ELECTRONIC DISPLACEMENT EFFECTS

Reactions intermediates:

Species obtained between reactant and product during reaction are called reaction intermediates.

Carbocation	Carbanion	Free radical
$\overset{}{\mathrm{C}}\mathrm{H}_{3}$	$\bar{\mathrm{C}}\mathrm{H}_{3}$	ĊH ₃
Highly unstable	Highly unstable	Highly unstable
Incomplete octet	Complete octet	Incomplete octet
Only 6e ⁻ in V. shell	8e-in V. shell	7e ⁻ in V. shell
Lewis Acid	Lewis Base	Neither
Bond Pair $e^- = 3$	Bond Pair $e^- = 3$	Bond Pair $e^- = 3$
Unpaird Pair $e^- = 0$	Unpaired $e^- = 0$	Unpaired $e^- = 1$
Lone Pair $e^- = 0$	Lone Pair $e^- = 1$	Lone Pair $e^- = 0$
Magnetic Moment = $\sqrt{n(n+2)} = 0$	Magnetic moment = 0	Magnetic moment = $\sqrt{3}$
Spin Multiplicity = $2 s + 1 = 1$	Spin Multiplicity = 1	Spin Multiplicity = 2
Singlet C -Intermediate	Singlet C -Intermediate	Doublet C-Intermediate
$Hyb. = sp^2$	$Hyb. = sp^3$	$Hyb. = sp^2$
Bond angle = 120°	Bond Angle = 107°	Bond Angle = 108°

$$* P - C_{r} \xrightarrow{r} + S^{-} \longrightarrow P \xrightarrow{r} (2 \text{ different product})$$

$$(2 \text{ different product})$$

$$(2 \text{ different product})$$

$$(3 \text{ different product})$$

Electron Displacement Effect : (EDE)

Effect because of displacement of electron is known as EDE.

Permanent Effect

- (i) Inductive Effect $(displacement \ of \ \sigma\text{-}e^-) \quad temp.$
- (ii) Resonance/Mesomeric effect (displacement of π e⁻)
- (iii) Hyperconjugation effect (displacement of σe^- in p-orbital)

Temporary Effect

- (i) Inductomeric Effect displacement of σ -e⁻
- (ii) Electromeric Effect $temp. \ displacement \ of \ \pi \ e^-$

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- (i) $\Delta x > \Delta x_1 > \Delta x_2 > \Delta x_3$
- (ii) $\delta = (\delta_1 + \delta_2 + \delta_3 + \delta_4)$
- (iii) $\delta > \delta_1 > \delta_2 > \delta_3 > \delta_4$
- (iv) $\delta_{4} \sim 0$ (experimentally)

Type of inductive effect:

–I-effect : (i) Permanent displacement of σ -e⁻ in a covalent bond because of any atom or group is known as I-effect of that atom. If the electron withdrawing power of group is higher than that of hydrogen then these groups are known as –I groups.

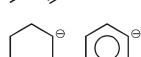
Decreasing order of e⁻ withdrawing tendency by inducting.

-I-Series:

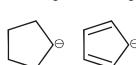
$$-\overset{+}{N}F_{3}>-\overset{+}{N}R_{3}>-\overset{+}{N}H_{3}>-NO_{2}>-CN>-SO_{3}H>-CHO>-COOH>-F>-Cl>-Br>-I>-OH>-NH_{2}>-C\equiv CH>-Ph>-CH\equiv CH_{2}>(H)$$

Hybridisation state of carbanion:

* $sp^3 sp^2$







+I effect:

If the electron donating power of group is higher than that of hydrogen then these groups are known as +I groups.

+I series:

$$-CH_{2}^{\Theta} > -NH^{\Theta} > -COO^{\Theta} > -COO^{\Theta} > -C-CH_{3} > -CH_{2} < CH_{3} > -CH_{2} - CH_{3} > -CH_{3} > -CH_{3}$$

$$-T > -D > -H$$

 $-CT_3 > -CD_3 > -CH_3$

Note:

- (i) For I-effect C–H bond is taken as reference.
- (ii) It is permanent and weak effect.
- (iii) During I-effect partial displacement takes place within orbitals.
- (iv) I-effect is distance dependent effect.
- (v) Practically, it is observed upto C₃ atom, after third atom its effect is negligible
- (vi) Experimentally proved, that 10% effect is transferred to next atom.

Magnitude: $\delta_5 > \delta_6 > \delta_1 > \delta_4 > \delta_2 > \delta_3$

Ex.2 (a)
$$-T$$
, $-D$, $-H$ $(+I)$

Heavier the molecule (atom), less is its oscillation frequency ⇒ Higher overlapping makes strong and small bond. So that as small displacement of e⁻ cause large I-effect. So

$$-T > -D > -H$$

(b)
$$-CH_3$$
, $-CH_2D$, $-CHD_2$, $-CD_3$ (+I) $-CH_3 < -CH_2D < -CHD_2 < -CD_3$

(c)
$$-CH_3$$
, $-CD_3$, $-CT_3$ (+1) $-CH_3 < -CD_3 < -CT_3$

(d)
$$-CH_3 - SiH_3$$
 (+I)
 $-CH_3 < -SiH_3$

(e)
$$-CH_3 - CCl_3$$
 (+I)
 $-CH_3 > -CCl_3$

□ RESONANCE

If a single structure can not explain all of the properties of a molecule then more than one structures are required then it is said that molecule is showing resonance. It is due to the delocalization of electrons within the molecule.

All the contributing structures in the resonance are called **resonating structures** or **canonical structures**.

- ◆ These structures are helpful in explanation of chemical reactivity or the chemical reaction of the compound.
 - (i) Resonating structure are not the real structures.
 - (ii) The real structure is a hybrid of all resonating structures which is called as **resonance hybrid**.

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□ CONDITIONS FOR RESONANCE

- 1. System must be planar.
- 2. System must be in conjugation (i.e. parallel p orbitals are required)

Following type of conjugation may be present in a molecule:-

1. $\pi \to \pi$ conjugation :

If there are two π bonds at alternate position then e^- of one π bond are transferred towards another π bond. (According to I–effect).

Example:

(i)
$$CH_2$$
 CH CH_2 CH_2 CH_2 CH_2 CH_3 CH_4 CH_5 CH_6 CH_7 CH_8 CH_8

(iii)
$$CH_3$$
 CH CH CH CH CH_2 CH_3 CH CH CH CH CH

2. Lone pair $\rightarrow \pi$ conjugation :

If there is one lone pair and one π bond are in parallel orbital then electrons of lone pair are delocalised through π bond.

Example:

$$(i) \qquad \stackrel{\longleftarrow}{\text{CH}_2} = \text{CH} \stackrel{\bigoplus}{\longrightarrow} \text{CH} + \stackrel{\bigoplus}{\longrightarrow} \text{CH}_2 - \text{CH} = \stackrel{\bigoplus}{\longrightarrow} \text{H}$$

(ii)
$$CH_2 = CH = CH_2$$
 $CH = CH_2$

(iii)
$$CH_2 = CH - O - CH_3 \longleftrightarrow CH_2 - CH = O - CH_3$$

(iv)
$$CH_2 = CH = O$$
 $CH_2 - CH = O$

3. $\pi \rightarrow$ vacant orbital conjugation :

If there is one vacant orbital and one π bond are in parallel orbital then electrons of π bond are delocalised towards vacant orbital.

Example:
$$CH_{\bullet} = CH_{\bullet} = CH_{\bullet} + CH_{\bullet} + CH_{\bullet} = CH_{\bullet} + CH_{\bullet} + CH_{\bullet} + CH_{\bullet} = CH_{\bullet} + CH_{\bullet} +$$

4. $\pi \rightarrow$ unpaired e⁻ conjugation :

If there is one free e^- and one π bond are at alternate position.

Example:

(i)
$$CH_2 = CH - \dot{C}H_2 \leftarrow - \rightarrow \dot{C}H_2 - CH = CH_2$$

(ii)
$$CH_3$$
— CH = CH — $\dot{C}H_2$ ← \longrightarrow CH_3 — $\dot{C}H$ — CH = CH_2

5. Lone pair \rightarrow +ve charge conjugation :

If there is one lone pair or negative charge and one positive charge are at adjacent atoms then e⁻ of lone pair or negative charge are transferred towards positive charge.

Example:
$$\overset{\oplus}{C}H_2 \xrightarrow{\bullet} \overset{\ominus}{O}H \longleftrightarrow CH_2 = \overset{\oplus}{O}H$$

Conditions of Resonating Structures: Resonance structures should fulfil following conditions:

(a) All resonating structures must have the same arrangement of atomic nuclei. Resonance differs from tautomerism in this very important aspect.

$$\begin{array}{ccc}
\bullet & \bullet & \bullet \\
\bullet & \bullet & \bullet \\
R - C & \bullet & \bullet & \bullet \\
\end{array}$$

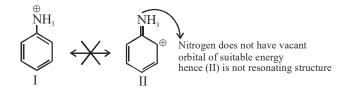
$$\begin{array}{cccc}
\bullet & \bullet & \bullet & \bullet \\
R - C & \bullet & \bullet & \bullet \\
\end{array}$$

Positions of atomic nuclei in (I) and (II) are same.

Position of hydrogen nuclei in (I) and (II) are different, hence (I) and (II) are not resonating structures, they are tautomer.

(b) The resonating structures must have the same numbers of paired and unpaired electrons. However, they differ in the way of distribution of electrons.

- ♦ The energy of the different resonating structures must be the same or nearly the same.
- ♦ All atoms that are part of the delocalisation system must be in a plane or be nearly planar.



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Examples of drawing resonating structures :

$$1. \quad \bigcirc \ddot{\text{OH}} \longleftrightarrow \bigcirc \ddot{\text{OH}}$$

5-Resonating structure

$$\mathbf{2.} \qquad \bigcirc \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\bigcirc} \overset{\mathrm{CH}_{2}}{\longleftrightarrow} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\bigcirc} \overset{\mathrm{CH}_{2}}{\longleftrightarrow} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\bigcirc} \overset{\mathrm{CH}_{2}}{\longleftrightarrow} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\bigcirc} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\mathrm{CH}_{2}} \overset{\bigcirc}{\longleftrightarrow} \overset{\bigcirc}{\mathrm{CH}_{2}} \overset{\bigcirc}{\longleftrightarrow} \overset{\bigcirc}{\mathrm{CH}_{2}} \longleftrightarrow \overset{\bigcirc}{\mathrm{CH}_{2}} \overset{\bigcirc}{\longleftrightarrow} \overset{\bigcirc}{\longleftrightarrow} \overset{\bigcirc}{\mathrm{CH}_{2}} \overset{\bigcirc}{\longleftrightarrow} \overset{\bigcirc}$$

5-Resonating structure

5-Resonating structure

5-Resonating structure

5-Resonating structure

6.
$$\bigcap_{N} \longleftrightarrow \bigcap_{H} \longleftrightarrow \bigcap_{N} \longleftrightarrow \bigcap_{H} \longleftrightarrow$$

5-Resonating structure

5-Resonating structure



☐ Hybrid resonating structure :

In the structure I C_1 — C_2 has double bond while in II and III C_1 — C_2 has single bond, so C_1 — C_2 shows bond length in between single and double bond similarly in structure I C_2 — C_3 has single bond. While in structure II and III C_2 — C_3 has double bond, so C_2 — C_3 shows bond length in between single and double bond.

