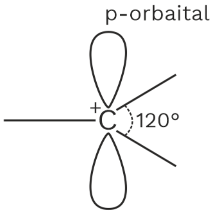
Reaction Mechanism

Carbocation

Carbocation are reactive intermediates in which carbon bearing the positive charge, sp^2 hybridised, plannar and having $6e^-$ in their valence shell.

Structure



Example

$\overset{+}{C}H_3$, $CH_2=CH\overset{+}{C}H_2$, $C_6H_5\overset{+}{C}H_2$ .....etc.

Note:

1. Alkyl group (R) disperse +ve charge over carbon.
2. Electron withdrawing groups pulls electron density away from C^+ carbon which decreases stability of carbocation.
3. More is the number of α-H attached to carbon atom having +ve charge, more is the number of hyperconjugative structures. Hence more stable is carbocation.

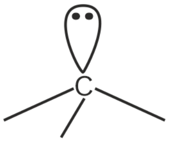
Stability of carbocation

$$\underset{3°}{(\overset{+}{C}H_3)_3-C} > \underset{2°}{(\overset{+}{C}H_3)_2-C} > \underset{1°}{\overset{+}{C}H_3CH_2} > \overset{+}{C}H_3$$

Carboanions

Carboanions are reactive intermediates in which carbon bearing the negative charge, sp^3 hybridised, pyramidal and having $8e^-$ in their valence shell.

Structure



Concept Ladder

Electrophiles are be electron deficient species, looking to attack an electron rich site (Nucleophilic Substrate). These are classified as follows:

Rack your Brain

How resonance is related to carbocation stability?

Previous Year's Questions

The most stable carbocation, among the following is **[NEET-2016]**

(1) $(CH_3)_3C-\overset{+}{C}H-CH_3$

(2) $CH_3-CH_2-\overset{+}{C}H-CH_2-CH_3$

(3) $CH_3-\overset{+}{C}H-CH_2-CH_2-CH_3$

(4) $CH_3-CH_2-\overset{+}{C}H_2$

Examples

$CH_2=CH-\bar{C}H_2$, $R_3\bar{C}$, $R\bar{C}H_2$ ..... etc.

Note:

1. Electron-withdrawing group increases stability whereas electron-releasing (R) group decreases the stability of carbanions.
2. The stability of carbanions increases with increase in 's' character (electron withdrawing).

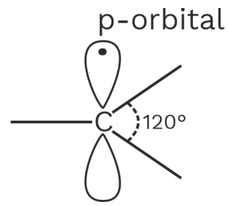
Stability of Carbanions

1. $\bar{C}H_3 > \underset{1°}{RH_2\bar{C}} > \underset{2°}{R_2H\bar{C}} > \underset{3°}{R_3\bar{C}}$
2. $\underset{50\%\ 's'\ (sp)}{R-C\equiv C} > \underset{33\%\ 's'\ (sp^2)}{RHC=CH} > \underset{25\%\ 's'\ (sp^3)}{R-H_2C}$

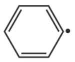
Free Radicals

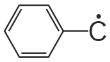
Free radical are reactive intermediates in which carbon bearing the unpaired electron, sp^2 hybridised, planar and having $7e^-$ in their valence shell.

Strucutre



Examples

$CH_2=CH$ (vinyl), $CH_2=CH-CH_2$ (allyl),  (benzyl),

 $-\dot{C}H_2$ (phenyl), ...etc.

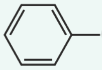
Note:

1. As the number of alpha H-atoms are increasing. The hyperconjugation effect is increasing and stability increasing.

Stability of Free Radicals

$\underset{1°}{(CH_3)_3\dot{C}} > \underset{2°}{(CH_3)_2\dot{C}H} > \underset{3°}{CH_3\dot{C}H_2} > \dot{C}H_3$

Previous Year's Question

The radical,  $-\dot{C}H_2$ is aromatic because it has

[NEET]

(1) 7 p-orbitals and 7 unpaired electrons
(2) 6 p-orbitals and 7 unpaired electrons
(3) 6 p-orbitals and 6 unpaired electrons
(4) 7 p-orbitals and 6 unpaired electrons

Rack your Brain

What are ambident nucleophiles?

Concept Ladder

Nucleophile are electron rich species, looking to attack a +ve charged centre. Nucleophiles may be charged:- H^-, OH^-; Neutral:- NH_3 H_2O; Ambident:-CN^-, O—N=O

Inductive Effect

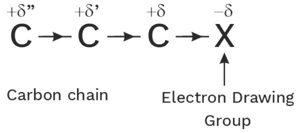
Displacement of an electron cloud along the carbon atom chain due to the presence of an electron withdrawing groups or electron releasing groups in the carbon chain is known as Inductive Effect.

Types of Inductive Effect

(1) -I Effect (2) +I Effect

(1) -I Effect

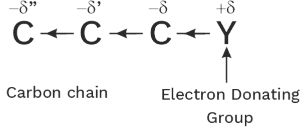
Any atom or group which attracts electrons more strongly than hydrogen is said to exert a negative effect (-I effect)



- I Effect

(2) +I Effect

An atom or group which attracts electrons less strongly than hydrogen is said to exert a positive inductive effect (+I effect).

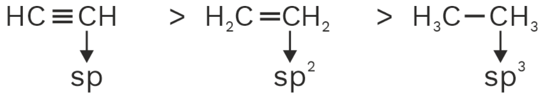


+ I Effect

Features

(1) Permanent Effect.

(2) Inductive effect is a weak effect.



$$\underset{sp}{HC\equiv CH} > \underset{sp^2}{H_2C=CH_2} > \underset{sp^3}{H_3C-CH_3}$$

Definitions

Inductive Effect is the phenomenon where a permanent dipole arises in a molecule due to the unequal sharing of the bonding electrons in the molecule.

Concept Ladder

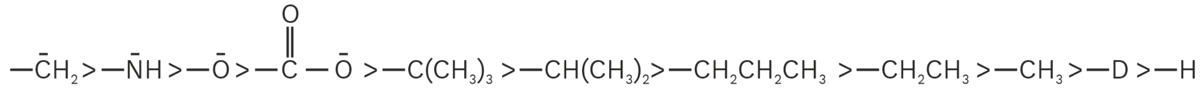
(1) Inductive effect depends upon the hybridisation of carbon atom.

(2) It is a distance dependent effect, after 3 or 4 carbon. Inductive effect will be zero.

(3) Any atom or group attracts electrons more strongly than hydrogen is said to exert a negative effect (-I effect); an atom or group which attracts electrons less strongly than hydrogen is said to exert a positive inductive effect (I-effect)

Hybridisation of C-atom	sp^3	sp^2	sp
% of s-character	25%	33%	50%
EN of C-atom	$sp^3 < sp^2 < sp$ (greater the s-character, greater will be the EN of the C-atom)		

Order of + I effect



- $—\bar{C}H_2 > —\bar{N}H > —\bar{O} > —\overset{\overset{O}{\|}}{C} — \bar{O} > —C(CH_3)_3 > —CH(CH_3)_2 > —CH_2CH_2CH_3 > —CH_2CH_3 > —CH_3 > —D > —H$

← Increasing +I Effect ——

- $—CT_3 > —CD_3 > —CH_3$ (+ I effect)

Order of -I effect

$—NO_2 > —CN \gg —SO_3H > —CHO > —COOH > —F > —Cl > —Br > —I > —OH > —OR > —NH_2$
$> HC \equiv C— > CH_2 = CH— > —C_6H_5 > —H$

← Increasing -I Effect ——

Note: Complete positive charge > +δ positive charge > EN Factor (-I effect)

Application of Inductive effect

(1) Stability of carbocation and free radical

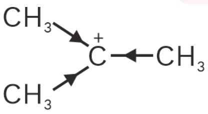
Ex. 1

$CH_3 \rightarrow \overset{+}{C}H_2$

1°Carbocation
(I)

$CH_3 \rightarrow \overset{+}{C}H \leftarrow CH_3$

2°Carbocation
(II)

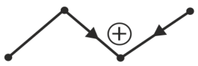


3°Carbocation
(III)

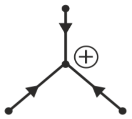
Stability of Carbocation: (III) > (II) > (I)

Ex. 2

1°Carbocation
I



2°Carbocation
II



3°Carbocation
III

Stability of Carbocation: III > II > I

Ex. 3

$\overset{\ominus}{C}H_3$

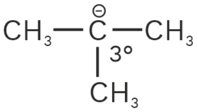
I

$CH_3—\overset{\ominus}{C}H_2$ 1°

II

$CH_3—\overset{\ominus}{C}H—CH_3$ 2°

III



$CH_3—\overset{\ominus}{\underset{CH_3}{\underset{|}{C}}}—CH_3$ 3°

IV

Stability of Free radical : III > II > I

Rack your Brain

Why do alkyl groups show +I effect?

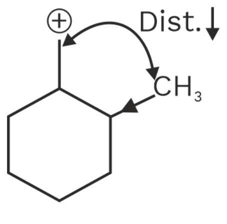
Previous Year's Question

Which of the following is correct with respect to – I effect of the substituents? (R = alkyl)

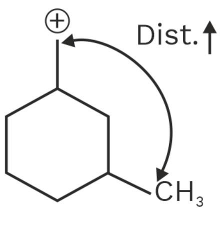
[NEET]

(1) $–NH_2 < –OR <– F$
(2) $–NR_2 < –OR < –F$
(3) $–NH_2 > –OR > –F$
(4) $–NR_2 > –OR > –F$

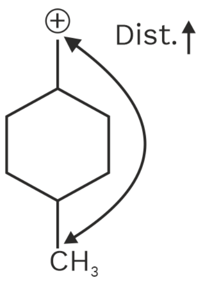
Ex. 4



I



II



III

Stability of Carbocation: I > II > III (Distance factor)

tertiary (3°) carbocation is more stable than that of secondary (2°) carbocation which is stable than that of primary (1°) carbocation. It is due to +I effect of the methyl group.

