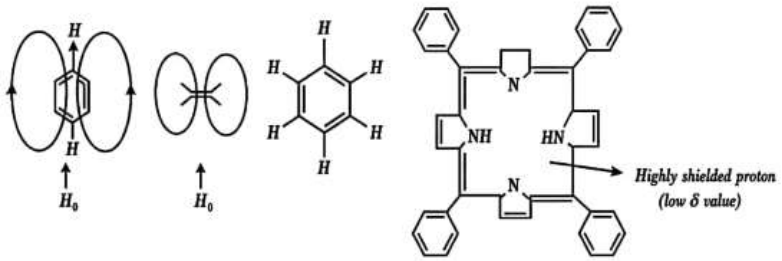
H_1 = induced magnetic field

   ✓ Clockwise direction in electron present for aromatic compound.



δ value $-sp^2 > sp > sp^3$ (decreasing order) due to arisototopic effect.

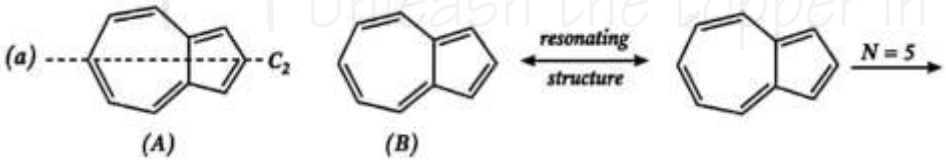
- ✓ Molecule in which outer protons are deshielded and inner protons are shielded is known as diatropic molecule. These type of molecules are always aromatic in nature.
- ✓ Similarly, molecule in which inner protons are shielded and outer protons are deshielded are known as paratropic molecule. Paratropic molecule is aromatic in nature.
- ✓ Antiaromatic compounds show paramagnetic ring current due to unpaired electron.



Hückel Rule: This is a very popular and useful rule to identify aromaticity in monocyclic conjugated compound. According to which a planar monocyclic conjugated system having $(4n + 2)\pi$ delocalised (Where n = 0, 1, 2, . …) electrons are known as aromatic compound. For example: Benzene, Naphthalene, Furan, Pyrrole etc

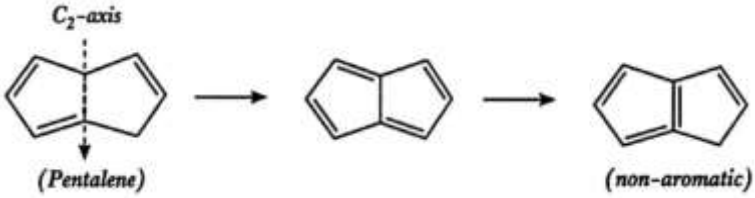
$n = 0$	$(4 \times 0 + 2)\pi e^- = 2\pi e^-$
$n = 1$	$(4 \times 1 + 2)\pi e^- = 6\pi e^-$
$n = 2$	$(4 \times 2 + 2)\pi e^- s10\pi e^-$
$n = 3$	$(4 \times 3 + 2)\pi e^- = 14\pi e^-$
$n = 4$	$(4 \times 4 + 2)\pi e^- = 18\pi e^-$

- ➢ **Craig's Rule:** This rule is applicable for polyclic non-benzenoid compounds. If molecule contain C_2-axis then count total number of double bonds (N) and calculate value of $N - 1$ which decide aromaticity in compound.
- ➢ (1) If $N - 1$ is odd, compound is non-aromatic.
- ➢ (2) If $N - 1$ is even, compound is aromatic.
- ➢ e.g. Azulene



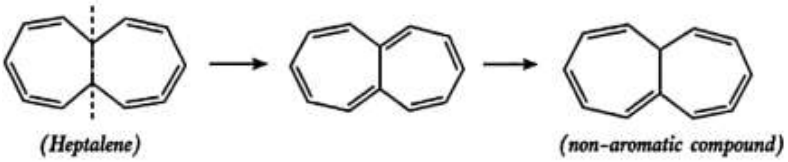
$N - 1 = 4\pi$ bond (aromatic)

- ➢ In system C_2-axis must be present



N = 4

N-1 = 3, odd, Hence, compound is non- aromatic.



N = 6

N – 1 = 5, odd. Hence compound is non-aromatic.