So hybrid resonating structure from all its resonating structures is:

Example:

(i)
$$\overrightarrow{CH_2} = \overrightarrow{CH} = \overrightarrow{OH}$$
 \longleftrightarrow $\overrightarrow{CH_2} = \overrightarrow{CH} = \overrightarrow{OH}$ \Longrightarrow $\overrightarrow{CH_2} = \overrightarrow{CH} = \overrightarrow{OH}$ \Longrightarrow $\overrightarrow{CH_2} = \overrightarrow{CH} = \overrightarrow{OH}$ (Resonating structure) (Hybrid structure)

(ii)
$$CH_2 = CH - \overset{\Theta}{C}H_2$$
 \longleftrightarrow $\overset{\Theta}{C}H_2 - CH = CH_2$ \longleftrightarrow $\overset{\delta^-}{C}H_2 = CH$ \longleftrightarrow $\overset{\delta^-}{C}H_2 = CH$ (Resonating structure) \longleftrightarrow (Hybrid structure)

Aromaticity:

Order of stability for prototype structure

Aromatic > Non Aromatic > Anti Aromatic

Aromatic compounds are highly stable molecules/ions

Aromatic compounds must be Cyclic, planar, having cyclic conjugation and also have $(4n + 2) \pi e^-$ [Huckel's Rule] n = integer $2\pi e^-, 6\pi e^-, 10\pi e^-, 14\pi e^-$

Antiaromatic:

- → Antiaromatic compounds are unstable molecules/ions
- # Antiaromatic compounds must be Cyclic, planar, having cyclic conjugation and also have $4n\pi e^-$ n=integer

 $4\pi e^{-}$, $8\pi e^{-}$, $12\pi e^{-}$, $16\pi e^{-}$

Compound		Cyclic	Planar	Cyclic conjugation	πe-	Aromaticity
1.		✓	✓	×	2πe ⁻	Non aromatic
2.		✓	✓	✓	2πe ⁻	Aromatic
3.	[©]	✓	✓	✓	$4\pi e^-$	Anti aromatic
4.		✓	✓	✓	4πe ⁻	Anti aromatic
5.	$\bigoplus_{\mathbb{Q}} \mathbb{Q}$	✓	✓	\checkmark	2πe ⁻	Aromatic
6.		✓	✓	✓	6πe-	Aromatic
7.		✓	×	×	$4\pi e^{-}$	Non Aromatic
8.	()	✓	✓	✓	4πe ⁻	Anti Aromatic
9.	 	✓	✓	✓	6πe-	Aromatic
10.		✓	✓	✓	6πe ⁻	Aromatic
11.	\bigoplus_{\oplus}	✓	√	✓	6πe-	Aromatic
12.		✓	✓	✓	10πe ⁻	Aromatic
13.	N H H	√	✓	✓	6πe ⁻	Aromatic

- 14. N
- \checkmark

- \checkmark
- $6\pi e^-$ Aromatic

- 15. B H
- \checkmark
- ✓
- \checkmark
- 4πe⁻ Anti Aromatic

- 16. N
- ✓
- ✓
- \checkmark
- $6\pi e^-$ Aromatic

- 17. N
- ✓
- ✓
- **√**
- $6\pi e^-$ Aromatic

- 18.
- **√**
- **√**
- ✓
- $6\pi e^-$ Aromatic

- 19.
- \checkmark
- ×
- ×
- $6\pi e^-$ Non Aromatic

- 20.
- \checkmark
- ×
- ×
- 8πe⁻ Non Aromatic

- 21.
- ✓
- \checkmark
- \checkmark
- $6\pi e^-$
- Aromatic

□ MESOMERIC EFFECT OR RESONANCE EFFECT

- Polarity developed in conjugated system by interaction of lone pair or π e⁻ present in parallel orbitals is known as mesomeric effect.
- ◆ If transfer of pi-bond electron takes place from conjugate system to group then it is known as **negative mesomeric** (−**M**) effect.

$$CH_2 = CH - N$$
 $O\Theta$
 $CH_2 - CH = N$
 $O\Theta$

- ◆ Due to –M effect positive charge generate over conjugate system or due to –M effect electron density decrease in conjugate system.
- ◆ Group which shows –M effect are --NO₂, –CN, –SO₃H, – CHO, –COR, –COX, –COOR, –COOH, –CONH₂ etc.
- ◆ If transfer of lone pair electrons takes place from group to conjugate system then it is known as **positive mesomeric (+M)** effect.

$$CH_{2} = CH - CH = CH - \overrightarrow{CH} = CH - \overrightarrow{N}H_{2}$$

$$CH_{2} = CH - \overrightarrow{CH} = CH - CH = CH - CH = \overrightarrow{N}H_{2}$$

$$CH_{2} = CH - \overrightarrow{CH} - CH = CH - CH = \overrightarrow{N}H_{2}$$

$$CH_{2} = CH - CH = CH - CH = \overrightarrow{N}H_{2}$$

$$CH_{2} - CH = CH - CH = CH - CH = \overrightarrow{N}H_{2}$$

- ◆ Due to + M effect negative charge comes over conjugate system or electron density increase on conjugate system such type of conjugate system will be more reactive towards electrophile or will be less reactive towards nucleophile.
- ◆ Group which shows + M effect are -

$$-\overset{\ominus}{O}, -\overset{\ominus}{NH}, -NR_2 \ , -NH_2, -NHR, -OH, -OR, -NH-\overset{O}{C}-R, -O-\overset{O}{C}-R, -F, -Cl, -Br \ etc.$$

♦ In mesomeric effect polarity or charge migrate from one end to another end. During charge transfer, energy releases from the conjugate system which increase the stability of conjugate system also.

ALLEN

Difference in energy between most stable resonating structure resonance hybride.

Resonance energy \(^\) with better overlapping.

(a) has more R.E. than (b)

$$\bigcirc$$
OH
$$(a) \qquad (b)$$

(a) has more R.E. than (b)

It is delocalisation of σ electron with p-orbital. Also known as $\sigma - \pi$ conjugation effect or no bond resonance. It may take place in alkene, alkyne, carbocation, free radical, alkyl benzene nucleus. It was given by Nathan and Baker.

Necessary Condition of H effect: Presence of at least one hydrogen at saturated carbon (sp³ carbon) which is α with respect to alkene, alkynes, carbocation, free radical, alkyl benzene nucleus. Carbon which is attached to sp² C is called as α –C and H which are attached to α -C are called as α -H.

1 Hyperconjugation in alkene:

If there is at least one C–H σ bond and π bond are at alternate position then there will be H-effect.

These resonating structures only suggest that there is some ionic character between C – H bond. carbon - carbon double bond acquires some single bond character.

2 Hyperconjugation in carbocation :

If there is one C–H σ bond and one positive charge are at alternate position then there will be H effect. All the structures are called as hyperconjugation structures.

If number of α – H are more then there will be more number of hyperconjugation structures, results more stable carbocation.

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3 Hyperconjugation in free radical:

If there is one $-C-H \sigma$ bond and one free electron are at alternate position then there will be H-effect.

$$\begin{array}{c} \stackrel{\longleftarrow}{\underset{H}{\overset{\alpha}{\subset}}} \stackrel{\longleftarrow}{\underset{C}{\overset{\dot{H}}{\hookrightarrow}}} \stackrel{\stackrel{\cdot}{\underset{H}{\longleftrightarrow}}}{\longleftrightarrow} \stackrel{\stackrel{\cdot}{\underset{H}{\longleftrightarrow}}} \stackrel{\stackrel{\cdot}{\underset{H}{\longleftrightarrow}}}{\longleftrightarrow} \stackrel{\stackrel{\cdot}{\underset{H}{\longleftrightarrow}}}{\longleftrightarrow}$$

4 Hyperconjugation in toluene :

Example:

Structure	Number of α-hydrogens	Total number of hyperconjugative structure	Number of hyperconjugative structure (involving C–H bond)
CH ₃ – CH = CH ₂	3	4	3
$CH_3 - CH_2 - CH = CH_2$	2	3	2
CH ₃ – CH = CH – CH ₃	6	7	6
CH ₃ – CH ₂	3	4	3
H ₃ C - CH ₃ CH ₃	9	10	9

5 Applications of hyperconjugation :

(1) **Stability of Alkenes:** More is the number of hyperconjugative structures, more stable is the alkene. So **"More alkylated alkenes are more stable".**

$$H_3C$$
 $C = C$ CH_3 H_3C $C = CH - CH_3$ H_3C $C = CH_2$

Stability in decreasing order

Example :
$$CH_3$$
— CH = CH_2 > CH_2 = CH_2
3 α -H Zero α -H

more stable

Example: Stability order of alkenes is

- (2) **Heat of hydrogenation :** Greater the number of α hydrogen results in greater stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation. So order for heat of hydrogenation of some alkene can be given as $CH_2 = CH_2 > CH_3 CH = CH_2 > CH_3 CH = CH CH_3$
- (3) **Bond Length:** Bond length is also affected by hyperconjugation

Example:
$$H_2C \xrightarrow{\vdash} HC = CH_2 \longrightarrow HC = CH - CH_2$$

- (i) Bond length of C(II) C(III) bond is less than normal C–C bond.
- (ii) Bond length of C(II) C(I) bond is more than normal C=C bond.
- (iii) C–H bond of C(III) is longer than normal C–H bond.
- (4) **Dipole moment :** Since hyperconjugation causes the development of charge, it also affects the dipole moment of the molecule.

Example : $CH_2 = CH_2 < CH_3 - CH = CH_2$ (Dipole moment)

(5) Stability of carbocation: If hyperconjugation structures are more then more is the stability.

Maximum stable

Example:
$$\bigcirc^{\oplus} CH_3 > \bigcirc^{\oplus} > \bigcirc^{\oplus}$$

Example:
$$CH_3 - \overset{\oplus}{C}H_2 > CH_3 - CH_2 - CH_2 - \overset{\oplus}{C}H_2 > \overset{CH_3}{\overset{\circ}{C}H_2} > CH - \overset{\oplus}{C}H_2 > \overset{CH_3}{\overset{\circ}{C}H_2} = CH_2 - \overset{\oplus}{C}H_2 > CH_2 - \overset{\oplus}{C}H_2 - \overset{\oplus}{C}H_2$$

(6) Stability of free radical: Greater the number of α -hydrogen results greater stability of carbon free radical.

Example :
$$\dot{C}H_3 < CH_3 - \dot{C}H_2 < CH_3 - \dot{C}H - CH_3 < CH_3 - \dot{C} - CH_3$$

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Heat of Combustion (HOC):

Enthalpy change when 1 mole of compound is oxidized.

HOC ∝ No. of C-atom

$$\propto \frac{1}{\text{stability}} \propto \text{strain}$$

Arrange in order of HOC

1. (I) / (III) / (IV) /

IV > III > II > I, \uparrow no. of C-atom

2. (I) (II)

I > II, II is more stable due to +H effect

3. (I) (II)

I > II, II is more stable due to resonance

4. (I) (II) (III) (IV)

IV > III > II > I, increase in no. of carbon.

I > II > III > IV the strain decrease from $I \rightarrow IV$

6. (I) (II)

II > I, more no. of C, more is H.O.C.

7. (I) (III) (III)

III > I > II, no. of C-atom increases increasing H.O.C.

8. (I) (II) (III)

I > II > III, segment attached ring of 3, 4 and 5

Order of HOC I > II > III,

10. From HOC data,

strain order:

Stability order:

(Chair)
$$\Leftrightarrow$$
 (Boat)

As the angle decreases, the outer bonds are more free to move.