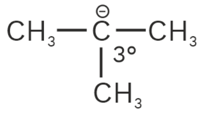
(2) Stability of Anion

Ex. 1

I: $\overset{\ominus}{C}H_3$

II: $CH_3-\underset{1°}{\overset{\ominus}{C}H_2}$

III: $CH_3-\underset{2°}{\overset{\ominus}{C}H}-CH_3$



IV: $CH_3-\underset{\underset{CH_3}{|}}{\overset{\ominus}{C}}-CH_3$ (3°)

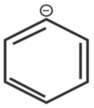
Stability of Carbocation: (I) > (II) > (III) > (IV)

Ex. 2

I: $CH_3-\overset{\ominus}{C}H_2$

II: $CH_2=\overset{\ominus}{C}H$

III: $CH\equiv\overset{\ominus}{C}$



IV

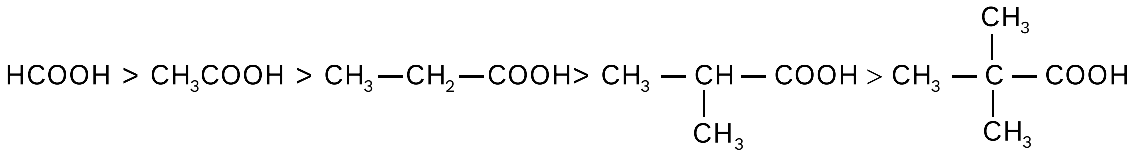
Stability of Carbocation: (III) > (IV) > (II) > (I)

Concept Ladder

1. Stability of anion
$\propto$ -I effect or 1/+I effect.
2. Stability of unsaturated anion > Stability of saturated anion

(3) Acidic Strength

$$\text{Acid strength} \propto \frac{1}{+\text{I effect}}$$



$$HCOOH > CH_3COOH > CH_3-CH_2-COOH > CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH > CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOH$$

- Acid strength $\propto$ –I effect

  $CH_3COOH < Cl–CH_2COOH < Cl_2CH–COOH < Cl_3C–COOH$
- Halogen having stronger –I effect makes an acid stronger. For example

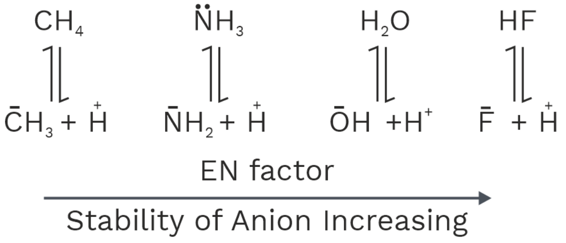
  $F–CH_2COOH > Cl–CH_2–COOH > Br–CH_2–COOH > I–CH_2–COOH$
- Increase in the number of halogen atoms on the α–carbon atom exerts greater inductive effect, thus increasing the –OH bond polarity, Consequently the acid becomes stronger.

  $CCl_3–COOH < CBr_3–COOH < CCl_3–COOH < CF_3–COOH$

  (Weakest acid) (Strongest acid)

Acidic strength acc. to periodic table

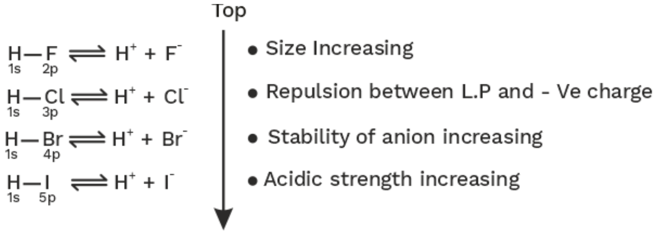
(a) Acidic strength in period



Acidic stability: $HF > H_2O > NH_3 > CH_4$

Strength of conjugate base: $\bar{C}H_3 > \bar{N}H_2 > \bar{O}H > \bar{F}$

(b) Acidic strength acc. to group



Acidic strength: $HI > HBr > HCl > HF$

Strength of conjugate Base: $I^- > Cl^- > Br^- > I^-$

Basicity of amines :

Basicity of aliphatic primary amines : In aliphatic amines, $R – NH_2$, the +I effect of alkyl group increases the electron density on nitrogen atom of $–NH_2$ group. As a result, its tendency to donate the electron pair to a proton increases.

basic strength of aliphatic primary amines is : $NH_3 < RNH_2$

Rack your Brain

Acidic strength of halogen acids increases down the group. Why?

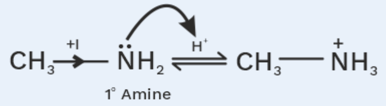
Concept Ladder

A Lewis acid is any species (molecule or ion) that can accept a pair of electrons, and a Lewis base is any species (molecule or ion) that can donate a pair of electrons.

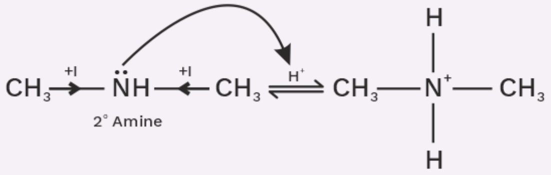
Basic strength of amine in different medium

(1) Basic Strength of amine in gaseous state

● Basic strength amine



$$CH_3 \xrightarrow{+I} \ddot{N}H_2 \overset{H^+}{\rightleftharpoons} CH_3-\overset{+}{N}H_3$$

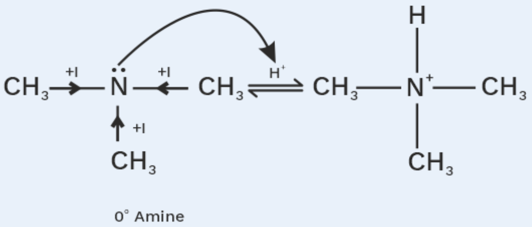


$$CH_3 \xrightarrow{+I} \ddot{N}H \xleftarrow{+I} CH_3 \overset{H^+}{\rightleftharpoons} CH_3-\overset{H}{\underset{H}{N^+}}-CH_3$$

$$\ddot{N}H_3 \overset{H^+}{\rightleftharpoons} NH_4^+$$

Ammonia

Strong acid (unstable)



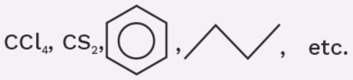
$$CH_3 \xrightarrow{+I} \overset{..}{N}(\uparrow^{+I} CH_3) \xleftarrow{+I} CH_3 \overset{H^+}{\rightleftharpoons} CH_3-\overset{H}{\underset{CH_3}{N^+}}-CH_3$$

weak conjugated acid (Stable)

Basic strength : 3° Amine > 2° Amine > 1° Amine > $\ddot{N}H_3$

(2) Basic strength of amine in case of non-polar medium

● Basic strength of amine in case of non- polar medium



CCl_4, CS_2, , , etc.

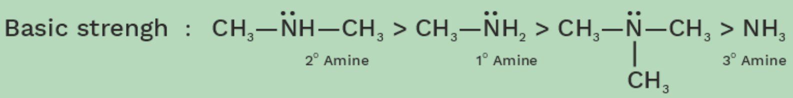
Non-polar Medium

Basic strength : 3° Amine > 2° Amine > 1° Amine > $\ddot{N}H_3$

Basic strength of amine in aqueous medium

(1) Basic strength of amine in case of methyl amine.

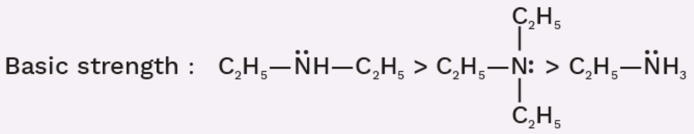
Basic Strength of methyl amines



Basic strengh : $\underset{2^\circ\ \text{Amine}}{CH_3-\ddot{N}H-CH_3} > \underset{1^\circ\ \text{Amine}}{CH_3-\ddot{N}H_2} > \underset{3^\circ\ \text{Amine}}{CH_3-\underset{\underset{CH_3}{|}}{\ddot{N}}-CH_3} > NH_3$

(2) Basic strength of amine in case of ethyl amine

Basic strength of ethyl amine.



Basic strength : $C_2H_5-\ddot{N}H-C_2H_5 > C_2H_5-\overset{\overset{C_2H_5}{|}}{\underset{\underset{C_2H_5}{|}}{N:}} > C_2H_5-\ddot{N}H_2$

Note:

(1) Basic strength $\propto$ +I effect $\propto \dfrac{1}{-\text{I effect}}$

(2) Basic strength $\propto$ Tendency donate lone pair of electrons to H^+ ion.

(3) Basic strength $\propto$ Stability of cation.

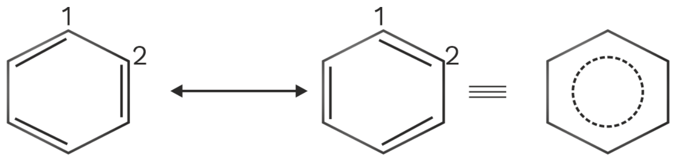
Resonance

- When properties of a molecules can not explain by single lewis dot structure even some time, we made more than 1 lewis dot structure that all structure canonical/resonating/ contributing structure but real structure is resonating hybrid. Which can explain all pp

Concept Ladder

The formula of the conjugate base is the formula of the acid less one hydrogen. The formula of the conjugate acid is the formula of the base plus one hydrogen ion.

and cp of molecule, for a resonance comp. must have conjugated system.