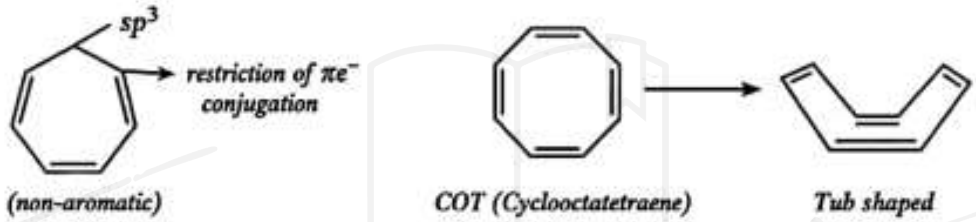
- Pentalene and heptalene is a non-aromatic compound. Since it does not follow craig's rule.
- The organic compound which show aromaticity are aromatic in nature or diatropic in nature and the protons (outside the rings) signal always exist away from the TMS (these protons are deshielded protons)
- Identification of aromatic, anti-aromatic and non-aromatic compounds.

Organic Compound :-

(1) Aromatic Compound	**(2) Anti-aromatic compound**	(3) Non-aromatic compound
(a) Hückel rule	$4n\pi e^-$ delocalized	restriction of delocalization
(i) Monocyclic system	$n = 1,2,3,4,5,$	$\pi e^{-'s}$
(ii) Polycyclic benzenoid	$n = 1 = 4\pi e^-$	
(b) Craig's rule	$n = 2 = 8\pi e^-$	
Polycyclic non-benzenoid	$n = 3 = 12\pi e^-$	
	system planar (sp and sp^2-hybridized)	
	(system conjugated)	

sp^3 non planar structure

s^3 hybridized carbon atom insert

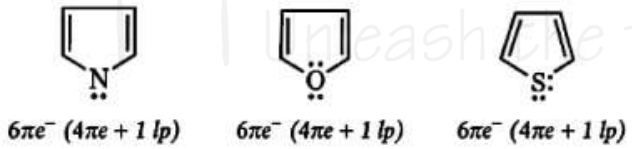


- **Order of stability and order of resonance energy :**
  Aromatic > Non-aromatic > Anti-aromatic.
- **Calculatin of π electrons :** During π -electron count double bond count 2 π electron and triple bond count 2 π electron. Also lone pair in conjugation is also counted.