Stability of Intermediates:

Stability of carbocation \propto EDG (+R/+H/+I)

Stability of carbon free radical \propto EDG (+R/+I)

Stability of carbonion \propto EWG (-R/-I)

1.
$$^{+}CH_{_{3}}$$
, $^{+}CH_{_{2}}$ - $CH_{_{3}}$, ^{+}CH $\stackrel{C}{\underset{CH_{_{3}}}{\leftarrow}}$, $\stackrel{CH_{_{3}}}{\underset{CH_{_{3}}}{\leftarrow}}$

IV > III > II > I

2.
$${}^{\bullet}CH_3$$
, ${}^{\bullet}CH_2$ ${}^{\bullet}CH_3$, ${}^{\bullet}CH_3$, ${}^{\bullet}CH_3$, ${}^{\bullet}CH_3$

IV > III > II > I

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3.
$$-CH_3$$
, $-CH_2$ - $-CH_3$, $-CH$ CH_3 , $-CH_3$ CH_3 CH_3 CH_3

I > II > III > IV

II > III > IV > I

IV < I < III < II

IV > I > III > II

- 7. $CH_3 CH_2^+$, $CH_2 = CH^+$, $CH = C^+$ I > II > III, + H in I
- 8. $CH_3-CH_2^+$, $CH_2=CH^+$, $CH=C^+$ I>II>III
- 9. $CH_3-CH_2^{\Theta}$, $CH_2=CH^{\Theta}$, $CH\equiv C^{\Theta}$ III>II>I

I > II > III

I > II > III

II > II > I

- 13. $Ph_3C^+, Ph_2CH^+, Ph-CH_2^+$ I > II > III
- 14. Ph_3C^{\bullet} , Ph_2CH^{\bullet} , $Ph-CH_2^{\bullet}$ I > II > III
- 15. $Ph_{3}C^{\Theta}, Ph_{2}CH^{\Theta}, Ph-CH^{\Theta}$ I > II > III

- **19.** CH₃-CH₂⁺, CD₃-CH₂⁺, CT₃-CH₂⁺
 I > II > III
- **20.** CH₃-CH₂•, CD₃-CH₂•, CT₃-CH₂•
 III > II > I
- **21.** $CH_3-CH_2^{\Theta}$, $CD_3-CH_2^{\Theta}$, $CT_3-CH_2^{\Theta}$ I>II>III
- **22.** CH_3^+ CD_3^+ CT_3^+ III > II
- 23. $CH_3^{\circ} CD_3^{\circ} CT_3^{\circ}$ III > II > I
- 24. ${}^{\Theta}CH_3$ ${}^{\Theta}CD_3$ ${}^{\Theta}CT_3$ I > II > III
- 25. (I) (II) II > I

- 26.
- $(I) \bigodot$
- (II)

II > I

- 27. (I)
- (II)

I > II

- **28.** (I) CH
- (II) CH_2

I > II

- **29.** (I) CH₂
- $\text{(II)} \bigcap^{\bullet} \mathring{\mathrm{C}} \mathrm{H}_2$

I > II

- **30.** (I) CH
- $\text{(II)} \overbrace{\bar{C}H_2}$

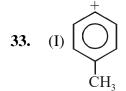
I > II

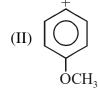
- **31.** (I
- $\text{(II)} \bigcup_{\text{OCH}_3}^{\text{\r{c}}\text{H}_2}$
- $(III) \bigcirc \bigvee_{NO}^{\stackrel{\leftarrow}{C}H_2}$

II > I > III

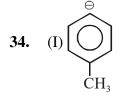
- 32. (I) CH
- $(II) \bigcirc CH_2$ OCH_3
- (III) $\bigvee_{NO}^{\overline{C}H_2}$

II < I < III





I > II > III



II > II > I

II > II > I

I > II > III

(II)
$$\oplus$$

II > I

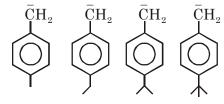
I > II

$$(II) \bigcirc \bigcirc$$

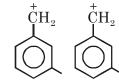
I > II

JEE-Chemistry

- 40.
- ${\rm \dot{C}H_2}$ ${\rm \dot{C}H_2}$ ${\rm \dot{C}H_2}$
- (I)
- (II)
- (III) (IV)
- I > II > III > IV
- 41.



- (I)
- (II)
- (III)
- (IV)
- IV > III > II > I



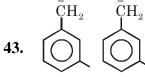
- ${\rm \dot{C}H_2}$
- (I)
- (II)
- (III)

 $\bar{\mathrm{CH}}_2$

(IV)

 $\bar{\mathrm{C}}\mathrm{H}_2$

IV > III > II > I



- (III)
 - (IV)
- (I) (II)I > II > III > IV
- 44.



- (III)

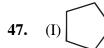
- **45.**

- (III)

- I > II > III
- **46.**

- (III)

III < I < II



I < II < III

I > I

I > II

IV > III > II > I

IV > I > II > III

52. (I)
$$\bigcirc$$
 \bigcirc \bigcirc (II) \bigcirc \bigcirc \bigcirc \bigcirc

I > II

 $Me \underbrace{ \oplus Me}_{C} Me$ (II)

II > I > III

 $(II) \qquad \bigcirc Me$

$$(III) \overset{\text{Me} \ \bigcirc}{C} Me$$

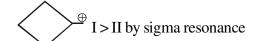
I > II > III

55.
$$\stackrel{+}{\bigvee}_{NO_2}$$
 $\stackrel{+}{\bigvee}_{NO_2}$ $\stackrel{+}{\bigvee}_{NO_2}$

node06/B0B0-BA/Kata/JEE[Advanced]/Leader/Che/Sheer/Electronic Displacement Effect/Eng.p65

 $\ominus_{\hbox{\scriptsize CH}_2}$

I > II





$$\binom{S}{S}$$

I > II > III



II > II > I

I > II

61.
$$\dot{C}F_3$$
 $\dot{C}Cl_3$

I > I

62.
$$\overset{\Theta}{C}F_3$$
 $\overset{\Theta}{C}Cl_3$

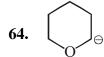
I > I







I > III > II







I > II > III

II > I

I > II > III > IV

67.
$$NO_2$$
 NO_2 NO_2

I < II < III

I > II > III

II > II > I

70.
$$CH_3 - CH_3^+$$
 $CH_3 - C-CH_2^+$ $CH_3 - C-CH_2^+$ CH_3

I > II

II > I

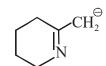
72.
$$CH_3 - CH_2^{\Theta} \stackrel{CH_3}{\underset{CH_3}{\leftarrow}} CH_2^{-2}$$

I > II

nodeO6\B0B0-BA\Kota\LEE[Advan.ced]\Lecder\Che\Sheer\Electronic Displacement Effect\Eng.p65

Ε

CH₂



II > II > I

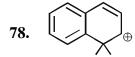
I > II > III

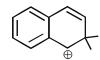
$$N \longrightarrow \emptyset$$

III > II > I

I > II

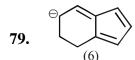
I > II





$$\bigcirc \bigcirc \bigcirc$$

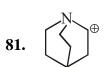
II < I < III



I > II

80.
$$\overset{\ominus}{C}\overset{\oplus}{H_2}\overset{\ominus}{-NR_3}\overset{\ominus}{C}\overset{\ominus}{H_2}\overset{\ominus}{-PR_3}$$

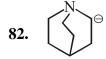
I < II







II > I > III





$$\bigcup_{\bigcirc}^{N}$$

I > II > III





II > I

Bayer's Angle Strain Theory:

→ For any sp³ carbon maximum stability is attained when bond angle is 109°.28'.



According to Bayer's:









$$\delta = \frac{1}{2} [109^{\circ}.28' - \alpha]$$

$$\alpha = 60^{\circ}, \ \delta = 24.5^{\circ}$$

$$\alpha=90^{\rm o},\,\delta=9.5^{\rm o}$$

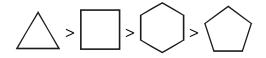
$$\alpha = 108^{\circ}, \, \delta = 0.5^{\circ}$$

$$\alpha = 120^{\circ}, \ \delta = -5.5^{\circ}$$

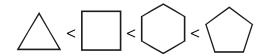
Ex.1:
$$1\rightarrow 24, 30\rightarrow 37, 43, 44$$

Stability
$$\propto \frac{1}{\text{strain}}$$

 \Rightarrow Strain order:



⇒ Stability order: (Acc. to Baeyer's strain theory)



EXERCISE # O-I

Q.1 Which of the following is false order of –I effect?

(A)
$$-F > -Cl > -Br > -I$$

(B)
$$\stackrel{\oplus}{-NR_3} > \stackrel{\oplus}{-NH_3} > -NO_2$$

(C)
$$-F > -OH > -NH_2$$

(D)
$$\bigcirc$$
 > -C = CH > -H

GC0001

Q.2 What is the correct order of inductive effect?

$$(A) -O^- > -CH_3 > -CMe_3$$

(B)
$$-CO_2^- > -O^- > CHMe_2$$

(C)
$$-O^- > -CH_2Me > -D > -H$$

GC0002

Q.3 Which of the following groups have + I effect:

$$(C)$$
 — $CH_{\underline{c}}$

$$\langle \rangle$$
 CH₃ (D) —CH = CH₂

GC0003

Q.4 Which of the following groups have –I effect:

(D)
$$--OCH_3$$

GC0004

Q.5 How many of the following groups have + I effect:

$$(d)$$
 $\stackrel{\circ}{--}$ $\stackrel{\circ}{N}$ H

(f) —
$$COO^{\Theta}$$

GC0005

- **Q.6** Which of the following statements is (are) true about resonance.
 - (a) Resonance is an intramolecular phenomenon.
 - (b) Resonance involves delocalization of both σ and π electrons.
 - (c) Resonance involves delocalization of $\boldsymbol{\pi}$ electrons only.
 - (d) Resonance decreases potential energy of an acyclic molecule.
 - (e) Resonance has no effect on the potential energy of a molecule.
 - (f) Resonance is the only way to increase molecular stability.
 - (g) Resonance is not the only way to increase molecular stability.
 - (h) Any resonating molecule is always more stable than any non resonating molecule.
 - (i) The canonical structure explains all features of a molecule.
 - (j) The resonance hybrid explains all features of a molecule.
 - (k) Resonating structures are real and resonance hybrid is imaginary.
 - (l) Resonance hybrid is real and resonating structures are imaginary.
 - (m) Resonance hybrid is always more stable than all canonical structures.

- **Q.7** Which of the following statement is incorrect?
 - (A) Resonating structure are real & have real existence
 - (B) Equivalent contributing structures make resonance hybrid very stable.
 - (C) Contributing structures are hypothetical having no real existance
 - (D) Contributing structures are less stable than the resonance hybrid.

GC0007

- **Q.8** Which of the following is most stable.
 - (A) Conjugated alkadiene ($CH_2 = CH CH = CH_2$)
 - (B) Isolated alkadiene ($CH_2 = CH CH_2 CH = CH_2$)
 - (C) Cumulated alkadiene ($CH_2 = C = CH_2$)
 - (D) All are equally stable

GC0008

0.9 Consider structural formulas A, B and C:

$$H_2\ddot{C}$$
— $N \equiv N$: $H_2C = N = \ddot{N}$: H_2C — $\ddot{N} = \ddot{N}$: (C)

- (a) Are A, B and C isomers, or are they resonance forms?
- (b) Which structures have a negatively charged carbon?
- (c) Which structures have a positively charged carbon?
- (d) Which structures have a positively charged nitrogen?
- (e) Which structures have a negatively charged nitrogen?
- (f) What is the net charge on each structure?
- (g) Which is a more stable structure, A or B? Why?
- (h) Which is a more stable structure, B or C? Why?

GC0009

Q.10 A canonical structure will be more stable if

- (A) it involves cyclic delocalization of $(4n + 2)\pi$ electrons than if it involves acyclic delocalization of $(4n + 2) \pi$ – electrons.
- (B) it involves cyclic delocalization (4n) π electrons than if it involves acyclic delocalization of (4n) π – electrons.
- (C) +ve charge is on more electronegative atom than if +ve charge is on less electronegative atom provided atoms are in the same period.
- (D) –ve charge is on more electronegative atom than if –ve charge is on less electronegative atom provided atoms are in the same period.