I II

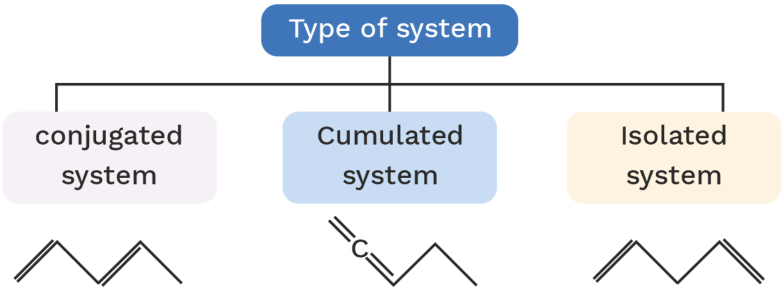
Bond Length between C—C atom= 1.39Å

Bond Length: $C_1—C_2$=1.54Å $C_1—C_2$=1.34Å

- Hypothetical concept.
- Permanent effect.
- General resonance is stabilizing phenomenon.
- In resonance we can't change position of atom. It involve only delocalisation of π–e^-s/ lone pair/ -ve charge/ free radical and +ve charge.
- Resonance is a intermolecular phenomenon.
- Atoms or orbital which are participate in resonance must be in the same plane (comp. must be planer or innerly planer only in resonance area)
- In resonance pure p-orbital/ pure d-orbitals are participated (anhydride orbitals)
- Hybrid orbital never participate in resonance.
- More stable resonating structure will give more contribution resonating hybrid.

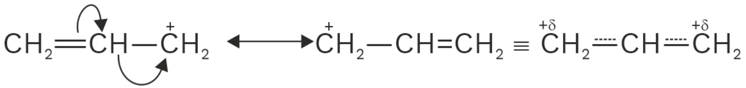
Concept Ladder

Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several resonance structures.



Condition for resonance/Mesmeric effect.

(1) Double bond/+ at conjugated position

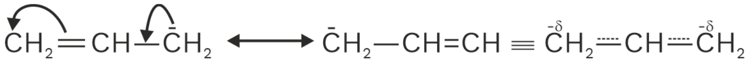


$$CH_2{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2 \equiv \overset{+\delta}{C}H_2 \cdots CH \cdots \overset{+\delta}{C}H_2$$

(allylication)I

Number of Resonating Structures (R.S) = 2

(2) =/- at conjugated position

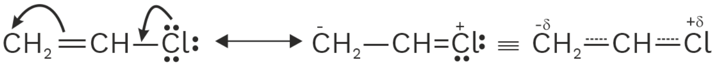


$$CH_2{=}CH{-}\bar{C}H_2 \longleftrightarrow \bar{C}H_2{-}CH{=}CH \equiv \overset{-\delta}{C}H_2 \text{-----} CH \text{-----} \overset{-\delta}{C}H_2$$

(allylic anion)

Number of Resonating Structures (R.S) = 2

(3) = / ⚇ at conjugated position



$$CH_2{=}CH{-}\ddot{C}l\colon \longleftrightarrow \bar{C}H_2{-}CH{=}\overset{+}{C}l\colon \equiv \overset{-\delta}{C}H_2 \text{-----} CH \text{-----} \overset{+\delta}{C}l$$

(Vinylic chloride)

Number of Resonating Structures (R.S) = 2

(4) =/Free radical at conjugated position

$$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$$

(Allylic F.R)

Number of Resonating Structures (R.S) = 2

Concept Ladder

Resonance structures are not in equilibrium with each other, they represent contributions to an overall resonance "Hybrid".

(5) =/conjugated with D.B.

(a)

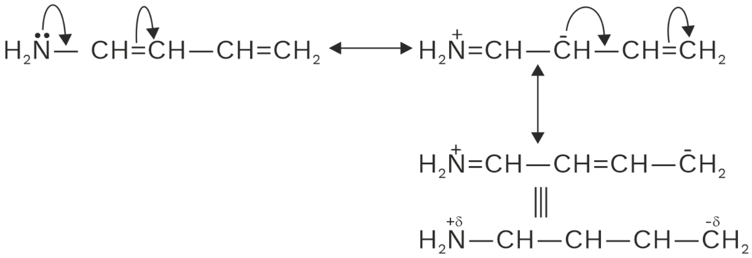
$$CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow \bar{C}H_2{-}CH{=}CH{-}\overset{+}{C}H_2$$

(1, 3—butadiene)

Number of Resonating Structures (R.S) = 2

In 1, 3-butadine resonance takes place in both the directions so it is bidirectional

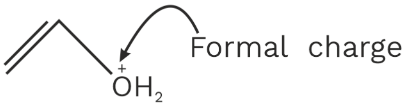
(b)

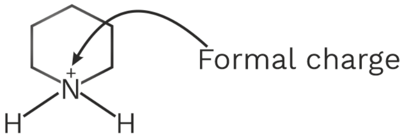


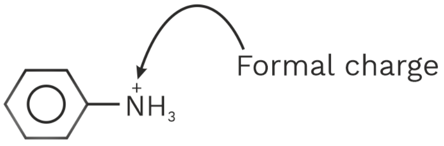
$$H_2\ddot{N}{-}CH{=}CH{-}CH{=}CH_2 \longleftrightarrow H_2\overset{+}{N}{=}CH{-}\bar{C}H{-}CH{=}CH_2$$
$$\updownarrow$$
$$H_2\overset{+}{N}{=}CH{-}CH{=}CH{-}\bar{C}H_2$$
$$|||$$
$$H_2\overset{+\delta}{N}{-}CH{-}CH{-}CH{-}\overset{-\delta}{C}H_2$$

Note:

- Formal charge never participate in resonance.



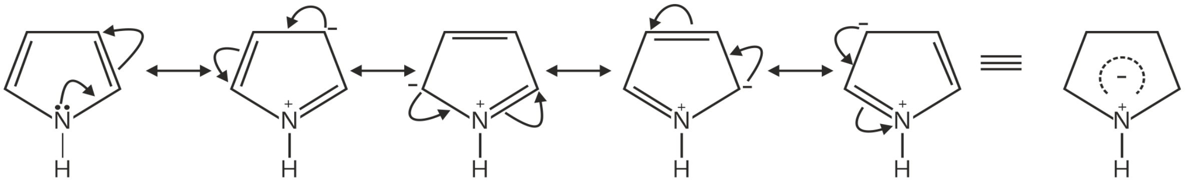




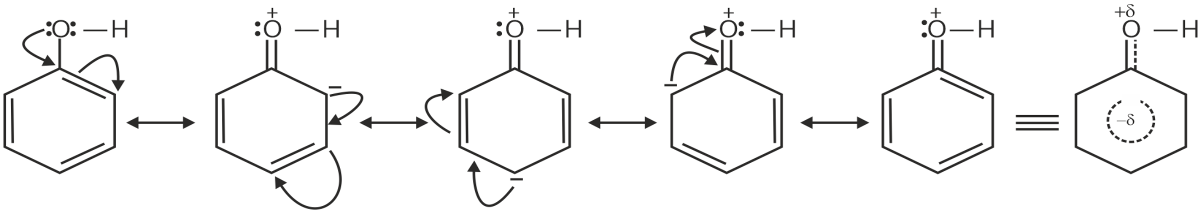
- Any compound must have 3 parallel p-orbitals for resonance.
- For ions must have two parallel p-orbital

Different Resonating Structures

(1)



(2)



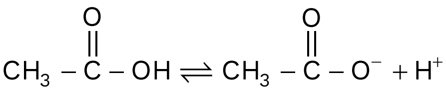
Note:

- In linear molecule, resonance effect observed at both terminal position .
- In benzene molecule, resonance effect observed at ortho and para position.

Equivalent Resonance

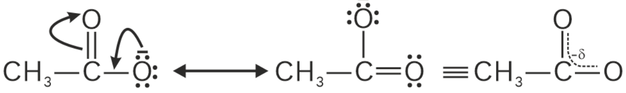
- It more effective than normal resonance.

(a)

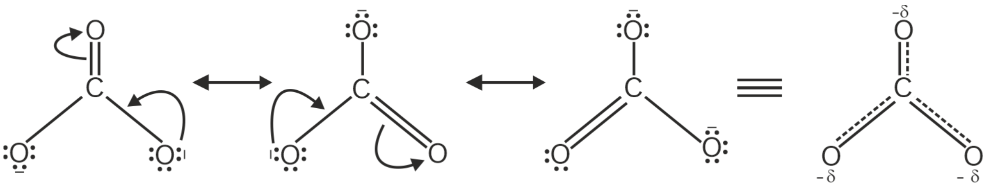


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightleftharpoons CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H^+$$

Acetic Acid Acetate ion



(b) $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{-2}$

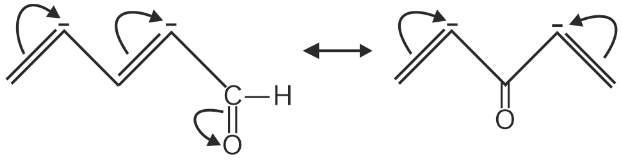


Concept Ladder

Resonance structures are not in equilibrium with each other, they represent contributions to an overall resonance "Hybrid".

Extended Resonance

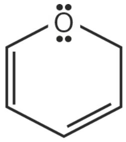
(a)



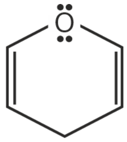
(I) (II)

Stability: I > II

(b)



(I)



(II)

Stability: I > II

Rack your Brain

Why carboxylic acids (RCOOH) are less stable than carboxylate ions ($RCOO^-$) ions?