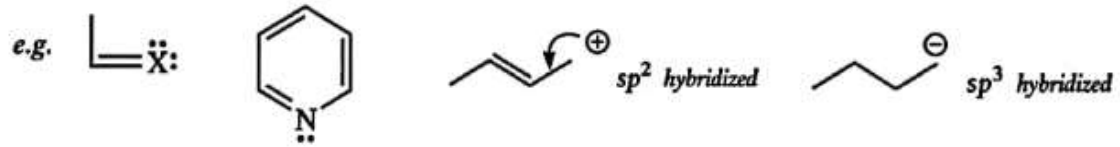
  $\Rightarrow 2\pi e^-$

  $\Rightarrow 2\pi e^-$

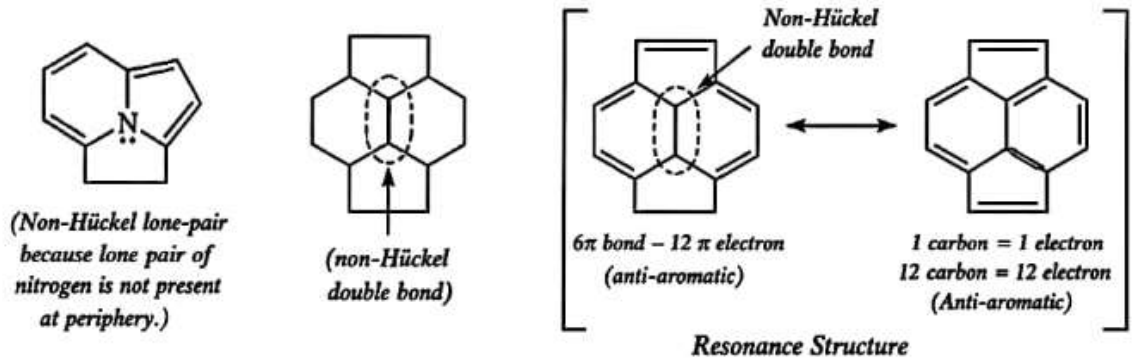
  1 lp $2e$

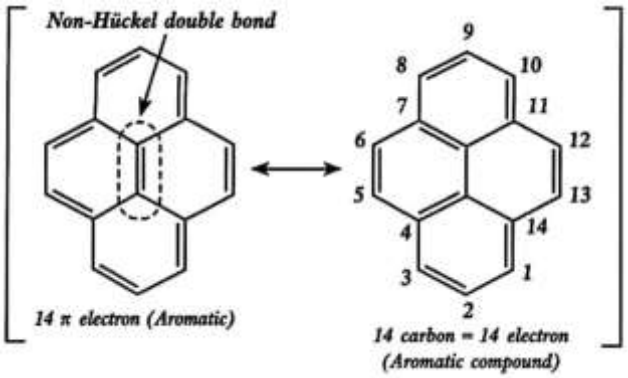


- **Species in which lone pair is not in conjugation can not be counted :**



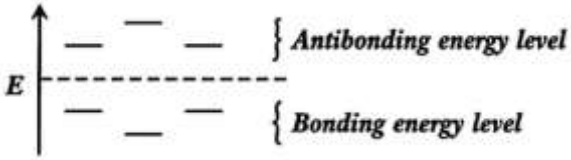
- Lone pair which participate in conjugation system and follow Huckel's rule are called Huckel lone pair while which lone pair does not participate in conjugation are known as non-Huckel lone pair.