GC0010

Q.11 Which one of the following pair of structures does not represent the phenomenon of resonance?

$$(A) \ H_{2}C = CH - C - H \ ; \ CH_{2} - CH = C - H \ (B) \ CH_{2} = CH - CH \ ; \ CH_{2} - CH = CH - CI$$

$$(C) \ (CH_{3})_{2}CH - C - O^{-}; \ (CH_{3})_{2}CH - C = O \ (D) \ CH_{3} - CH_{2} - C - CH_{3}; \ CH_{3} - CH = C - CH_{3}$$

Q.12 In which of the following, lone-pair indicated is involved in resonance:









(e)
$$CH_2 = CH - CH_2^{\Theta}$$

(e)
$$CH_2 = CH - CH_2^{\Theta}$$
 (f) $CH_2 = CH - CH = NH$

GC0012

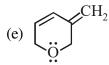
Q.13 In which of the following lone-pair indicated is not involved in resonance:

(a)
$$CH_2 = CH - NH - CH_3$$

(b)
$$CH_2 = CH - CH = O$$

(c)
$$CH_2 = CH - O - CH = CH_2$$

(d)
$$CH_2 = CH - C \equiv N_\bullet$$





GC0013

Q.14 Which of the following groups cannot participate in resonance with other suitable group:

$$(d) - \overset{\oplus}{N}H_3$$

(e)
$$-\overset{\oplus}{\mathbf{C}}\mathbf{H}_{2}$$

GC0014

Q.15 Identify electron donating groups in resonance among the following:

$$(b) - NO_2$$

$$(f)-NHCOCH_{3} \\$$

GC0015

Q.16 Identify electron withdrawing groups in resonance among the following:

$$(d) - CN$$

(e)
$$-O - CH = CH_2$$
 (f)

GC0016

Q.17 Which of the following groups can either donate or withdraw a pair of electrons in resonance depending upon situation:

$$(c) - CH = CH_2$$

$$(d) - CHO$$

(e)
$$-NH_2$$

$$(f) - N = NH$$

Q.18 Draw the resonance forms to show the delocalization of charges in the following ions

(a)
$$CH_3-C-CH_2$$

$$(e) \hspace{-0.1cm} \begin{array}{c} \hspace{-0.1cm} & \hspace{-0.1cm}$$

GC0018





$$(h) \bigcap_{O}$$

(i)
$$CH_3 - CH = CH - CH = CH - \overset{+}{C}H - CH_3$$
 (j) $CH_3 - CH = CH - CH = CH - \overset{+}{C}H_2$

(j)
$$CH_3 - CH = CH - CH = CH - CH_2$$

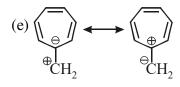
GC0019

Q.19 Identify less stable canonical structure in each of the following pairs:

(a)
$$\overset{\oplus}{C}H_2 - O - CH_3 \longleftrightarrow CH_2 = \overset{\oplus}{O} - CH_3$$

$$(b) \qquad \longleftrightarrow \qquad \bigcirc$$

$$(c) \overset{\Theta}{\underset{CH_2}{\overset{O}{\longrightarrow}}} \overset{O}{\underset{CH_2}{\overset{O}{\longrightarrow}}}$$



GC0020

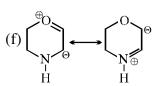
Q.20 Identify more stable canonical structure in each of the following pairs:

$$(b) \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc$$

$$(c) \bigcirc \bigvee_{N \ominus} \longleftrightarrow \bigcirc$$

$$(d) \bigoplus_{\bigoplus CH_2} \longleftarrow \bigoplus_{\Theta \mid CH_2}$$

(e)
$$\overset{\oplus}{\text{C}}\text{H}_2 - \text{CH} = \text{CH} - \overset{\Theta}{\text{O}} \longleftrightarrow \text{CH}_2 = \text{CH} - \text{CH} = \text{O}$$



- **Q.21** Which of the following group can participate in resonance with other suitable group:
 - (a) -OH
- (b) $-CH_2 \overline{C}H_2$ (c) $-CH_2 \overset{\oplus}{C}H_2$

GC0022

(e)
$$CH = CH$$
 (f) $-BH_2$ (g) $-\stackrel{\oplus}{P}Ph_3$

GC0023

- Q.22 Arrange the following resonating structure according to their contribution towards resonance hybrid?
 - (a) $CH_2 = \overset{\oplus}{N} = \overset{\Theta}{N}$ (b) $\overset{\Theta}{C}H_2 N = \overset{\Theta}{N}$ (c) $\overset{\Theta}{C}H_2 \overset{\Theta}{N} = \overset{\Theta}{N}$ (d) $\overset{\Theta}{C}H_2 \overset{\Theta}{N} = \overset{\Theta}{N}$

- (A) a > d > c > b (B) b > a > c > d (C) a > c > b > d (D) d > a > b > c

GC0024

Q.23 In each of the following pairs of resonating structure which resonating structure is more stable:

(a)
$$\left[CH_3 - \overline{C}H - C = N^* \right] \leftarrow CH_3 - CH = C = N^* - CH$$

(b)
$$CH_3 - C - \overline{C}H - C - CH_3 \longleftrightarrow CH_3 - C = CH - C - CH_3$$

(c)
$$\begin{bmatrix} NH_2 & NH_2 \\ CH_3 - CH_2 - C - NH_2 & \longleftrightarrow CH_3 - CH_2 - C = NH_2 \end{bmatrix}$$

GC0025

Q.24 Formic acid is considered as a hybrid of the four structures

Which of the following order is correct for the stability of four contributing structures.

- (A) I > II > III > IV
- (B) I > II > IV > III (C) I > III > IV > IV > III > II

GC0026

E

Q.25 In the given pair of compounds select the one in each pair having lesser resonance energy:

(a)
$$\bigwedge_{O}$$
 and \bigwedge_{OH}

(c)
$$\bigcap_{NO_2}$$
 and \bigcap_{NO_2}

$$(d) \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \end{array} \right) \text{ and } \left(\begin{array}{c} \\ \\ \\ \\ \\ \end{array} \right)$$

GC0027

Q.26 Resonance energy of resonance hybrid of a molecule will be more if:

- (a) canonical structures are equivalent than if canonical structures are non-equivalent
- (b) molecule is aromatic than if molecule is not aromatic.

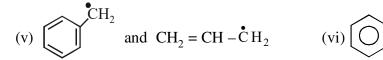
GC0028

Q.27 In the given pair of compounds select the one in each pair having higher resonance energy:

(i)
$$\bigcap_{N}$$
 and \bigcap_{H}

(i)
$$\left(\begin{array}{c} \\ \\ \\ \\ \\ \end{array}\right)$$
 and $\left(\begin{array}{c} \\ \\ \\ \\ \end{array}\right)$ (ii) $CH_2 = CH - O - CH = CH_2$ and $CH_2 = CH - NH - CH = CH_2$

(iii) $CH_2 = CH - \stackrel{\Theta}{N}H$ and $HN = CH - \stackrel{\Theta}{N}H$ (iv) $CH_2 = CH - F$ and $CH_2 = CH - Br$



GC0029

(ix) $CH_2 = CH - OH$ and $CH_2 = CH - CH = CH - OH$

(xi) CH₃COOH and CH₃COONa

(xii)
$$CH_2 = CH - \overset{\Theta}{O}$$
 and $CH_2 = CH - OH$

$$(xiii) \bigcirc \hspace{-0.5cm} \bigcap^{COO^\Theta} \text{and} \bigcirc \hspace{-0.5cm} \bigcap^{O^\Theta}$$

(xv) and
$$CH_2 = CH - CH = CH - CH = CH_2$$

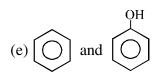
GC0030

Ε

Q.28 In the given pair of compounds select the one in each pair having lesser resonance energy:

(a) CO₃²⁻ and HCOO⁻

- (b) Θ and $CH_2 = CH CH_2$
- and $CH_2 = CH CH = CH_2$ (d) \oplus and $CH_2 = CH \overset{\oplus}{C}H_2$



GC0031

Q.29 In which of the following pairs first one is having more resonance energy than the second one -

- (D) None of these

GC0032

Q.30 In which of the following molecules π – electron density in ring is minimum:

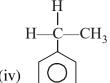
GC0033

Q.31 In which of the following molecules π – electron density in ring is maximum:

GC0034

Q.32 Arrange following compounds in decreasing order of reactivity of ring towards attack of electron deficient species -





- (A) i > ii > iii > iv
- (B) iii > iv > ii > i
- (C) i > iv > ii > iii
- (D) i > ii > iv > iii

- Q.33 In which of the following molecule all the effect namely inductive, mesomeric & hyperconjugation operate:

GC0036

- Q.34 Which one of the following molecules has all the effect, namely inductive, mesomeric and hyperconjugative?
 - (A) CH₂Cl

- (B) CH_3 – $CH = CH_2$
- (D) $CH_2 = CH CH = CH_2$

GC0037

- **Q.35** Select the correct statement.
 - (i) Delocalisation of σ -electron is hyperconjugation.
 - (ii) Delocalisation of π -electron is resonance.
 - (iii) Permanent partial displacement of σ -electron is inductive effect.
 - (A) i & iii
- (B) ii & iii
- (C) i & ii
- (D) i, ii, iii

GC0038

- Q.36 Which of the following compound is correctly matched with number of hyperconjugating structures (involving C—H bond):

- (C) \oplus (8) (D) $CH_3-C \equiv C-CH_3$ (5)

GC0039

$$\mathbf{Q.37} \stackrel{2}{\stackrel{1}{\checkmark}} \stackrel{1}{\longleftrightarrow} \longleftrightarrow \stackrel{2}{\stackrel{1}{\longleftrightarrow}} \stackrel{1}{\longleftrightarrow} \stackrel{2}{\longleftrightarrow} \stackrel{1}{\longleftrightarrow} \stackrel{2}{\longleftrightarrow} \stackrel{1}{\longleftrightarrow} \stackrel{1}{\longleftrightarrow} \stackrel{2}{\longleftrightarrow} \stackrel{1}{\longleftrightarrow} \stackrel{1}{\longleftrightarrow$$

These are three canonical structures of naphthalene. Examine them and find correct statement among the following:

- (A) All C C bonds are of same length
- (B) C1 C2 bond is shorter than C2 C3 bond.
- (C) C1 C2 bond is longer than C2 C3 bond (D) None

GC0040

Q.38 Which of the following has longest C – O bond:





GC0041

nodeO6\B0B0-BA\Kota\JEE[Advanced]\Leader\Che\Sheet\Electronic Displacement Effect\Eng.p65

$$CH_2 = NH$$

I

II

III

IV

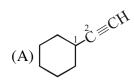
Among these compounds, the correct order of C – N bond lengths is:

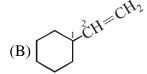
(B)
$$III > I > II > IV$$
 (C) $III > II > IV$

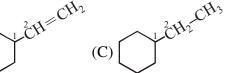
(D)
$$III > I > IV > II$$

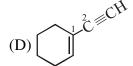
GC0042

 $\mathbf{Q.40}$ C1 – C2 bond is shortest in









GC0043

Q.41 Which of the following molecule has longest C=C bond length?

(A)
$$CH_2=C=CH_2$$
 (B) $CH_3-CH=CH_2$ (C) $CH_3-C=CH_2$ (D) $CH_3-C=CH_2$ (D) $CH_3-C=CH_2$ (D) $CH_3-C=CH_2$

GC0044

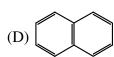
Q.42 Which of the following molecule has shortest C=C bond length?