Stability of Resonating Structure

- No. of covalent bonds
- Stability or non - polar R.S. > Stability of polar R.S
- At more EN atom -ve charge stable and at lest EN atom + ve charge stable
- stability of polar R.S with complete octate > stability of polar R.S with incom octate

Distance factor

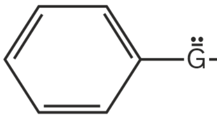
- +/-]Distance Decreases → Stability Increases
  Distance Increases → Stability Decreases
- +/+]Distance Decreases → Stability Decreases
  -/-]Distance Increases → Stability Increases

Types of Resonance / Mesomeric effect

+M/+R effect → Electron releasing effect

-M/-R effect → Electron withdrawing effect

(1) +M/+R effect



→ All lone pair containing + All -ve charge

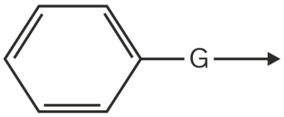
↓

If lone pair and -ve charge involve in Resonance → +R/+M

+M/+R groups

$—CH_2$, $—N(CH_3)_2$, $—NHCH_3$, $—NH_2$, —OH, $—OCH_3$ —Cl, etc.

(2) -M/-R effects

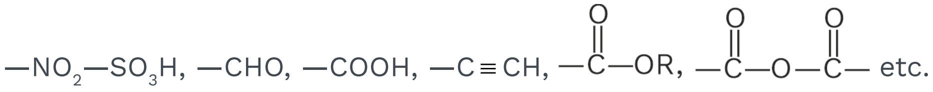


All polar π -bond + All vacant orbital containing group

↓

If polar π-bond and vacant orbital involve in resonance ⟶ -M/-R effect

-M/-R groups



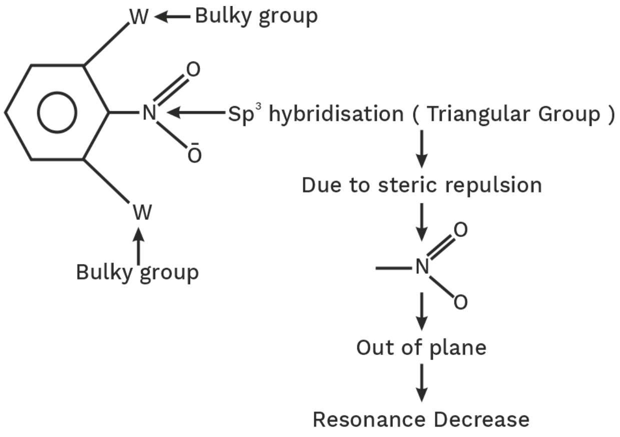
$—NO_2—SO_3H$, $—CHO$, $—COOH$, $—C\equiv CH$, $—\overset{O}{\overset{\|}{C}}—OR$, $—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—$ etc.

Note:

$$\text{Stability of anion} \propto -M/-I \propto \frac{1}{+M/+I} \propto \text{extent of resonance}$$

Steric inhibition of Resonance [SIR]

Whenever bulky group at ortho position of triangular group due to steric repulsion triangular group change its plane [Out of plane] so tendency of resonance with benzene decrease this is known as SIR.



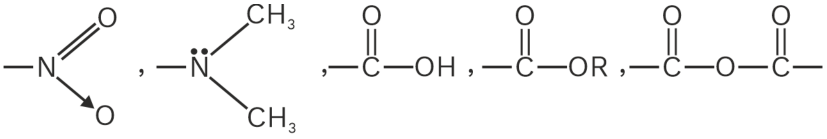
Previous Year's Question

A tertiary butyl carbocation is more stable than asecondary butyl carbocation because of which of the following?

[NEET]

(1)–I effect of – CH_3 groups
(2)+R effect of – CH_3 groups
(3)–R effect of –CH_3 groups
(4)Hyperconjugation

(a) All triangular group

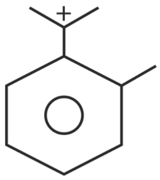


(b) Bulky group

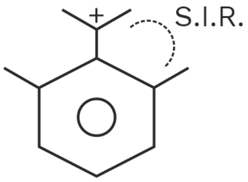
All triangular group + all alkyl group

Examples:

(1)



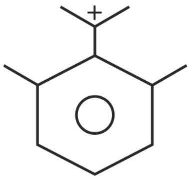
(I)



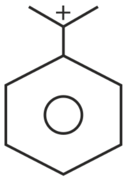
(II)

Stability: I > II

(2)



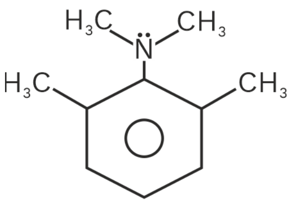
(I)



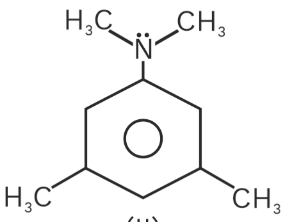
(II)

Stability: II > I

(3)



(I)



(II)

Stability: II > I

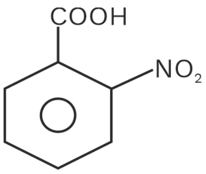
Note:

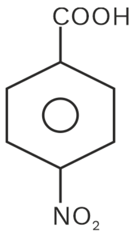
Ortho Effect (For only aromatic carboxylic acid)

1. Ortho effect is the application of SIR.
2. Ortho substituted aromatic acid is more acidic than para and meta substituted carboxylic acid, this effect is known as ortho effect.

Example

(1)





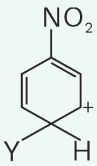
(I) (II)

Acidic Strength: I > II

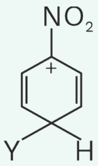
Previous Year's Question

Which of the following carbocations is expected to be most stable? **[NEET]**

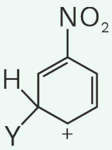
(1)



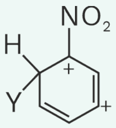
(2)



(3)



(4)



Rack your Brain

Ortho substituted aromatic acid is more acidic than para and meta substituted carboxylic acid. Why?

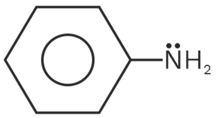
Note:

$$\text{Basic Strength} \propto \frac{1}{\text{Resonating Structures}}$$

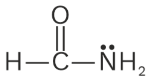
$$\text{Basic Strength} \propto \frac{1}{\%\ \text{s} - \text{Character of Donor atom}}$$

$$\text{Basic Strength} \propto +\text{I}/+\text{M} \propto \frac{1}{-\text{I}/-\text{M}}$$

(2)



(I)

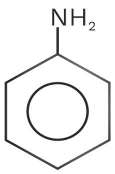


$H-\overset{\overset{\large O}{\|}}{C}-\ddot{N}H_2$

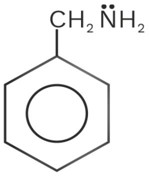
(II)

Basic strength: I > II

(3)



(I)



(II)

$CH_3-\ddot{N}H-CH_3$

(III)

Basic strength: III > II > I

Concept Ladder

There are thousands of aromatic compounds that are not monocyclic such as naphthalene, azzulene, anthracene etc. are polycyclic aromatic hydrocarbons.

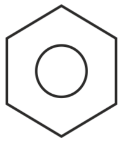
Aromaticity (Huckel's Rule)

Aromaticity (Huckel's Rule)

- Aromatic Compound
- Non - Aromatic Compound
- Anti Aromatic Compound

Example:

(a)



↓

Resonance + extra factor

Aromatic

Resonance Energy

= -36 K cal/mole

↓

Only Resonance

Resonance Energy

= -22 K cal/mole

Rack your Brain

How % s-character of donor atom is related to basic strength?

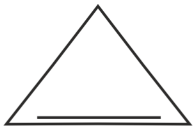
Stability

Aromatic	>	Non Aromatic	>	Anti Aromatic
Cyclic, Resonance and All e^- in BMO		Non-Cyclic, Resonance and All e^- in BMO		Cyclic, Resonance and But all e^- ABMO

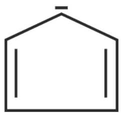
Aromatic	Non-Aromatic	Anti-aromatic
Compound must be cyclic	Out of four, as disscoused in aromatic condition. If any one of condition violated then compound behave as non-aromatic	Compound must be cycle
Compound must be planer		Compound must be planer
Compound must have cyclic resonance over the entire cyclic		Compound must have cyclic resonance
Compound must follow Huckel's rule $(4n + 2)\ \pi\ e^-$		Compound must follow Hucket's rule $(4n)\ \pi\ e^-$
n = 0,1,2,3,4,5,......., etc.		n = 1,2,3,4,5,......., etc.
Trick $2\pi e^-$, $6\pi e^-$, $10\ \pi e^-$, $14\ \pi e^-$, $22\ \pi e^-$ etc		Trick $4\pi e^-$, $8\pi e^-$, $12\ \pi e^-$, etc

Examples of Aromatic Compounds:

(1)

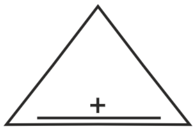


(2)



Examples of Non Aromatic Compounds:

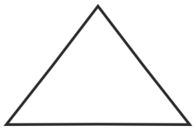
(1)



Rack your Brain

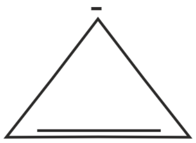
In case of anti aromatic species delocalisation of p-electrons dows not takes place. Why?