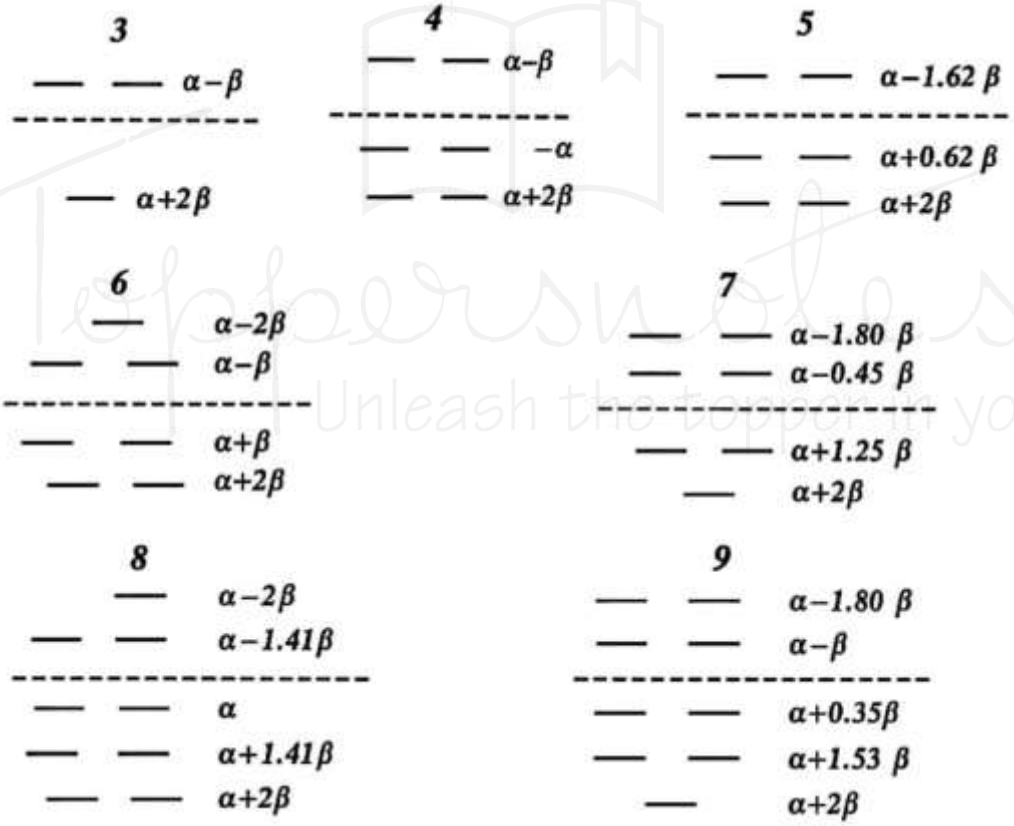


Resonance Structure

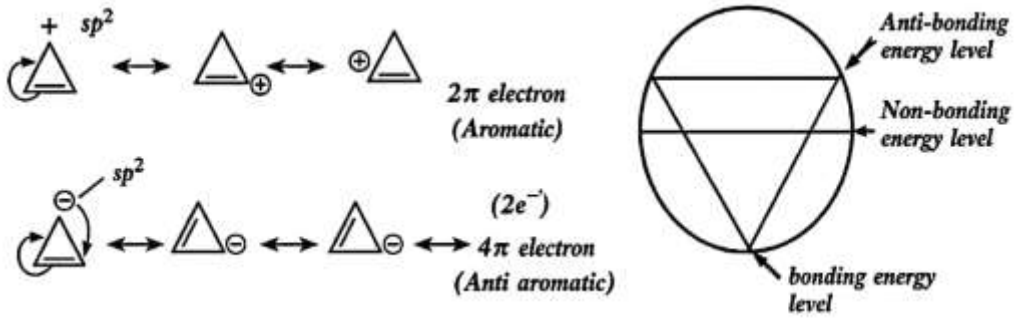
- Energy level of aromatic and anti-aromatic compounds can be shown by using frost circle or diagram. Energy levels of regular planar polygonic molecules with an even number of atoms form a symmetrical pattern as shown below.



- If all bonding energy levels are filled then it is aromatic [Hückel criterion also required].



- **Figure :** HMO energies for conjugated planar ring systems of three to nine carbon atoms.



- Anti-aromatic compound behaves as a biradical
- Frost Diagram for Cyclopropenyl system
- In anti-aromatic compounds two unpaired electron are present which are all paired.
- Oxygen also behave as biradical and triplet state.
- Carbene-triplet state are biradical.

Types of Aromatic Compounds

(A) 2π-electron system .

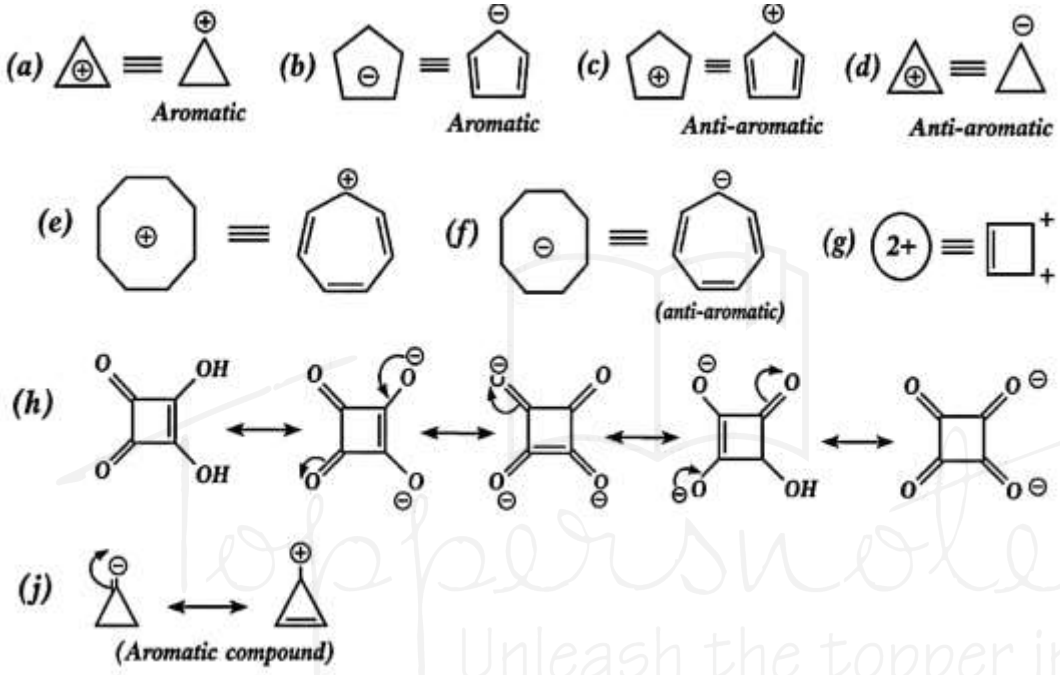
(i) It follow $(4n+2)\pi e^-$system.

(ii) If electron delocalised then compound is aromatic.

(iii) If electrons not delocalised then compound is non-aromatic

(iv) Compound will never be antiaromatic.

Examples:



- ✓ Displacement of electrons takes place towards higher electronegative atom.