(A)
$$CH_2=C=CH_2$$
 (B) $CH_3-CH=CH_2$ (C) $CH_3-C-CH=CH_2$ (D) $CH_3-C=CH_2$ (E) CH_3

GC0045

Q.43 C—C and C=C bond lengths are unequal in :

- (A) Benzene
- (B) 1,3-buta-di-ene (C) 1,3-cyclohexa-di-ene (D)



GC0046

Q.44 Among the following molecules, the correct order of C - C bond length is (C_6H_6) is benzene

$${\rm (A)}\ {\rm C_2H_6} > {\rm C_2H_4} > {\rm C_6H_6} > {\rm C_2H_2}$$

(B)
$$C_2H_6 > C_6H_6 > C_2H_4 > C_2H_2$$

(C)
$$C_2H_4 > C_2H_6 > C_2H_2 > C_6H_6$$

(D)
$$C_2H_6 > C_2H_4 > C_2H_2 > C_6H_6$$

GC0047

 $Q.45 \text{ CH}_3\text{O} - \text{CH} = \text{CH} - \text{NO}_2$

$$CH_2 = CH - NO_2$$

$$CH_2 = CH - Cl$$

$$CH_2 = CH_2$$

Which of the following is the correct order of C – C bond lengths among these compounds:

$$(A) I > II > III > IV$$

(B)
$$IV > III > II > I$$

(C)
$$I > III > II > IV$$
 (D) $II > III > I > IV$

(D)
$$\Pi > \Pi > I > IV$$

GC0048

E

Q.46 Which of the following is (are) the correct order of bond lengths:

(A)
$$C - C > C = C > C \equiv C > C \equiv N$$

(B)
$$C = N > C = O > C = C$$

$$(C) C = C > C = N > C = O$$

(D)
$$C - C > C = C > C \equiv C > C - H$$

GC0049

Q.47 In which of the following pairs, indicated bond having less bond dissociation energy:

(a)
$$\leftarrow$$
 and $CH_2 = CH_2$

(b)
$$CH_3 - C \equiv CH$$
 and $HC \equiv CH$

(c)
$$CH_2 = CH$$
 $CH = CH_2$ and $CH_2 = CH$ $CH = CH_2$

$$CH = CH_2$$

$$CH = CH_2$$

$$CH = CH_2$$

$$CH = CH_2$$

GC0050

(d)
$$\underset{\text{H}_2\text{N}}{\overset{\text{O}}{\text{C}}}$$
 and $\underset{\text{CH}_3}{\overset{\text{O}}{\text{C}}}$ (e) $\underset{\text{Cl}}{\overset{\text{O}}{\text{Cl}}}$ and $\underset{\text{CH}_3}{\overset{\text{O}}{\text{C}}}$

(e)
$$CI$$
 and CH_3 CI

$$(f) \underset{H_2N}{\overset{O}{\underset{H_2}{\overset{\parallel}{\longleftarrow}}}} \underset{NH_2}{\overset{O}{\underset{H_2}{\overset{\parallel}{\longleftarrow}}}} \text{ and } \underset{H}{\overset{O}{\underset{NH_2}{\overset{\parallel}{\longleftarrow}}}}$$

GC0051

Q.48 In which of the following pairs, indicated bond is of greater strength:

(a)
$$CH_3 - CH_2 - Br$$
 and $CH_3 - CH_2 - CH_3 - C$

(a)
$$CH_3 - CH_2 - Br$$
 and $CH_3 - CH_2 - C1$ (b) $CH_3 - CH = CH - Br$ and $CH_3 - CH - CH_3 \rightarrow Rr$

(c)
$$CH_3$$
 CI and $CH_3 - CH_2 - CI$ (d) $CH_2 = CH - CH = CH_2$ and $CH_2 = CH_2 - CH_2 - CH_3$
GC0052

(e)
$$CH_2 = CH - CH = CH_2$$
 and $CH_2 = CH - NO_2$ (f) CH_3 and $CH_2 = CH_5$

GC0053

Q.49.
$$H_{3}C - C - C H - C H_{2} - H$$

$$C H_{2} = C - H$$

the correct order of bond dissociation energy (provided bond undergoes homolytic cleavage):

(A)
$$C^2-H > C^3-H > C^4-H > C^1-H$$
 (B) $C^2-H > C^3-H > C^1-H > C^4-H$

(B)
$$C^2$$
– $H > C^3$ – $H > C^1$ – $H > C^4$ – H

(C)
$$C^1-H > C^4-H > C^2-H > C^3-H$$
 (D) $C^1-H > C^4-H > C^3-H > C^2-H$

(D)
$$C^1$$
-H > C^4 -H > C^3 -H > C^2 -H

Q.50 Compare the C–N bond-length in the following species:

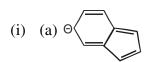
GC0055

Q.51 In which case, C – O bond length is shorter for Ist compound :

(A)
$$C_{\overline{a}} OH$$
 $C_{\overline{b}} OH$ (B) $C_{\overline{b}} OH$ (C) $C_{\overline{b}} OH$ (D) $C_{\overline{b}} OH$ (D) $C_{\overline{b}} OH$

EXERCISE # O-II

Q.1 In each set of species select the aromatic species.



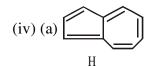


GC0057

GC0058



GC0059









(e) H-N: N-H N-H N-B N-H

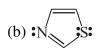


GC0060

Q.2 Which of the given compound is aromatic, antiaromatic or nonaromatic.



isoxazole



1,3-thiazole



pyran



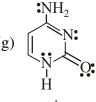
pyrylium ion



γ-pyrone



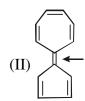
1,2-dihydropyridine



cytosine

Q.3





Compare carbon-carbon bond rotation across I, II, III.

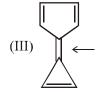
- (A) I > II > III
- (B) I > III > II
- (C) II > I > III
- (D) II > III > I

GC0062

Q.4 Which of the given compunds has minimum rotation energy barrier across indicated carbon-carbon bond.







(A) I

(B) II

- (C) III
- (D) All are equal

GC0063

Q.5 Which species is not aromatic?







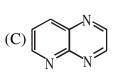


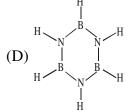
GC0064

Q.6 Which of the following are non-aromatic









GC0065

Q.7 Write down the structure of the following molecule and comment on aromaticity?

- (a) $B_3H_3O_3$
- (b) $C_3N_3 (NH_2)_3$
- (c) Trimer of isocyanic acid $(HN = C = O)_3$

- **Q.8** Select the least stable one:
 - (A) $CH_3 CH_2^{\oplus}$

(B) $CH_3 - CH_2 - CH_2^{\oplus}$

(C) $\underset{\text{H},C}{\text{H}_3C} > \text{CH} - \text{CH}_2^{\oplus}$

(D) $\underset{H}{\overset{H_3C}{\subset}} C - \overset{\oplus}{\overset{C}{\subset}} H_2$

GC0067

- **Q.9** Write stability in decreasing order of following intermediates:

 - (i) (a) $CH_3 \overset{\oplus}{CH}_2$ (b) $CH_3 \overset{\oplus}{CH} CH_3$ (c) $CH_3 \overset{|}{C} \oplus$
- ĊН

GC0068

GC0069

GC0070

GC0071

- (v) (a) $CF_3 \overset{+}{C}H_2$ (b) $CCl_3 \overset{+}{C}H_2$
- (c) $CBr_3 \overset{+}{C}H_2$

GC0072

GC0073

- (vii)(a) $HC \equiv \overset{\oplus}{C}$ (b) $CH_2 = \overset{\oplus}{CH}$ (c) $CH_3 \overset{\oplus}{CH}_2$

GC0074

- $({\rm viii}) \ ({\rm a}) \ {\rm C_6 H_5}^+ \qquad \qquad ({\rm b}) \ {\rm p-NO_2(C_6 H_4)^+} \qquad ({\rm c}) \ {\rm p-CH_3-(C_6 H_4)^+} \qquad ({\rm d}) \ {\rm p-Cl-C_6 H_4^+}$

(ix) (a)
$$CH_2^{\oplus}$$

$$(c) \bigcirc \bigcap^{CH_2^{\bigoplus}}$$

GC0076

$$(x)$$
 (a) OH_2^{\oplus} OH_2

GC0077

$$(xi) (a) \qquad \begin{array}{c} CH_2^{\oplus} \\ H & H \end{array}$$

(c)
$$CH_2^{\oplus}$$
 C_{-H}^{H}

GC0078

$$(xii) (a) \bigcirc CH_2^{\oplus}$$

$$CH_3$$

$$(b) \bigcirc CH_2^{\oplus}$$

$$CH_2Me$$

(c)
$$CH_2^{\oplus}$$
 $CH Me_2$

$$(d) \bigcirc CH_2^{\oplus}$$

$$CMe_3$$

GC0079

$$(xiii) (a) \ Me - C^{+} \qquad (b) \ Ph - C^{+} \qquad (c) \ Me - CH_{2} \\ Me \qquad \qquad Ph$$

GC0080

$$(xv)(a)$$
 $\stackrel{+}{\swarrow}$

GC0082



GC0083

Q.10 Consider the following statements:

- (I) CH_3OCH_2 is more stable than CH_3CH_2
- (II) Me₂CH is more stable than CH₃CH₂CH₂
- (III) $CH_2 = CH \overset{\oplus}{C}H_2$ is more stable than $CH_3CH_2\overset{\oplus}{C}H_2$ (IV) $CH_2 = \overset{\oplus}{C}H$ is more stable than $CH_3\overset{\oplus}{C}H_2$ Of these statements:
- (A) I and II are correct

(B) III and IV are correct

(C) I, II and III are correct

(D) II, III and IV are correct

GC0084

Q.11 In each of the following pairs of ions which ion is more stable:

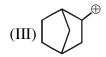
- (a) (I) $C_6H_5-\overset{\oplus}{CH}_2$ and (II) CH_2 = $CH-\overset{\oplus}{CH}_2$ (b) (I) $CH_3-\overset{\oplus}{CH}_2$ and (II) CH_2 = $\overset{\oplus}{CH}$
- (d) (I) $CH_3 CH CH_3$ and (II) $CH_3 N CH_3$ $CH_3 \begin{matrix} & & & \\$

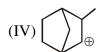
GC0085

Q.12 Find out correct stability order in the following carbocations-









- (A) IV > I > III > II
- (B) IV > III > I > II
- (C) I > IV > III > II (D) I > III > IV > II

GC0086

Q.13 Which of the following carbonium ion is most stable?

- $(A) Ph_2C^+$
- (B) $(CH_2)_2 C^+$
- (C) $(CH_3)_2 CH^+$ (D) $CH_2 = CH CH_2^+$

Q.14 Consider the following carbocations

(a)
$$CH_3O-\langle O \rangle - \overset{\oplus}{C}H_2$$

(c)
$$CH_3 - CH_2$$

(d)
$$CH_3$$
— $\overset{\oplus}{C}H_2$

The relative stabilities of these carbocations are such that :-

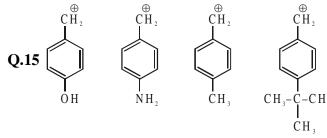
(A)
$$d < b < c < a$$

(B)
$$b < d < c < a$$

(C)
$$d < b < a < c$$

(D)
$$b < d < a < c$$

GC0088



Correct order of carbocation stability is:

(A)
$$2 > 1 > 4 > 3$$

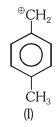
(B)
$$1 > 2 > 4 > 3$$

(C)
$$3 > 4 > 2 > 1$$

(D)
$$2 > 1 > 3 > 4$$

GC0089

Q.16 Arrange the following carbocation in the increasing order of stability:



$$(A) I < II < III$$

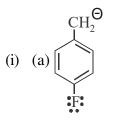
(B)
$$II < III < I$$

$$(C)$$
 III $<$ II $<$ I

(D)
$$III < I < II$$

GC0090

Q.17 Rank the following sets of intermediates in increasing order of their stability.