(2)

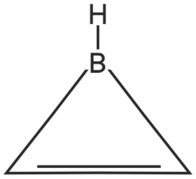


Examples of Anti Aromatic Compounds:

(1)



(2)

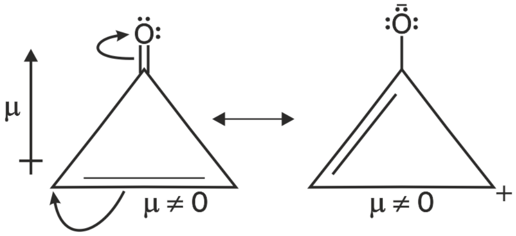


Quasi aromatic compound

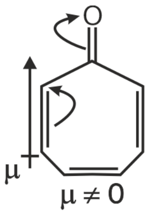
- Ionisied aromatic compound is known as Quasi aromatic compound.
- Quasi aromatic compound have always non-zero dipole moment.
- Quasi aromatic compound soluble in polar solvent.

Examples:

(a)



(b)



Tropopone

Previous Year's Question

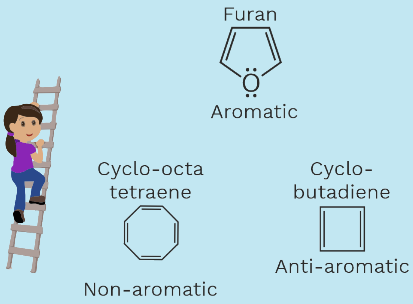
Cyclic hydrocarbon 'A' has all the carbon and hydrogen atoms in a single plane. All the carbon–carbon bonds have the same length, less than 1.54Å, but more than 1.34Å. The bond angle will be **[AIPMT]**

(1) 109°28']
(2) 100°
(3) 180°
(4) 120°

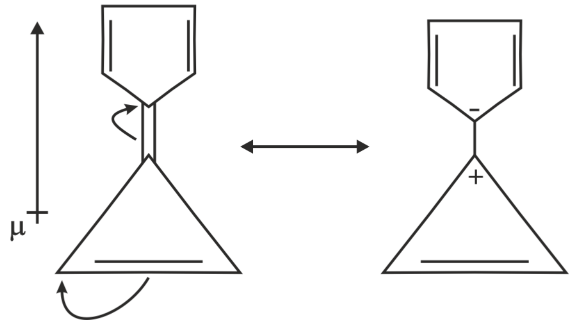
Rack your Brain

Why tropylium ion is aromatic in nature?

Concept Ladder



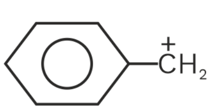
(c)



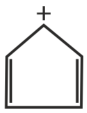
Rack your Brain

Benzyl anion, Benzyl free radical, aniline, phenol and benzyl cation are all aromatic compounds. Why?

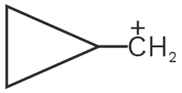
Q.1 Write down the stability of the following species?



I



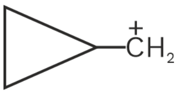
II



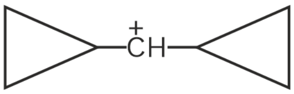
III

A.1 Stability: III > I > II

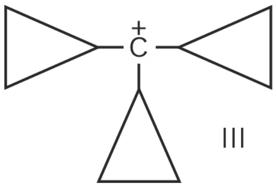
Q.2 Write down the stability of the following species?



I



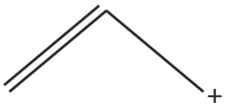
II



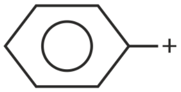
III

A.2 Stability: III > II > I

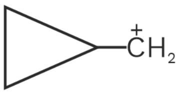
Q.3 Write down the stability of the following species?



I



II

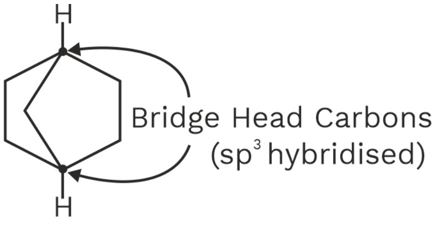


III

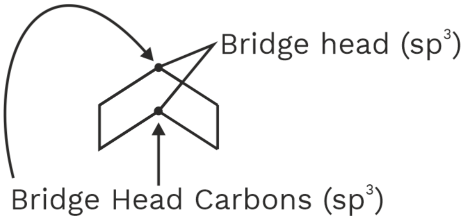
A.3 Stability: III > II > I

Bredt's Rule

It states that a double bond cannot be placed at the bridgehead of bridged ring system, unless the ring are large enough.



(Bridge bicyclo compound)



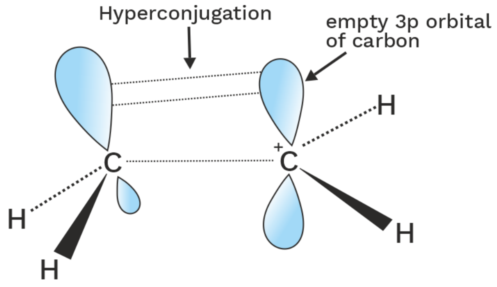
Note:

Dancing Resonance

(a) Only in cyclo proply methyl cation.

(b) Generally dancing resonance is more effective than normal resonance.

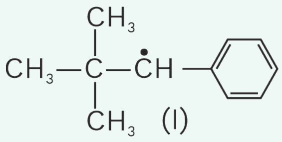
Hyper-conjugation Effect (+H effect)



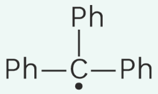
- Permanent effect.
- Hypothetical concept.
- In H.C. effect unparallel p-orbital participate.
- H.C. is week effect than resonance.
- H.C effect explain stability of carbo cation, free Radical, alkene which have atleast one α-hydrogen atom alkyl having at least 1 a hydrogen.
- H.C effect can not explain stability of carboanion due to repulsion factor.
- H.C. effect also known as Natnan Bekar effect/ No bond Resonance.
- Following conjugator system given hyper conjugation effect.

Previous Year's Question

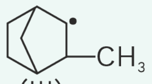
Consider the following Compounds :



(I)



(II)

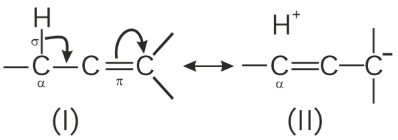


(III)

Hyperconjugation occurs in

[NEET]

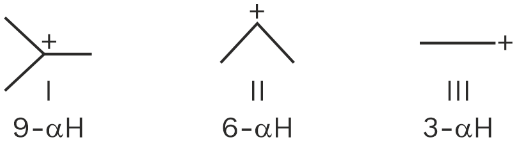
(1) III only
(2) I and III
(3) I only
(4) II only



Applications

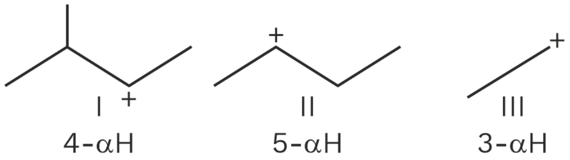
1. Stability of carbocation

(i)



Stability: I > II > III

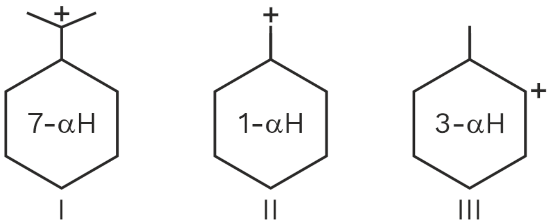
(ii)



Stability: II > I > III

II > I > III

(iii)



Stability: I > III > II

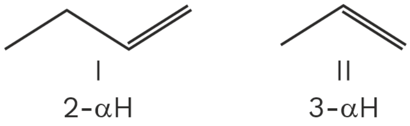
2. Stability of alkene

(i)

$CH_3—CH=CH_2$	$CH_2=CH_2$
I	II
3-αH	0-αH

Stability: I > II

(ii)



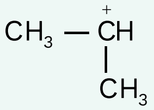
Stability: II > I

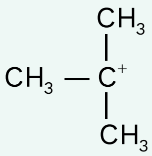
Previous Year's Question

Which amongst the following is the most stable carbocation? **[NEET]**

(1) $\overset{+}{C}H_3$

(2) $CH_3\overset{+}{C}H_2$

(3)

$CH_3—\overset{+}{C}H(CH_3)$

(4)

$CH_3—C^+(CH_3)_2$

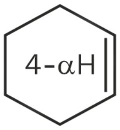
Rack your Brain

Why 3° allyl cation is more stable then that of 2° allyl cation?

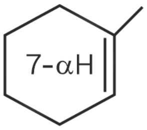
Concept Ladder

In order to achieve stabililty, carbocation go through rearrangement through shift of hydride ion (H^-) or methide ion (CH_3^-) from adjacent carbon atom. These shift are known as 1, 2 shifts.

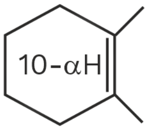
(iii)



I



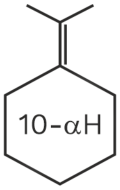
II



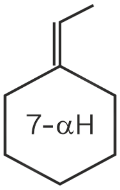
III

Stability: I > III > II

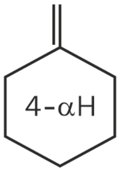
(iv)



I



II



III

Stability: I > II > III

Previous Year's Question

Which of the following is the most stable carbocation (carbonium ion)?

[NEET]

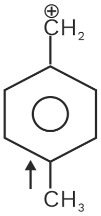
(1) $CH_3\overset{+}{C}H_2$

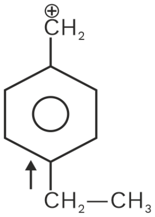
(2) $(CH_3)_2\overset{+}{C}H_2$

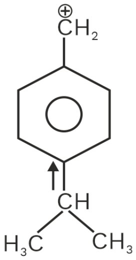
(3) $(CH_3)_3\overset{+}{C}$

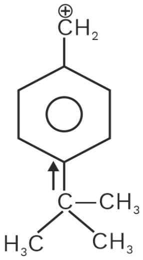
(4) $C_6H_5\overset{+}{C}H_2$

Q.4 Write down the stability of the following species?