(B) 4π-electronic system:

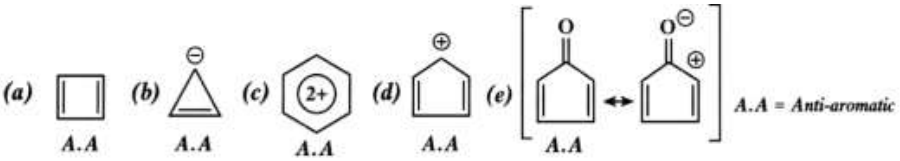
(i) Belongs to $4n\pi e^-$system doesnot follow Hückel rule.

(ii) If electron is delocalised then compound is antiaromatic.

(iii) If electron does not delocalised then compound never antiaromatic

(iv) If electron does not delocalised then compound is non-aromatic.

Examples:



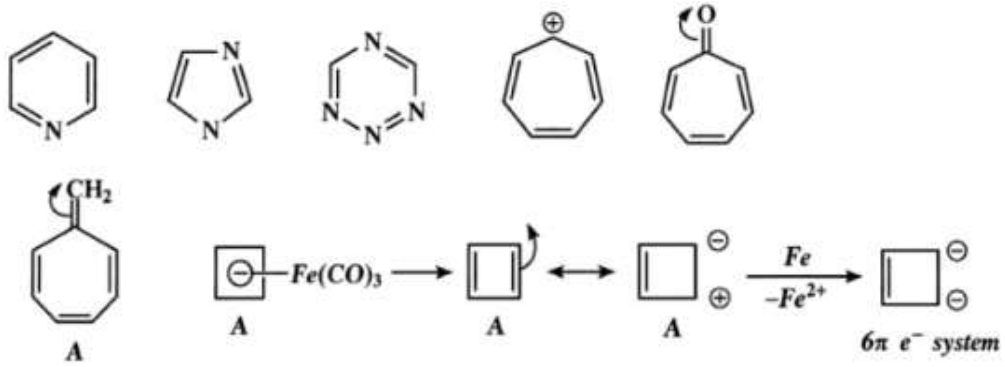
(C) 6π electron system:

(i) Belongs to $(4n+2)\pi e^-$system

(ii) If electron is delocalised then compound will be aromatic.

(iii) If electron does not delocalise then compound must be non-aromatic

For example:

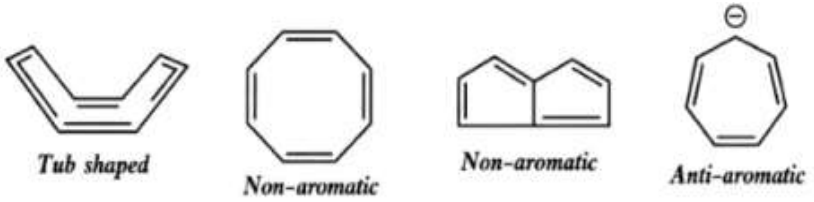


(D) 8π electronic system :

(i) Belongs (4n) πe^-rule

(ii) If electron is delocalised the compound must be anti-aromatic

(iii) If electron does not delocalise then compound is non-aromatic.



(E) 10π electronic system:

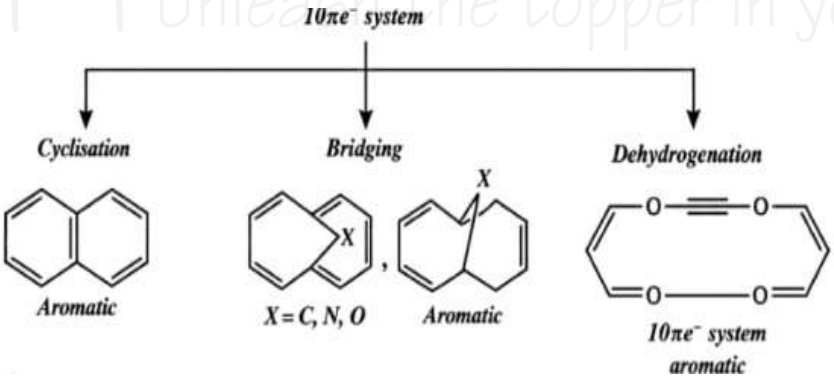
(i) Belongs $(4n+2)\pi e^-$system.

(ii) If electron delocalised then compound aromatic in nature.