(b)
$$\operatorname{NO}_2^{\mathsf{CH}_2^{\mathsf{C}}}$$

GC0091

(ii) (a)
$$\bigcap_{Cl}^{CH_2^C}$$

$$(c) \bigcirc CH_{2}^{C}$$

$$C \equiv N$$

$$\operatorname{CH}_{2}^{\mathsf{C}}$$

GC0092

(iii) (a)
$$\overset{\Theta}{\operatorname{CH}}_2$$
 – CH $\overset{\parallel}{\underset{\Theta}{\operatorname{CH}}}$

(b)
$$CH_2 - CH_3$$

GC0093

E

(iv) (a)
$$\bigcirc$$
 (b) \bigcirc

GC0094

$$(b) \bigcup_{NO_2}^{CH_2^-}$$

$$(c) \bigcirc \overline{CH}_2$$

GC0095

GC0096

GC0097



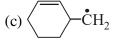


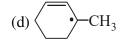
GC0098

GC0099

(x) (a)
$$CH_2 = CH$$

(x) (a)
$$CH_2 = CH$$
 (b) $CH_2 = CH - CH_2$ (c) $\leftarrow CH_2$





GC0100

Q.18 Most stable carbanion is :-

- (A) $HC \equiv C^{\Theta}$
- (B) $C_6H_5^{\Theta}$
- (C) $(CH_3)_3C-CH_2^{\circ}$ (D) $(CH_3)_2C=CH^{\circ}$

GC0101

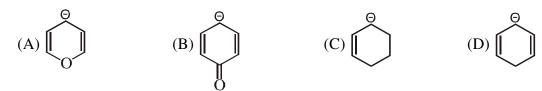
Q.19 Most stable carbanion is:

(A) CH_3^{Θ} (B) $CH_2 = CH - \overset{\Theta}{C}H_2$ (C)





Q.20 Identify the most stable anion.



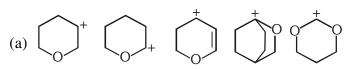
GC0103

Q.21 Correct order of stability:

(D)
$$CH_2 = CH - \dot{C} + \dot{C}H_3 + CH_2 = CH - \dot{C}H_2 + CH_3 - \dot{C}H_2 + CH_2 = \dot{C}H$$

GC0104

Q.22 Rank the following sets of intermediates in increasing order of their stability giving appropriate reasons for your choice.



GC0105

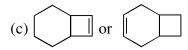
Q.23 Select the correct order of stability of carbon free radicals:

$$(A) \ IV > III > I > II \qquad (B) \ IV > III > II > II < (C) \ I > III > III > IV \qquad (D) \ I > III > IV$$

- **Q.24** $CH_2 = CH CH = CH CH_3$ is more stable than $CH_3 CH = C = CH CH_3$ because (I)
 - (A) there is resonance in I but not in II
- (B) there is tautomerism in I but not in II
- (C) there is hyperconjugation in I but not in II (D) II has more cononical structures than I.

GC0107

- Q.25 Choose the more stable alkene in each of the following pairs. Explain your reasoning.
 - (a) 1-Methylcyclohexene or 3-methylcyclohexene
 - (b) Isopropenylcyclopentane or allylcyclopentane



GC0108

Q.26 Match each alkene with the appropriate heat of combustion:

Heats of combustion (kJ/mol): 5293; 4658; 4650; 4638; 4632

(a) 1-Heptene

(b) 2,4-Dimethyl-1-pentene

(c) 2,4-Dimethyl-2-pentene

- (d) 4,4-Dimethyl-2-pentene
- (e) 2,4,4-Trimethyl-2-pentene

GC0109

Q.27 Stability of:

(II)
$$CH_3 - C = C - CH_3$$

 CH_3

(III)
$$CH_3 - C = CH_2$$

 CH_3

(IV)
$$CH_3 - C = CH - CH_3$$

 CH_3

in the increasing order is:

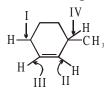
(A) I < III < IV < II

(B) I < II < III < IV

(C) I < IV < III < I

(D) II < III < IV < I

Q.28 Which of the following C-H bonds participate in hyperconjugation?



- (A) I and II
- (B) I and IV
- (C) I and III
- (D) III and IV

GC0111

GC0110

Q.29 Rank the following alkenes in decreasing order of heat of combustion values:







- (I)
- m'

- (III)
- (IV)

- (A) II > III > IV > I
- ,

- (B) II > IV > III > I
 - > 1

(C) I > III > IV > II

(D) I > IV > III > II

Q.30 Write decreasing order of heat of hydrogenation:

GC0113

GC0114

(iii) (a)
$$CH_3$$
 (b) CH_3 CH_3

GC0115

GC0116

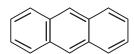
(v) (a)
$$CH_3$$
 $C = C$ CH_3 (b) $C = C$ H

GC0117

(vi) (a)
$$CH_2 = CH - CH < CH_3 CH_3$$
 (b) $CH_2 = C < CH_3 CH_2-CH_3$

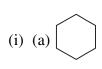
GC0118

Q.31 Write increasing order of heat of hydrogenation:

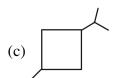


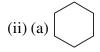
(HOH per benzene ring)

Q.32 Give decreasing order of heat of combustion (HOC):











GC0120

Q.33 Among the following pairs identify the one which gives higher heat of hydrogenation:

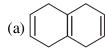
(c)
$$CH_3 - CH = CH - CH_3$$
 and $CH_3 - CH_2 - CH = CH_2$

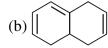
(d)
$$CH_2$$
 and CH_3 CH_3

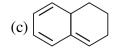
GC0121

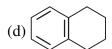
Q.34 Arrange the following compounds in order of:

- (I) Stability
- (II) Heat of hydrogenation









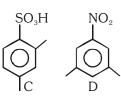
GC0122

Q.35 If Heat of hydrogenation of 1-butene is 30 Kcal/mol then heat of hydrogenation of 1,3-butadiene is ?

- (A) 30
- (B) 60
- (C) 57
- (D) 25

GC0123

 $\mathbf{Q.36} \quad \bigcirc \\ \mathbf{NM}e_2 \qquad \bigcirc \\ \mathbf{NH}_2 \\ \bigcirc \\ \mathbf{R}$

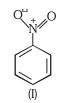




Steric inhibition of resonance takes place:

- (A) In A,B only
- (B) In A, B, C, E
- (C) C only
- (D) In A only

Q.37 Consider the following two structures and choose the correct statements -



- (A) carbon-nitrogen bond length structure I is greater than that in structure II
- (B) carbon-nitrogen bond length in structure I is less than in structure II
- (C) carbon-nitorogen bond length in both structure is same
- (D) It can not be compared

GC0125

Q.38 Which of the following statements would be true about this compound:

$$NO_2 = \bigcup_{\substack{1 \\ NO_2 \\ Br}}^{NO_2} NO_2$$

- (A) All three C N bonds are of same length.
- (B) Cl N and C3 N bonds are of same length but shorter than C5 N bond.
- (C) Cl N and C3 N bonds are of same length but longer than C5 N bond.
- (D) Cl N and C3 N bonds are of different length but both are longer than C5 N bond

GC0126

Q.39 Arrange given compounds in decreasing order of dipole moment:

(i) (a)
$$CH_3$$





GC0127

(c)
$$\bigcap_{C_1}^{NO_2}$$

GC0128

GC0129

EXERCISE # S-I

- **Q.1** Cyclopentadienyl anion is much more stable than allyl anion because:
 - (A) Cyclic anion is more stable than acyclic anion
 - (B) Delocalised anion is more stable than localised anion
 - (C) Cyclopentadienyl anion is aromatic in nature
 - (D) None of these

GC0131

Q.2 Select correct statement regarding given compounds:

$$\begin{array}{ccc} \mathrm{CH_3OCH_3} & & \mathrm{C_2H_5OH} \\ \mathrm{II} & & \mathrm{II} \end{array}$$

- (A) Boiling point of II is higher than I
- (B) Boiling point of II is lower than I
- (C) Compound I forms intramolecular H-bonding
- (D) Compound II forms intermolecular H-bonding

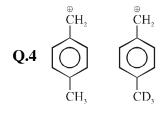
GC0132

- **Q.3** In the compund, CH_3 —CH=CH— $C\equiv N$, the most electronegative carbon is :
 - (A) I

(B) II

- (C) III
- (D) IV

GC0133



(I)

(II)

Carbocation (I) is more stable than carbocation (II), because:

- (A) —CD₃ has more + I effect than —CH₃
- (B) — CH_3 has more + I effect than — CD_3
- (C) —CH₃ has more + H effect than —CD₃
- (D) —CD₃ has more + H effect than —CH₃

GC0134

- **Q.5** Select correct statement:
 - (A) Carbon-oxygen bonds are of equal length in acetate ion
 - (B) Resonating structures of acetate ion are equivalent
 - (C) Carbon-oxygen bonds are of unequal length in formate ion
 - (D) Resonating structures of formate ion are equivalent

GC0135

nade06\B0B0-BA\Kata\LEE[Advanced]\Leader\Che\Sheet\Electronic Displacement Effed\Eng.p65

Q.6 Match the column I with column II.

Column-I

(Group attached with benzene ring)

- (A) — NO_2
- (B) —O⁻
- $(C) O CH_{2}$
- (D) —C = N

Column-II

(Effect shown by the group)

- (P) R effect
- (Q) + R effect
- (R) + I effect
- (S) I effect

GC0136

O.7 Column- I

(Groups attached to phenyl ring)

- (A) $-\ddot{N} = O$
- (B) —CH₃
- (C) $-\ddot{N}H C < CH_3$
- (D) $-C OCH_3$

Column-II

(Effect shown)

- (P) +M
- (Q) -M
- (R) +H
- (S) -I

GC0137

Q.8 Match the column:

Column-I

- (A) Group donate e⁻ inductively but does not donate / withdraw by resonance
- (B) Group withdraw e⁻ inductively but does not donate / withdraw by resonance
- (C) Group withdraw e⁻ inductively & donate e⁻ by resonance
- (D) Group withdraw e⁻ inductively & withdraw e⁻ by resonance

Column-II

(P) -OH

- (Q) -NO₂
- (R) $-CH_2-CH_3$
- $(S) \stackrel{+}{N} H_3$
- (T) -NH₂

Column-I

Column-II

- (P) Aromatic
- (Q) Non-aromatic
- (R) Anti-aromatic
- (S) Cyclic structure

GC0139

Q.10 Statement-I: -a \square OEt



$$C - C - C$$
 bond length $a < b$

Because

Statement-II: More is the double bond character less is the bond legnth.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

GC0140

Q.11 Statement-I: Me₃ C is more stable than Me₂ CH and Me₂ CH is more stable than the MeCH₂.

Because

Statement-II: Greater the number of hyperconjugative structures, more is the stability of carbocation.

- (A)Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

GC0141

Q.12 Statement-I: The potential energy barrier for rotation about C = C bond in 2-butene is much higher than that in ethylene.

Because

Statement-II: Hyperconjugation effect decreases the double bond character.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
- (C) Statement-1 is true, statement-2 is false
- (D) Statement-1 is false, statement-2 is true.

Paragraph for Question 13 to 15

The intramolecular delocalisation of π and non-bonding electrons without any change in the position of atoms is called resonance. Delocalisation may occur in conjugated system involving carbon atom and atom other than carbon. Delocalisation makes system stable. More is the number of resonating structures, more is the stability of the system. A resonating structure is less stable when a higher electronegative atom has positive charge and when identical charges are present on adjacent atoms.

Q.13 The decreasing order of stability of the following resonating structures

$$CH_{2} = CH - \overset{\cdot}{C}I: \longleftrightarrow :\overset{\cdot}{C}H_{2} - CH = \overset{+}{C}I: \longleftrightarrow \overset{+}{C}H_{2} - CH = \overset{\cdot}{C}I: \quad is:$$

$$(I) \qquad \qquad (II) \qquad (III)$$

$$(A) \ I > II > III \qquad (B) \ II > III > I \qquad (C) \ III > II > I$$

- (D) I > III > II

GC0143

Q.14 If A is PhCH₂ and B is CH₂=CH—CH₂, the greater number of resonating structure is of -

(A) A

- (B) B
- (C) both A and B (D) None of these

GC0144

Q.15 Which of the following pairs represent resonance?