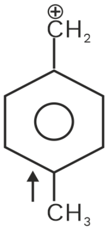




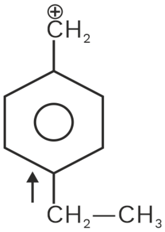




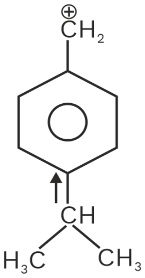
A.4



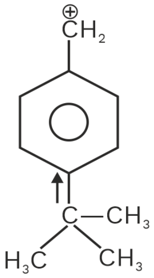
3–αH &
Hyper
conjugation



2–αH &
Hyper
conjugation



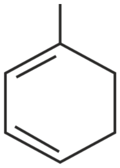
1αH &
Hyper
conjugation

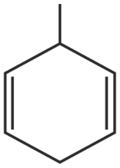


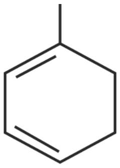
+I Effect
Only

Stability: I > II > III > IV

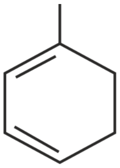
Q.5 Write down the stability of the following species?

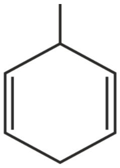

(I)

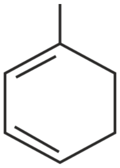

(II)


(III)

A.5


7-αH
(I)


No Resonance
(II)


3-αH & Resonance
(III)

Stability: I > III > II

Q.6 Discuss the bond energy of the following species.

$CH_3—CH_2—H$ (I) $CH_2=CH—H$ (II) $CH≡CH—H$ (III)

A.6

(I) $CH_3—CH_2—H \downarrow CH_3—\dot{C}H_2$

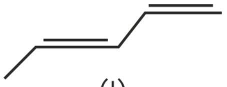
Max. Stable
free radical,
Min. B.E

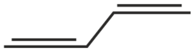
(II) $CH_2=CH—H \downarrow CH_2=\dot{C}H$

(III) $CH≡CH—H \downarrow CH_2≡\dot{C}H$

Min. Stable
free radical,
Max. B.E

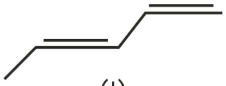
Q.7 Write down the stability of the following species?

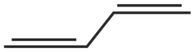

(I)


(II)


(III)

A.7

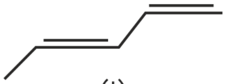

(I)
3–αH & Resonance

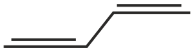

(II)
Only Resonance


(III)
No Resonance

Stability: I > II > III

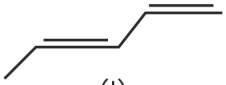
Q.8 Write down the stability of the following species?

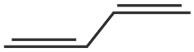

(I)


(II)


(III)

A.8

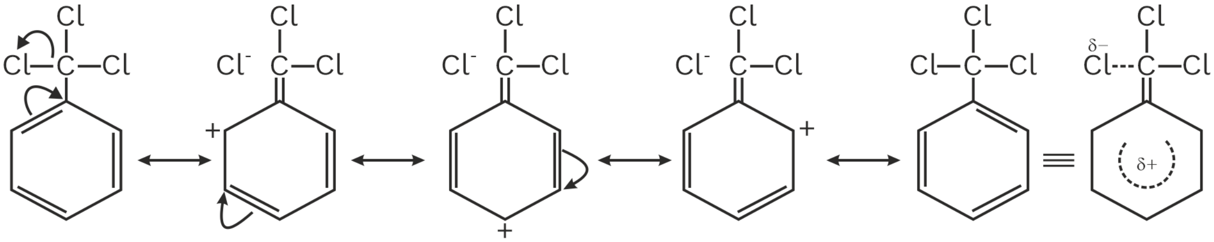

(I)
3–αH & Resonance


(II)
Only Resonance


(III)
No Resonance

Stability: I > II > III

Reverse hyper conjugation or -H effect



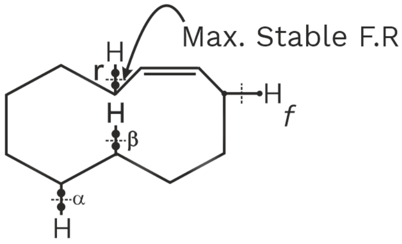
Note:

- Reverse hyper conjugation Results decrease in electron density.
- It deactivat the ring.
- Reverse hyper conjugation shown by m-directing group.

Bond Energy

$$\text{Bond Energy} \propto \frac{1}{\text{Stability of free radical}}$$

Note:



Bond energy: α > *f* > β > r

Heat of combustion (H.O.C)

Amount of heat released when a substance undergoes complete combustion with oxygen under standard candtion.

Rack your Brain

Bond energy is inversely proportional to stability of free radical. Why?

Definitions

Heat of combustion is defined as the amount of heat liberated when a given amount of the substance undergoes combustion.

Note:

1. Heat of combustion $\propto$ No of carbon atom
2. If number of carbon atoms are equal then

   Heat of combustion $\propto \dfrac{1}{\text{stability of comp.}}$

Examples

(1)


I


II

H.O.C: I > II

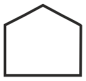
(2)


I


II

H.O.C: I > II

(3)


I


II

H.O.C: II > I

(4)


I

Cis


II

Tran

H.O.C: I > II

Heat of Hydrogenation (H.O.H)

Amoung of heat release when 1 mole of unsotaurated hydrocarbon completely hydrogenated into saturated compound.

Note:

Heat of hydrogenation number of π–bond (Except aromatic)

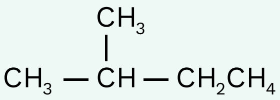
- If number of π-bond are equal, then heat of hydrogenation $\propto \dfrac{1}{\text{Stability of alkene}}$.

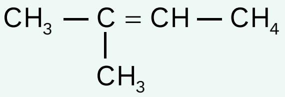
Rack your Brain

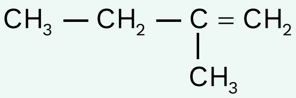
Why heat of combustion is inversely proportional to stability of the compound?

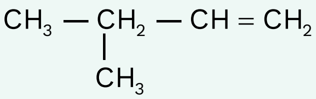
Previous Year's Questions

2-Methyl-2-butene will be represented as **[NEET]**

(1) 
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2CH_4$

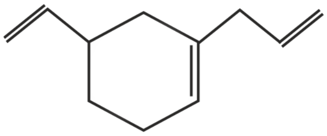
(2) 
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_4$

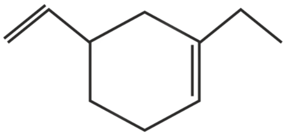
(3) 
$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2$

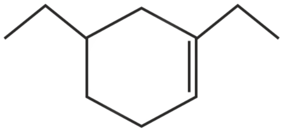
(4) 
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH_2}-CH=CH_2$

Examples

(1)

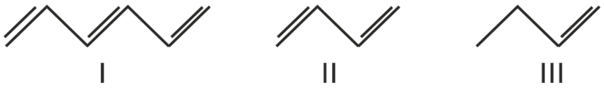

I


II


III

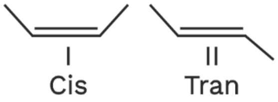
HOH: I > II > III

(2)



HOH: I > II > III

(3)



HOH: II > I

Note:

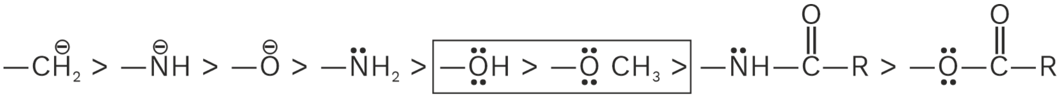
Order of Effect

Resonance > Hyper conjugation > -I Effect

Concept Ladder

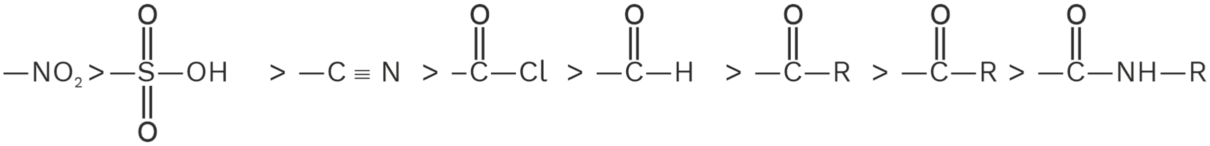
Keto-enol tautomerism is possible only in those ketones and aldehydes in which at least one α-hydrogen atom is present so that it may convert the carbonyl group to enol group.

Order of +M effect



$$-\overset{\ominus}{C}H_2 > -\overset{\ominus}{N}H > -\overset{\ominus}{O} > -\ddot{N}H_2 > \boxed{-\underset{\cdot\cdot}{\ddot{O}}H > -\underset{\cdot\cdot}{\ddot{O}}\,CH_3 >} -\ddot{N}H-\overset{\overset{O}{\|}}{C}-R > -\underset{\cdot\cdot}{\ddot{O}}-\overset{\overset{O}{\|}}{C}-R$$

Order of -M effect



$$-NO_2 > -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH > -C\equiv N > -\overset{\overset{O}{\|}}{C}-Cl > -\overset{\overset{O}{\|}}{C}-H > -\overset{\overset{O}{\|}}{C}-R > -\overset{\overset{O}{\|}}{C}-R > -\overset{\overset{O}{\|}}{C}-NH-R$$

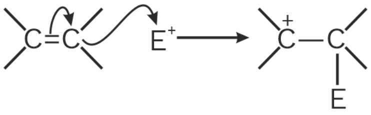
Electromeric effect (E effect)

- Temporary effect
- It involve complete delocalization of electrons.
- It operates only in molecules having π-electrons (i.e, multiple bonded compounds).
- It induced by the attracking reagents (nucleophiles & electrophiles) in a chemical reaction.