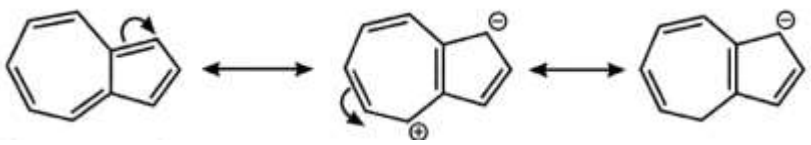
(iii) If electron does not delocalise then compound will be non-aromatic

(iv) Compound never be anti-aromatic.

(Repulsion between H-hydrogen atoms, causes the compound to be non planar. So, compound is non-aromatic)

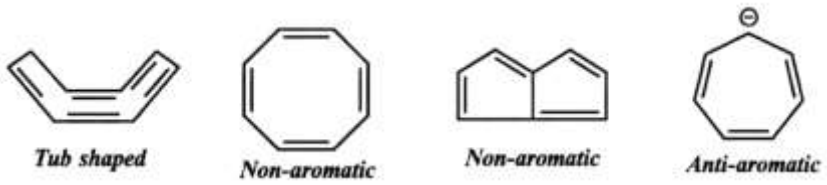


Azulene:



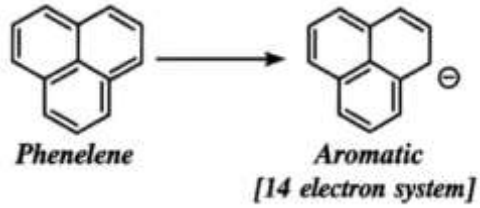
($10\pi e^-$system)

- ✓ Azulene is the isomer of Naphthalene
- ✓ Azulene is less stable than naphthalene
- ✓ Azulene gives electrophilic substitution reaction
- ✓ Five membered ring gives substitution reaction (because small size, electronegativity)



G. Phenelene is acidic in nature why?

✓ Proton (H^+)remove from the phenaline and acidic in nature and system gain aromaticity.



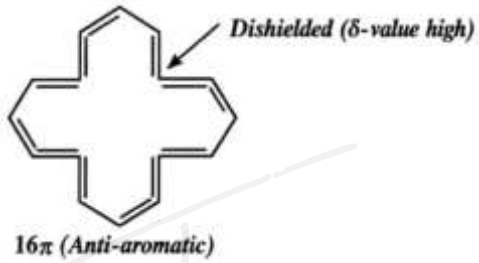
(H) 16π electronic system:

(i) Belongs to $4n\pi e^-$rule.

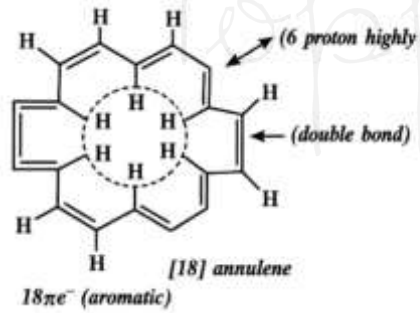
(ii) If electron is delocalised then compound is anti-aromatic.

(iii) If electron does not delocalised then compound will be non-aromatic

(iv) It never be aromatic.

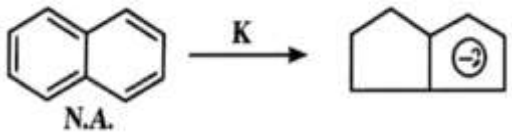


(I) 18π electronic system:



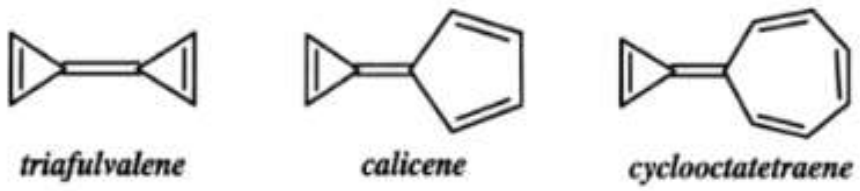
Completely conjugated monocyclic system called annulene

✓ 18 Annulene contain 3 cis close bond.