(A)
$$CH_2 = CHOH$$
; CH_3CHO

(B)
$$\overset{\ominus}{\text{CH}}_2$$
-CHO ; H_2C =CH- $\overset{\ominus}{\text{O}}$

(C)
$$CH_3$$
— C — CH_3 ; CH_3 — $C = CH_2$

GC0145

Paragraph for Question 16 to 18

Carbocation is a specie with positively charged carbon atom having six electrons in the valence shell after sharing. Carbocations are formed in the heterolysis of a bond and are planar species. Stability of carbocation is determined by inductive effect, hyperconjugation and resonance effect. Greater the number of contributing structures, more is the stability of a Carbocation. Electron releasing groups (+I effect) increases the stability of a carbocation whereas the electron withdrawing groups (–I effect) have an opposite effect.

Q.16 Which of the following is most stable carbocation?

(B)
$$CH_3 - \overset{+}{C}H - CH_3$$
 (C) $CH_3 - \overset{+}{C}H_2$ (D) $CH_3 - \overset{+}{C} - CH_3$

Q.17 The most stable carbocation among the following:

$$(A) \bigvee^{\oplus} \qquad (B) \bigvee_{\oplus} \qquad (C) \bigvee^{\oplus} \bigvee$$

GC0147

Q.18 In which of the following cases, the carbocation (I) is less stable than the carbocation (II)?

(A)
$$C_6H_5$$
— $\dot{C}H_2$ (I), $CH_2 = CH$ — $\dot{C}H_2$ (II) (B) $\dot{C}H_2$ (I), $\dot{C}H_2$ (II)

(C)
$$CH_2 = \overset{+}{C}H(I)$$
, $CH_3 - \overset{+}{C}H_2(II)$ (D) $H_3C - \overset{+}{C}H_2(I)$, $CH_2 - \overset{\oplus}{C}H_2(II)$

GC0148

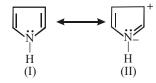
Q.19 Examine the structures I and II for nitromethane and choose the statement correctly:

$$CH_{3} \xrightarrow{+} \stackrel{+}{N} \stackrel{\circ}{} \stackrel{:}{\longleftrightarrow} CH_{3} \xrightarrow{+} \stackrel{+}{N} \stackrel{\circ}{} \stackrel{\circ}{} \stackrel{:}{\longleftrightarrow} CH_{3} \xrightarrow{+} N \stackrel{+}{N} \stackrel{\circ}{} \stackrel{\circ}{} \stackrel{:}{\longleftrightarrow} CH_{3} \xrightarrow{+} N \stackrel{\circ}{} \stackrel{\circ}{} \stackrel{:}{\longleftrightarrow} N \stackrel{\circ}{} \stackrel{\circ}{} \stackrel{:}{\longleftrightarrow} N \stackrel{\circ}{} \stackrel{\circ}{} \stackrel{:}{\longleftrightarrow} N \stackrel{\circ}{} \stackrel{\circ}{} \stackrel{:}{\longleftrightarrow} N \stackrel{\circ}{} \stackrel{\circ}{\to} \stackrel{\circ}{\to} N \stackrel{\circ}{} \stackrel{\circ}{\to} \stackrel{\circ}{\to} N \stackrel{\circ}{} \stackrel{\circ}{\to} \stackrel{\circ}{\to} N \stackrel{\circ}{\to}$$

- (A) Structure II is unlikely representation because electrons have shifted to oxygen
- (B) Structure II is unlikely representation because nitrogen has sextet of electrons
- (C) Structure II is acceptable and important
- (D) None of these

GC0149

Q.20 Examine the following two structures for pyrrole and choose the correct statement given below



- (A) II is not an acceptable resonating structure because carbonium ions is less stable than nitride ion
- (B) II is not an acceptable resonating structure because there is charge separation
- (C) II is not an acceptable resonating structure because nitrogen has ten valance electrons
- (D) II is an acceptable resonating structure

GC0150

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- **Q.21** Delocalization of electrons increases molecular stability because :
 - (A) Potential energy of the molecule decreases (B) Electron-electron repulsion decreases
 - (C) Both (A) and (B)

(D) Electron-electron repulsion increases

GC0151

Q.22 The most stable and the least stable carbocation among



- (II) $CH_2 = CH \overset{+}{C}H_2$ (III) $C_6H_5 \overset{+}{C}H_2$ (IV) $CH_3 \overset{+}{C}H CH_3$

are respectively:

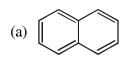
- (A) II, I
- (B) III, IV
- (C) I, II
- (D) I, IV

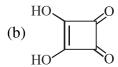
GC0152

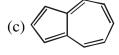
- **Q.23** Most stable carbocation is formed by the heterolysis of :
 - (A) (CH₃)₃CBr
- (B) $(C_6H_5)_3CBr$
- $(C) (C_6H_5)_2CHBr$
- (D) $C_6H_5CH_2Br$

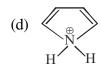
GC0153

Q.24 Total number of aromatic compounds









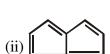




GC0154

Q.25 Identify total number of compounds which are unstable at room temperature?

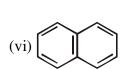














EXERCISE # J-MAIN

Q.1 In the following benzyl/allyl system

[AIEEE-2002]

R–CH=CH
$$_2$$
 or \bigcirc

(R is alkyl group)

decreasing order of inductive effect is-

- $(1) (CH_3)_3C-> (CH_3)_2CH-> CH_3CH_2-$
- (2) $CH_3 CH_2 > (CH_3)_2 CH > (CH_3)_3 C -$
- $(3) (CH_3)_2CH -> CH_3CH_2 -> (CH_3)_3CH -$
- (4) None of these

GC0156

- Q.2 In the anion HCOO the two carbon-oxygen bonds are found to be of equal length. What is the reason for it-[AIEEE-2003]
 - (1) Electronic orbits of carbon atoms are hybridised
 - (2) The C=O bond is weaker than the C-O bond
 - (3) The anion HCOO has two resonating structure
 - (4) The anion is obtained by removal of a proton form the acid molecule

GC0157

Q.3 Which one of the following does not have sp² hybridised carbon

[AIEEE-2004]

- (1) Acetamide
- (2) Acetic acid
- (3) Acetonitrile
- (4) Acetone

GC0158

Q.4 Due to the presence of an unpaired electron, free radicals are -

[AIEEE-2005]

(1) Chemically inactive

(2) Chemically reactive

(3) Cations

(4) Anions

GC0159

Q.5 The increasing order of stability of the following free radicals is

[AIEEE-2006]

- (1) $(C_6H_5)_3 \overset{\bullet}{C} < (C_6H_5)_2 \overset{\bullet}{C} H < (CH_3)_3 \overset{\bullet}{C} < (CH_3)_2 \overset{\bullet}{C} H$
- (2) $(C_6H_5)_2 CH < (C_6H_5)_3 C < (CH_3)_3 C < (CH_3)_2 CH$
- (3) $(CH_3)_2 CH < (CH_3)_3 C < (C_6H_5)_3 C < (C_6H_5)_2 CH$
- $(4) (CH_3)_2 CH < (CH_3)_3 C < (C_6H_5)_2 CH < (C_6H_5)_3 C$

GC0160

- **Q.6** Arrange the carbanions, $(CH_3)_3\overline{C}$, \overline{CCl}_3 , $(CH_3)_2\overline{CH}$, $C_6H_5\overline{CH}_2$, in order of their decreasing stability [AIEEE-2009]

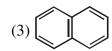
 - (1) $\overline{CCl}_3 > C_cH_5\overline{CH}_2 > (CH_3)_2\overline{CH} > (CH_3)_3\overline{C}$ (2) $(CH_3)_3\overline{C} > (CH_3)_2\overline{CH} > C_cH_5\overline{CH}_2 > \overline{CCl}_3$
 - $(3) C₆H₅\overline{C}H₂ > \overline{C}Cl₃ > (CH₃)₂\overline{C} > (CH₃)₂\overline{C}H$ $(4) (CH₃)₂\overline{C}H > \overline{C}Cl₃ > C₆H₅\overline{C}H₂ > (CH₃)₂\overline{C}H$

Q.7 The non aromatic compound among the following is:-

[AIEEE-2011]









GC0162

- Q.8 ortho-Nitrophenol is less soluble in water than p- and m- Nitrophenols because :-
 - (1) Melting point of o-Nitrophenol is lower than those of m- and p- isomers

[AIEEE-2012]

- (2) o-Nitrophenol is more volatile in steam than those of m- and p- isomers
- (3) o-Nitrophenol shows Intramolecular H-bonding
- (4) o-Nitrophenol shows Intermolecular H-bonding

GC0163

Q.9 Which of the following compounds are antiaromatic:

[AIEEE-2012(Online)]









- (1) (III) and (VI)
- (2) (II) and (V)
- (3) (I) and (V)
- (4) (V) and (VI)

GC0164

- Q.10 Among the following the molecule with the lowest dipole moment is: [AIEEE-2012(Online)]
 - (1) CHCl₃
- $(2) CH_2Cl_2$
- (3) CCl₄
- (4) CH₃Cl

GC0165

Q.11 The order of stability of the following carbocations

[JEE-MAIN-2013]

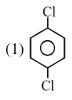
$$CH_2=CH-\overset{\oplus}{C}H_2$$
; $CH_3-CH_2-\overset{\dagger}{C}H_2$; III is:

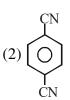
- (1) III > II > I
- (2) II > III > I
- (3) I > II > III
- (4) III > I > II

GC0166

Q.12 For which of the following molecule significant $\mu \neq 0$

[JEE-MAIN-2014]









- (1) Only (3)
- (2) (3) and (4)
- (3) Only (1)
- (4) (1) and (2)

GC0175

Q.13 Which of the following molecules is least resonance stabilized? [JEE-MAIN-2017] GC0168 **14.** Which of the following compounds is not aromatic? [JEE(Main)-Jan-2019] GC0169 Which compound(s) out of the following is/are not aromatic? [JEE(Main)-Jan-2019] **15.** (C) (D) (A) (3) A and C (1) C and D (2) B, C and D (4) BGC0170 16. The correct order of stability for the following alkoxides is: [JEE(Main)-Jan-2020] NO, (A) (B) (2) (C) > (A) > (B) (3) (B) > (C) > (A)(1) (C) > (B) > (A)(4) (B) > (A) > (C)GC0171 Arrange the following compounds in increasing order of C-OH bond length: **17.** methanol, phenol, p-ethoxyphenol [JEE(Main)-Jan-2020] (1) phenol < methanol < p-ethoxyphenol (2) phenol < p-ethoxyphenol < methanol (3) methanol < p-ethoxyphenol < phenol (4) methanol < phenol < p-ethoxyphenol GC0172 **18.** Which of the following has the shortest C-Cl bond? [JEE(Main)-Jan-2020] (1) Cl-CH=CH-OCH₃ (2) C1-CH=CH-CH₃ (3) C1-CH=CH₂ (4) C1-CH=CH-NO₂ GC0173 **19.** The number of sp² hybrid orbitals in a molecule of benzene is : [JEE(Main)-Jan-2020] (1)24(3) 12(2) 6(4) 18GC0174 **20.** The correct order of heat of combustion for following alkadienes is: [JEE(Main)-Jan-2020] (1) (a) < (b) < (c)(2) (b) < (c) < (a) (3) (c) < (b) < (a)(4) (a) < (c) < (b)

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EXERCISE # J-ADVANCED

- Q.1 Which one of the following has the smallest heat of hydrogenation per mole of H_2 ? [IIT-93]
 - (A) 1-Butene
- (B) trans-2-Butene (C) cis-2-Butene
- (D) 1, 3-Butadiene

GC0176

Q.2 Most stable carbonium ion is

[IIT-95]

- (A) $p-NO_2-C_6H_4-C_1H_2$
- (B) $C_6H_5\overset{\oplus}{C}H_2$

(C) p-Cl— C_6H_4 — $\overset{\oplus}{C}H_7$

(D) p-CH₃O— C_6H_4 — $\overset{\oplus}{C}H_2$

GC0177

Q.3 Arrange the following compounds in order of increasing dipole moment:

[IIT-96]

toluene (I)

m-dichloroobenzene (II)

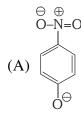
o-dichlorobenzene (III)

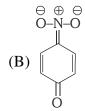
p-dichlorobenzene (IV)

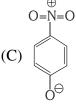
(B)
$$IV < I < II < III$$
 (C) $IV < I < III < II$ (D) $IV < II < III$

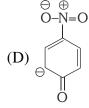
GC0178

Q.4 The most unlikely representation of resonance structure of p-nitrophenoxide ion is -[HT-99]









GC0179

Q.5 An aromatic molecule will not

[IIT-99]

(A) have $4n \pi$ electrons

(B) have $(4n + 2)\pi$ electrons

(C) be planar

(D) be cyclic

GC0180

Q.6 Statement-I: p-Hydroxybenzoic acid has a lower boiling point that o-hydroxybenzoic acid.