Type of Electromeric effect

1. +E effect **2.** –E effect

+E Effect: In presence of electrophiles (E^+), π-electrons shifts to other carbon to make adjustment for the incoming electrophile to be added.



$$>C=C< \quad E^+ \longrightarrow\ >\overset{+}{C}-\underset{E}{\underset{|}{C}}<$$

Previous Year's Questions

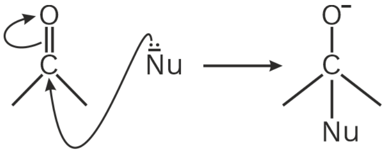
Which of the following statements is not correct for a nucleophile?

[NEET]

(1) Ammonia is a nucleophile
(2) Nucleophiles attack low e^- density sites
(3) Nucleophiles are not electron seeking
(4) Nucleophile is a Lewis acid

Observe that E^+ (electrophile) adds to the atom (group) where electrons are transferred. Such effect is known as +E effect i.e., when the transfer of electrons takes place towards the attacking reagent. .

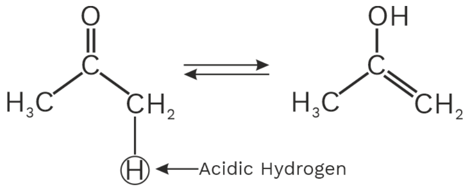
-E Effect: In polar bonds, in presence of attacking reagent, a complete transfer of electron (one of π e^- pair) to more electronegative atom takes place, e.g., $\rangle\overset{\delta+}{C}=\overset{\delta-}{\ddot{O}}$ in presence of nucleophiles like R^-, CN^-, HSO_3^-, p electrons shifts over to O.



Observe that CN^- (nucleophile) adds to the atom (group) from where electrons are transferred. Such effect is known as -E effect i.e., when the transfer of electrons takes place away from the attacking reagent.

Tautomerism (Chemistry of α-H)

Compound having same. molecular formula but different structural formula due to transfer of acidic Hydrogen is known as tautomer's and phenomenon is Tautomerism.



Keto form Enol form

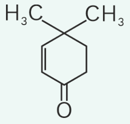
- Two tautomers have dynamic equation that's why tautomerism also known as Desmotropism.
- Due to rapid shifting of H^+ ion tautomerism also known as cationotropy/ prototropy.
- All tautomer also have functional group I but periorty given to tautomerism.
- Two tautomeric structure are real in nature while two resonanting structure are hypothetical.

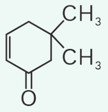
Rack your Brain

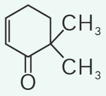
Why electromeric effect is a temporary polarising effect?

Previous Year's Questions

Given


(I)


(II)

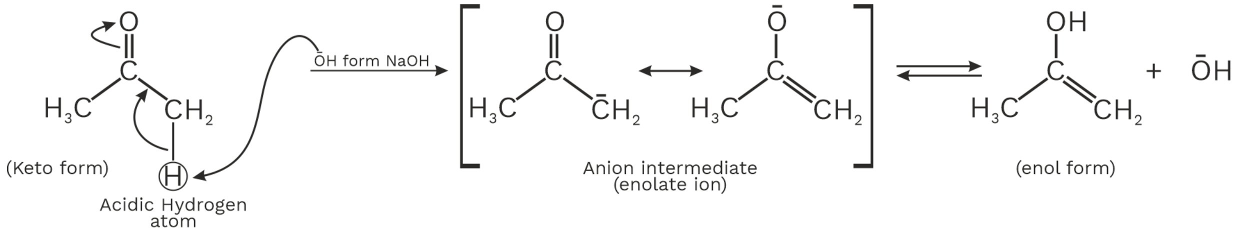

(III)

Which of the given compounds can exhibit tautomerism?

[NEET]

(1) II and III
(2) I, II and III
(3) I and II
(4) I and III

- Due to rapid shifting of H^+ ions between two atoms of same molecule due to acid/ base rxn is known as tautomerism.

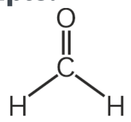


Note:

- If acidic character in C—H bond increasing, then stability of Anion Increasing, Rate determing step should be fast, reaction farours to the forward direction and enol content increasing.

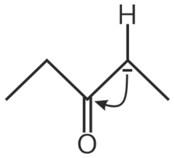
Example:

(1)



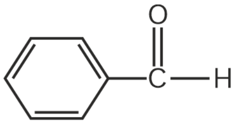
No α-H
No. tautomeric form

(2)



α-H is present
tautomeric form possible

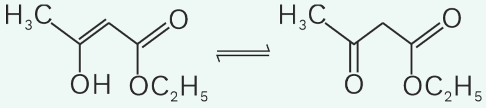
(3)



No. α-H
No. tautomeric form

Previous Year's Questions

The enolic form of ethyl acetoacetate as shown below has

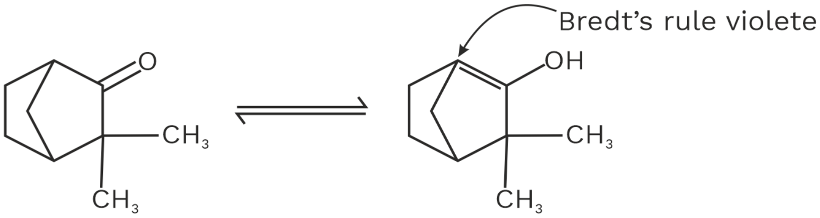


[NEET]

(1) 9 sigma bonds and 2 pi-bonds
(2) 9 sigma bonds and 1 pi-bond
(3) 18 sigma bonds and 2 pi-bonds
(4) 16 sigma bonds and 1 pi-bond

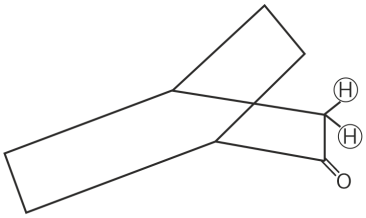
Bredt's Rule in tautomerism

If Bredt's rule violate in enol form then compound does not exit tautomerism.



No Tautomerism
No Enol form

According to Bredt's rule a double bond cannot be placed at the bridgehead of a bridged ring system, unless the rings are large enough.

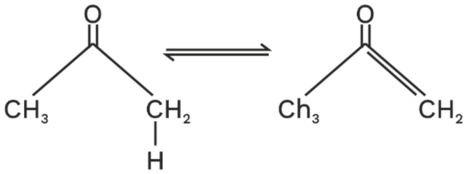


Tautomerism is possible

Type of tautomerism

Keto–enol tautomerism

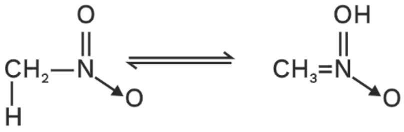
1.



Keto form
triad system

⇒ 6 deutrium exchange

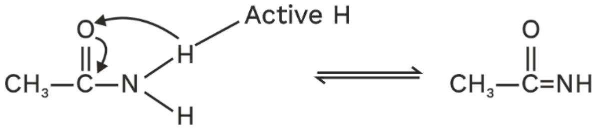
2. Nitro – Aci fom



Nitro form

Aci form

3. Amido–imido form tauto

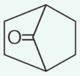


Amido form

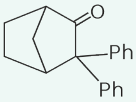
Imido form

Previous Year's Questions

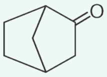
Which among the given molecules can exhibit tautomerism?



(I)



(II)



(III)

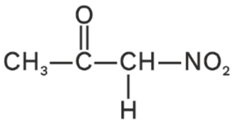
[AIPMT]

(1) III only
(2) Both I and III
(3) Both I and II
(4) Both II and III

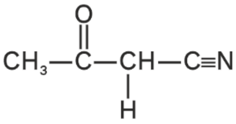
Concept Ladder

Keto-enol equilibrium more fvavourable by stabilizing the enol form such as extended conjugation, intramolecular H-bonding and aromatic characters etc.

Q.9 Which of the following species has maximum enol content.


$CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{CH}}-NO_2$

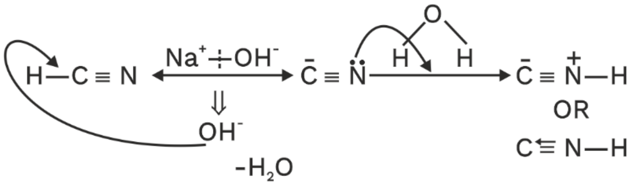
(I)


$CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{CH}}-C\equiv N$

(II)

A.9 enol content: I > II

4. Cyano–isocyano tauto



Cyano form
Diad system

Isocyano form

Keto-enol content

- Generally keto form is more stable than its enol form because (C = 0) is thermodynamically more stable bond.
- It as covalent as well as extra ionic character that why reaction favours to direction of (C = 0).
- Enol form may be stable than its keto form if following factors are present in enol form.

1. Hydrogen bonding
2. Resonance
3. Armoaticity
4. Acidic character in C—H bond.

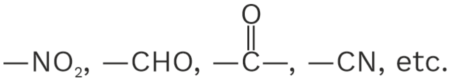
Note:

Active methylene

Whenever CH_2 having strong e^- withdrawing goup then it is called active methylene.

In case of active methylene enol content form always more than 50%.