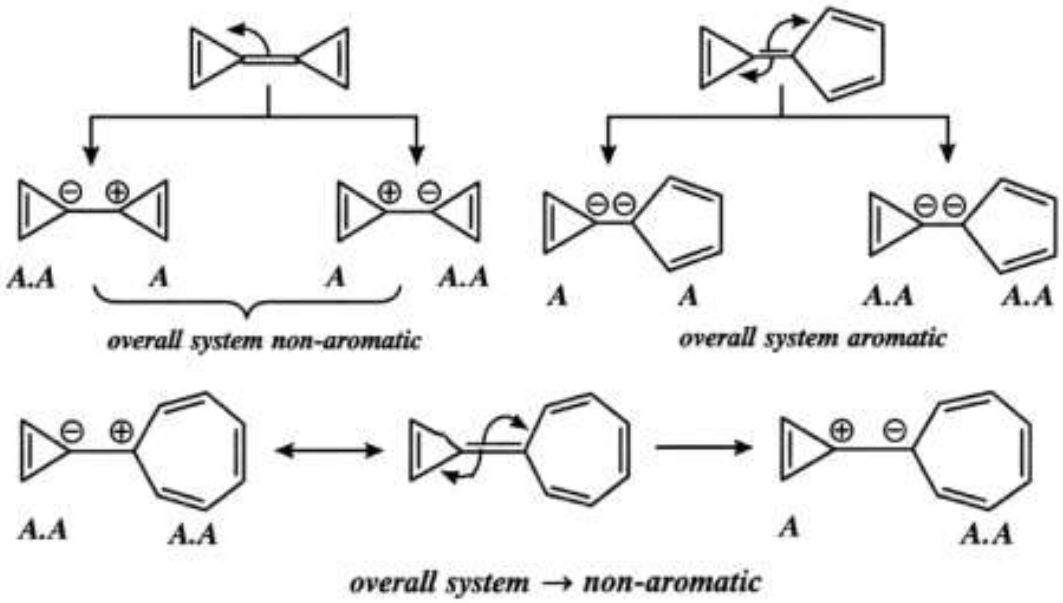
Other Aromatic System:

➢ Fused ring aromatic.



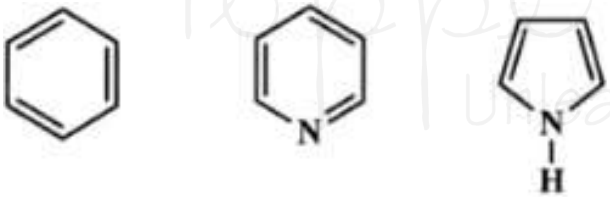
➢ Such type of systems is aromatic or non-aromatic but never be anti-aromatic

- If such type of system is aromatic then both ring must be aromatic after displacement of common double bond.
- **Otherwise both ring will not be aromatic**



- **Resonance energy of some aromatic system:**

- **Pyrrole is called as super aromatic compound**

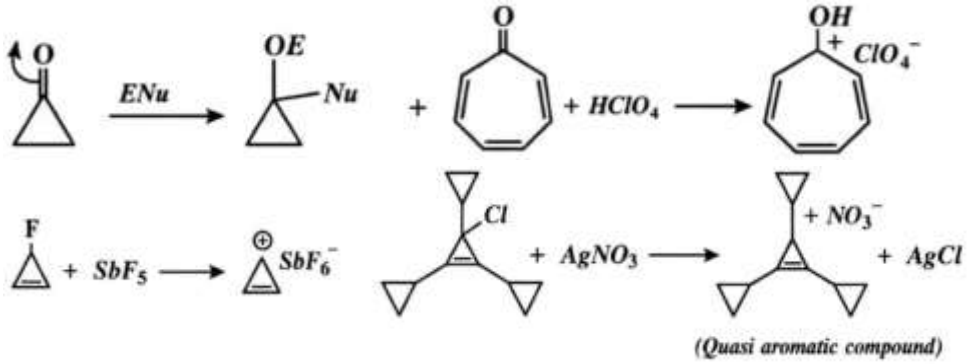


$36 = \frac{6}{6} = 1$ for C-atom energy, $\frac{(total\ \pi e^-)}{(total\ C-atom)}\frac{6}{5} = 1.2$ per C-atom

- According to electron density at per C-atom, pyrrole is electronically rich. So, pyrrole gives electrophilic substitution reaction more easily than benzene.
- Electrophilic substitution reaction $\propto \frac{1}{resonance\ energy\ (aromaticity)}$

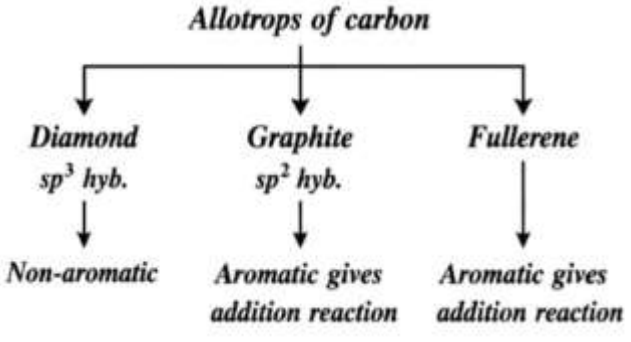
Quasi Aromatic Compound:

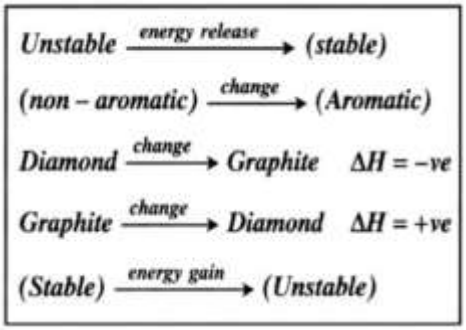
- These are generally ionic aromatic compound



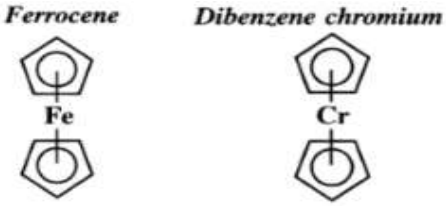
Allotops of Carbon:

(i) Diamond (ii) Graphite (iii) Fullerene



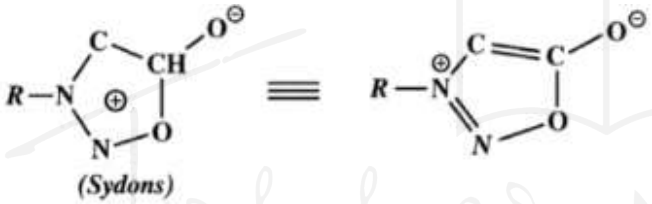


Organometallic aromatic compound:



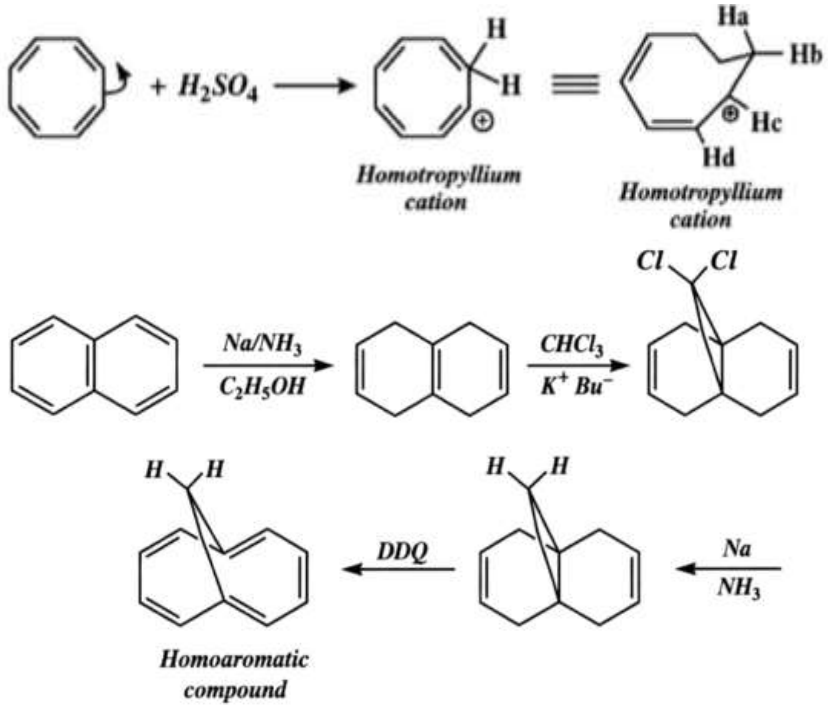
Mesoionic Compound:

- ✓ Sydons is the first meso-ionic compound which show aromaticity.
- ✓ Meso-ionic compound gives electrophilic substitution reaction
- ✓ Meso-ionic compound also known as internal salt.



Homo-aromatic compound :

- ✓ Compound that contain one or more sp ^{3}-hybridized C-atom in a conjugate cycle but s^3-hybridized carbon atom are force to lie almost vertically above the plane of the aromatic system known as homoaromatic compounds.



Stability: Aromatic > Homo-aromatic > non-aromatic > antiaromatic