Because

Statement-II: o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

[IIT 2003]

- (A) Statement-I is True, Statement-II is True; Statement-II is a correct explanation for Statement-I
- (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I
- (C) Statement-I is True, Statement-II is False.
- (D) Statement-I is False, Statement-II is True.

GC0181

Q.7 Among the following, the molecule with the highest dipole moment is

[IIT-2003]

- (A) CH₃Cl
- (B) CH₂Cl₂
- (C) CHCl₃
- (D) CCl₄

Q.8 Give resonating structures of following compound.

[IIT 2003]

GC0183

Q.9 Which of the following is least stable:

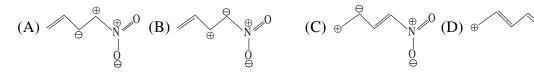
[IIT-2005]

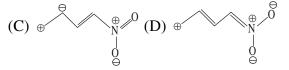
- (A) $CH_3 \overrightarrow{O} = CH \overrightarrow{CH} HC = CH_3$
- (B) $CH_3 \overset{\oplus}{O} = CH CH = HC \overset{\ominus}{C}H_3$
- (C) $CH_3-0-\overset{\oplus}{C}H-\overset{\ominus}{C}H-HC=CH_7$
- (D) $CH_3 O CH CH CH = CH_2$

GC0184

Q.10 Among the following, the least stable resonance structure is -

[IIT-2007]

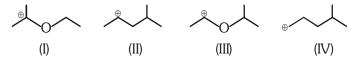




GC0185

Q.11 The correct stability order for the following species is:

[IIT-2008]



- (A) II > IV > I > III (B) I > II > III > IV
- (C) II > I > IV > III (D) I > III > II > IV

GC0186

Q.12 The correct stability order of the following resonance structures is

[IIT-2009]

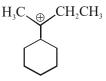
- (I) $H_2C = N = \overline{N}$
- (II) $H_2 \overset{+}{C} N = \overline{N}$ (III) $H_2 \overset{-}{C} \overset{+}{N} = N$ (IV) $H_2 \overset{-}{C} N = \overset{+}{N}$

(A)(I) > (II) > (IV) > (III)

- (B) (I) > (III) > (IV)
- (C) (II) > (I) > (III) > (IV)
- (D) (III) > (I) > (IV) > (II)

GC0187

Q.13 The total number of contributing structures showing hyperconjugation (involving C-H bonds) for the following carbocation is. [IIT-2011]



GC0188

Q.14 Which of the following molecules, in pure from , is (are) unstable at room temperature? [IIT-2012]









Q.15 The hyperconjugative stbilities of tert-butyl cation and 2-butene, respectively, are due to

(A) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi$ electron delocalisations

[IIT-2013]

- (B) $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ electron delocalisations
- (C) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations
- (D) p (filled) $\rightarrow \sigma$ and $\sigma \rightarrow \pi$ electron delocalisations

GC0190

Q.16 The total number of lone-pairs of electrons in melamine is

[IIT-2013] GC0191

Q.17 The number of resonance structures for N is:

$$\stackrel{\mathrm{OH}}{\longrightarrow} \mathrm{NaOH} \to \mathrm{N}$$

GC0192

18. Among the following, the number of aromatic compound (s) is[JEE - Adv. 2017]





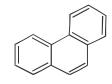












ANSWER-KEY

EXERCISE # O-I

Q.1 **(D)** Q.2 (C)

Q.3 (B)

Q.4 (A,B,D)

 $Q.5 \ 4(b, d, f, g)$

Q.6

 $(a), (c), (d), (g), (j), (\ell), (m)$

 $\mathbf{Q.7}$ (A)

 $\mathbf{Q.8}$ (A)

Q.9 Q.10 A,D

(a) Resonance forms, (b) A, (c) C, (d) A & B, (e) B & C, (f) 0, (g) B, (h) B

Q.13 b, d, e

Q.14 (d)

Q.15 c, f

Q.16 a, b, c, d, f

Q.11 (D) Q.17 b, c, f

Q.19 a-I, b-II, c-II, d-II, e-I

Q.20 a-I,b-I, c-I, d-I, e-II, f-II

Q.21 a, e, f, g

Q.12 b, d, e

Q.22(A)

Q.23(a) II; (b) II; (c) II

Q.24 (A)

Q.25 a-II, b-II, c-II, d-II

Q.26 a & b

Q.27 (i)-I, (ii)-II, (iii)-II, (iv)-I, (v)-I, (vi)-II, (vii)-II, (viii)-II, (ix)-II, (x)-II, (xi)-II, (xii)-I, (xiii)-I, (xiv)-I,(xv)-I

Q.28 a-II, b-I, c-I, d-II, e-I

Q.29(B)

Q.30(D)

Q.40(D)

Q.31(B)

Q.32 (C)

Q.33 (C)

Q.37 (B)

Q.34 (C)

Q.35(D)

Q.36(A,B,C)

Q.41(D)

Q.42(A)

Q.43 (B,C,D)

Q.38 (B) **Q.44** (**B**) Q.39(C) Q.45(A)

Q.46(A,C,D)

Q.47 a-I, b-I, c-II, d-I, e-I, f-I

Q.51 (A)

Q.48 a-II ,b-I, c-I, d-I, e-II, f-II Q.49(D)

Q.50 C > B > A

EXERCISE # O-II

Q.1 (i) a, b; (ii) a, c; (iii) b, c, d; (iv) a, b, c, d, e, f

0.2 Aromatic \rightarrow a, b, d, e, g; Non-aromatic \rightarrow c, f **O.3** (C)

O.4 (C)

O.5 (B)

Q.6 (A)

Q.8 (D)

Q.9

(i) c > b > a (ii) c > b > a

(iii) b > c > a

(iv) d > c > b > a

(v) c > b > a

(vi) b > c > a (vii) c > b > a

(viii) c>a>d>b

(ix) b > c > a

(x) c > a > b

(xi) c > a > b (xii) a > b > c > d (xiii) b > a > c > d (xiv) d > e > b > a > c

 $(xv) a > c > b \quad (xvi) b > c > a$

Q.10 (C)

Q.11 (a) I; (b) I; (c) II; (d) II; Q.12 (C)

O.13 (A)

Q.14 (A)

Q.15 (D)

Q.16 (B)

62 **IEE-Chemistry**

- Q.17 (i) a < b
- (ii) d < a < c < b (iii) b < a
- (iv) c < b < a (v) c < a < b (vi) a < c < b

- $(vii) c < b < a \quad (viii) c < b < a$
- (ix) b < a
- (x) a < c < b < d
- Q.18 (A)

- Q.19 (D)
- Q.20 (B)
- Q.21(D)
- Q.22 (a) IV < I < II < III < V (b) III < IV < I < II
- Q.23(B)
- Q.24(A)

Q.28(B)

- Q.25 (a) -I; (b) -I; (c) II
- Q.26 (a) 4658; (b) 4638 (c) 4632; (d) 4650; (e) 5293 Q.27 (A)
- Q.29 (D)
- Q.30 (i) d > c > b > a; (ii) e > c > d > b > a; (iii) b > a (iv) a > b (v) b > a; (vi) a > b
- Q.31 (i) a < b; (ii) e < d < c < b < a; (iii) a < c < b; (iv) a > b > c
- Q.32 (i) c > b > a; (ii) a > b > c > d; (iii) a > b; (iv) c > b > a
- Q.33 a I ; b I ; c II, d I
- Q.34 Stability order: d>c>b>a; HOH order: a>b>c>d

- Q.35 (C)
- Q.36 (D)
- Q.37 (B)
- Q.38(C)

- Q.39 (i) c > b > a
- (ii) a > b > c
- (iii) a > b

EXERCISE # S-I

- Q.1 **(C)**
- Q.2 (A,D)
- Q.3 (D)
- Q.4 (C)
- Q.5 (A,B,D)

- Q.6 (A)-P,S;(B)-Q,R;(C)-Q,S;(D)-P,S
- **Q.7** $(A) \rightarrow P, Q, S; (B) \rightarrow R; (C) \rightarrow P, S; (D) \rightarrow Q, S$
- **Q.8** (A)-R; (B)-S; (C)-P, T; (D)-Q Q.9 (A)-Q,S; (B)-P, S; (C)-P, S; (D)-R, S
- Q.10 (D)
- Q.11 (A)
- Q.12 (D)
- Q.13 (A)
- Q.14(A)
- Q.15 (B)

- Q.16 (D)
- Q.17 (C)
- Q.18 (C)
- Q.19 (B)
- Q.20(C)
- Q.21 (C)

- Q.22 (D)
- Q.23 (B)
- Q.24 (4)
- Q.25 (4)

EXERCISE # (J-MAIN)

- Q.1 **(1)**
- $\mathbf{Q.2}$ (3)
- Q.3 (3)
- Q.4 (2)
- Q.5 (4)
- Q.6 (1)

- **Q.7 (1)**
- **Q.8** (3)
- Q.9 (4)
- Q.10(3)
- Q.11(4)
- Q.12 (2)

- Q.13 (4)
- 14. Ans. (3)
- 15. Ans. (2)

- **16. Ans.** (1)
- **Sol.** (C) > (B) > (A)

17. Ans.(2)

Sol. H_3C – OH (100% single bond)

C-OH bond has partial double bond character

(C-OH bond has some double bond character but double bond character is less)

Ans.
$$CH_3OH > \bigcirc OH$$
 (p-ethoxyphenol) > $\bigcirc OH$

Due to –M effect of –NO $_2$ and + M effect of Cl more D.B. character between C – Cl bond. So shortest bond length.

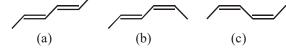
Each carbon atom is sp² hybridized

Therefore each carbon has 3 sp² hybrid orbitals.

Hence total sp² hybrid orbitals are 18.

20. Ans. (1)

Sol.



(Trans, Trans)

ns) (Trans, Cis)

(Cis, Cis)

:. Generally trans is more stable then cis form.

Heat of combustion (HOC) $\propto \frac{1}{\text{Stability}}$

Stability: a > b > cHOC: c > b > a

EXERCISE # J-ADVANCED

Q.1 (D)	Q.2 (D)	Q.3 (B)	Q.4 (C)	Q.5 (A)	Q.6 (D)
$\mathbf{Q.7}$ (A)	Q.9 (D)	Q.10 (A)	Q.11 (D)	Q.12(B)	Q.13 (6)
Q.14 (B,C)	Q.15 (A)	Q.16 (6)	Q.17(9)	Q.18 (5)	

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