Electron withdrawing group:



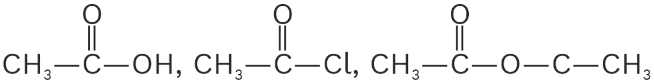
$$-NO_2,\ -CHO,\ -\overset{\overset{O}{\|}}{C}-,\ -CN, \text{ etc.}$$

enol content > 50%

Note:

Generally acid and acid derivaties formed less enol content.

Ex.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH,\ CH_3-\overset{\overset{O}{\|}}{C}-Cl,\ CH_3-\overset{\overset{O}{\|}}{C}-O-C-CH_3$$

Previous Year's Questions

Tautomerism is exhibited by

[AIPMT]

(1) R_3CNO_2
(2) RCH_2NO_2
(3) $(CH_3)_3CNO$
(4) $(CH_3)_2NH$

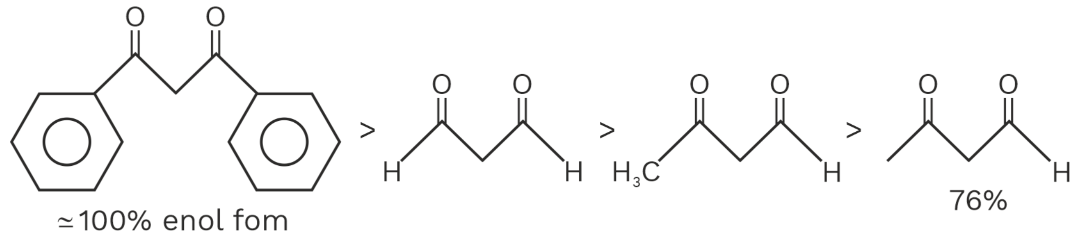
Concept Ladder

Keto-enol tautomerism is possible only in those ketones and aldehydes in which at least one α-hydrogen atom is present so that it may convert the carbonyl group to enol group.

Rack your Brain

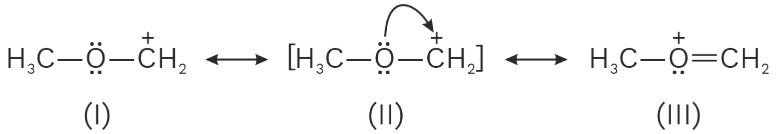
In most of the cases, the keto form is more stable than the enol form. Why?

Enol content



Q.10 Draw the possible resonance structure for $CH_3-\ddot{O}-\overset{+}{C}H_2$ and predict which of the structures is more stable. Give the reason for your answer.

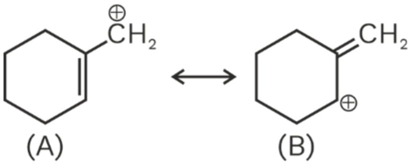
A.10



$$H_3C-\ddot{O}-\overset{+}{C}H_2 \longleftrightarrow [H_3C-\ddot{O}-\overset{+}{C}H_2] \longleftrightarrow H_3C-\overset{+}{O}=CH_2$$

The structure A is less stable than that of the structure C because structure C has complete octet of all the atoms, whereas, in structure A, carbon atom have a positive charge and incomplete octet (8 electrons in its valence shell).

Q.11 Which of the following ions is more stable? Use resonance to explain your answer.

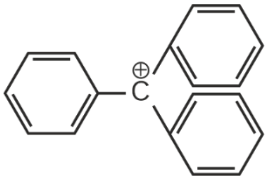


A.11 allylic > 3° > 2° > 1° > methyl

The stability of carbocation is decided by hyperconjugation, resonance and inductive effect.

As structure A is having a primary (allylic) carbocation, whereas the carbocation in structure B has secondary (allylic) carbocation.

Q.12 The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the cause of the high stability of this cation.



A.12 Triphenylmethyl cation is tertiary carbocation and the positive charge is on the carbon atom which is stabilized by three phenyl group by resonance. Due to the resonance the stability increases.

Q.13 Identify the most stable species in the following set of ions giving reasons.

$\overset{+}{C}H_3, \overset{+}{C}H_2Br, \overset{+}{C}HBr_2, \overset{+}{C}Br_3$

$\overset{-}{C}H_3, \overset{-}{C}H_2Cl, \overset{-}{C}HCl_2, \overset{-}{C}Cl_3$

A.13 (i) Bromine atom is an electron-accepting (electron-withdrawing) group and has a lone pair of electrons, Br-atom destabilizes the positive charge on a C-atom. Hence CH_3^+ will be more stable.

(ii) $\bar{C}Cl_3$ will be most stable because Cl is electron-accepting (electron-withdrawing) atom and the negative charge on C-atom will be stabilized by the Cl-atom. As the number of Cl-atom attached to carbocation increases the stability also increases.

Q.14 Give two points of difference between the inductive effect and resonance effect.

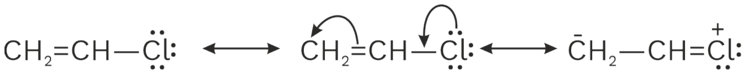
A.14

Inductive Effect	Resonance Effect
The transmission of the electron is only from sigma bond.	The transmission occurs from both sigma and pi bond.
It is possible when the polarization of bond takes place.	It is possible only if the system is conjugated.

Q.15 Draw the resonance structures of the following compounds.

$CH_2 = CH - \ddot{\underset{..}{Cl}}:$

A.15



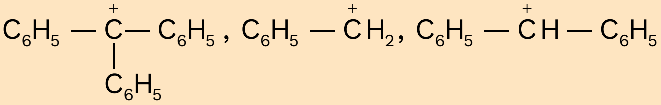
$CH_2{=}CH{-}\ddot{\underset{..}{Cl}}: \longleftrightarrow CH_2{=}CH{-}\ddot{\underset{..}{Cl}}: \longleftrightarrow \bar{C}H_2{-}CH{=}\overset{+}{\underset{..}{Cl}}:$

(I) (II) (III)

Q.16 Why does SO_3 act as an electrophile?

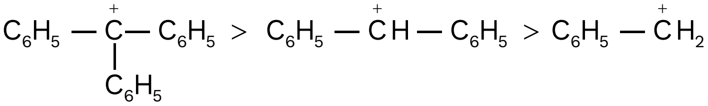
A.16 Oxygen is more EN than sulphur. The electron density at S in SO_3 is reduced by the oxygen atoms therefore to suppress the partial positive charge SO_3 acts as an electrophile

Q.17 Write down the stability of the following species.



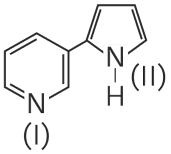
$C_6H_5 - \underset{\displaystyle C_6H_5}{\overset{+}{C}} - C_6H_5,\ C_6H_5 - \overset{+}{C}H_2,\ C_6H_5 - \overset{+}{C}H - C_6H_5$

A.17 More is the number of resonanting strucutres dispersing the +ve charge over carbon, more is teh carbocation stability e.g.



$C_6H_5 - \underset{\displaystyle C_6H_5}{\overset{+}{C}} - C_6H_5 > C_6H_5 - \overset{+}{C}H - C_6H_5 > C_6H_5 - \overset{+}{C}H_2$

Q.18 Hybridisation of nitrogen I and II in the following compound is:



A.18 In pyridine ring electron pair of N atom is localized due to sp^2 hybridization and it is not the part of close loop. While in pyrrole electron pair of N is delocalized and it is part of close loop, hence hybridization state of this N atom is sp^2 not sp^3.

Q.19 Explain the hyperconjugative stability of tert-butyl cation and 2-butene?

A.19 Hyperconjugation is tert-butyl carbocation refers to delocalisation of σ-electrons of C—H bond over the empty p-orbital of carbocation. In 2-butene, it refers to delocalisation of σ-electrons of C—H bond over the π^* orbitals of C=C.

Chapter Summary

1. Bond length

   (i) $\underset{1.54Å}{C_{(sp^3)} - C_{(sp^3)}} > \underset{1.48Å}{C_{(sp^2)} - C_{(sp^2)}} > \underset{1.38Å}{C_{(sp)} - C_{(sp)}}$

   (ii) $\underset{1.5Å}{C - C} > \underset{1.34Å}{C = C} > \underset{1.20Å}{C = C}$

   (iii) Benzene - C—C bond length = 1.34Å

   Resonance energy of benzene = 36.0 K cal/mol = 150.62 KJ.

2. (i) Electron withdrawing group showing –I effect (decreasing order)

   $R_3N^+ > NO_2 > CN > COOH > F > Cl > Br > I > OCH_3 > OH$

   (ii) Electron donating group showing +I effect (decreasing order)

   $O^- > COO^- > (CH_3)_3C > (CH_3)_2CH > CH_3CH_2CH_2 > CH_3$

3. Hyperconjugation effect is weaker than resonance effect.

4. Resonance effect is powerful than inductive effect.

5. Stability of carbocations:

   (i) $(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > C_6H_5\overset{+}{C}H_2 > CH_2 = CH — \overset{+}{C}H_2 > R — \overset{+}{C} = CH_2 >$
   $CH_3\overset{+}{C}H_2 > R — CH = \overset{+}{C}H > C_6H_5^+ > \overset{\oplus}{C}H_3 > HC = \overset{\oplus}{C}$

   (ii) 3° benzylic > 2° benzylic > 1° benzylic

6. Aromatic: Cyclic, planar, complete conjugation (4n + 2)π e^-s, where n = 0, 1, 2....

7. Anti-aromatic: Cyclic planar, complete conjugation, 4nπ e^-s, where n = 1, 2 ....

8. Non-aromatic: Not cyclic or not planar or not completely conjugated.

9. Resonance: When a ion/molecule can be represented by two or more different type of structures but the same arrangement of atomic nuclei but differ in distribution of electrons, the phenomenon is called as Resonance.

10. Hyperconjugation is also known as no-bond resoancne.