GENERAL ORGANIC CHEMISTRY-1 (GOC-1)

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JEE (Advanced) Syllabus

Inductive, Resonance mesomeric and Hyperconjugation Effect, Applications of Electronic Effects, Aromaticity.

JEE (Main) Syllabus

Electronic displacement in a covalent bond; inductive effect, electromeric effect, resonance and hyperconjugation.

GENERAL ORGANIC CHEMISTRY-1

ELECTRONIC EFFECTS IN ORGANIC REACTIONS

Introduction

(i) Effects because of displacement of electrons is known as electronic effects.

(ii) When a chemical bond is broken and a new chemical bond is formed during a chemical reaction, it is electronic displacement that decides which is the preferred direction of movement of electrons.

(iii) Type of electronic effects-

(A) Inductive effect or Induction effect or transmission effect.

(B) Resonance effect or Mesomeric effect.

- (C) Hyperconjugation effect or No-bond resonance.
- (D) Electromeric effect.

(iv) Inductive, resonance, hyperconjugation effects are permanent effect and electromeric effect is temporary effect.

1. Inductive effect/Transmission effect/Induction effect

Inductive effect is polarisation of shared pair of σ electrons towards more electronegative atom. Let us first consider a molecule of ethane.

$$\begin{array}{ccc} H & H \\ H & - \begin{matrix} I \\ - \begin{matrix} I \\ - \end{matrix} \\ - \begin{matrix} I \\ - \end{matrix} \\ - \begin{matrix} I \\ - \end{matrix} \\ H & H \end{matrix} H$$

In ethane molecule, the two electrons of C–C bond are centrally located i.e. both the carbons have equal hold on this shared pair of electrons and no polarisation of electron density is observed. Now consider choloromethane.

$$H \xrightarrow{H} Cl^{\delta^+} Cl^{\delta^-}$$

In chloromethane, the shared pair of electrons between carbon and chlorine are attracted strongly towards chlorine since later has greater electronegative than former.

The above effect of polarisation of shared pair of electrons towards more electronegative atom is known as inductive effect.

Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole (Polar bond).

Some important points are:

(i) It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.

(ii) It is also called transmission effect.

(iii) It causes permanent polarisation in molecule, hence it is a permanent effect.

(iv) The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.

(v) The electrons never leave their original atomic orbital.

(vi) Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.

(vii) The inductive effect is always operative through σ bond, does not involve π bond electrons.

Types of inductive effects

(a) –I Effect :

The group which withdraws electron cloud is known as –I group and its effect is called –I effect. Various groups are listed in their decreasing –I strength as follows.

$$\begin{array}{ccc} \oplus & \oplus \\ -\operatorname{NR}_3 &> -\operatorname{SR}_2 &> -\operatorname{NH}_3 &> -\operatorname{NO}_2 &> -\operatorname{SO}_2 R &> -\operatorname{CN} &> -\operatorname{COOH} &> -\operatorname{F} &> -\operatorname{CI} &> \\ -\operatorname{Br} &> -\operatorname{I} &> -\operatorname{OAr} &> -\operatorname{OR} &> -\operatorname{OH} &> -\operatorname{C} &= \operatorname{CR} &> -\operatorname{Ar} &> -\operatorname{CH} &= \operatorname{CR}_2 \end{array}$$

(b) +I Effect :

The group which release electron cloud is known as + I group and effect is + I effect.

 $-O^{\circ} > -COO^{\circ} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > -D > -H_3$

The hydrogen atom is reference for + I and - I series. The inductive effect of hydrogen is assumed to be zero.



Since –CN is – I group it pulls or withdraws electron from cyclohexane ring making it electron deficient.

(ii) Let us consider effect of -COOH & -COO⁻ in carbon chain.

(a) HOOC $\leftarrow \overset{\delta^+}{C}H_2 \leftarrow \overset{\delta\delta_+}{C}H_3$ (b) $\overset{\Theta}{O}OC \rightarrow \overset{\delta^-}{C}H_2 \rightarrow \overset{\delta\delta^-}{C}H_2 - CH_3$

Due to e^- attracting nature of –COOH, (–I effect) carbon chain will have partial positive charge but due to electron donating nature of – COO⁻ (+I effect), cabon chain has become partially negative charge.



2. Resonance

(1) It is stabilising phenomenon.

(2) When we can not explain all the properties of the molecule by single Lewis structure then phenomenon of resonance comes in our mind.

(3) For explaining all the properties of the molecule, different hypothetical Lewis structures are imagined by transfer/ delocalisation of π -electrons.

(4) Resonance structures : These hypothetical Lewis structures are called resonance structures/canonical structures/contributing structures.



(5) Characteristics of resonance structures

(a) They are hypothetical.

(b) Each resonance structure will have same skeleton, net charge, paired/unpaired electrons, approximate same energy.

(c) Hybridisation of atoms do not change.

(d) They will differ only in the distribution/delocalisation of π -electrons.

(i) $R - C = \overset{\Theta}{O} - H$ (Positions of atomic nuclei in both are same.)

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

(I) (II)

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

(6) Resonance hybrid

(i) It is real, most stable structure and contributed by all resonance structures.

(ii) Percentage contribution of each resonance structure in the resonance hybrid depends on the stability of each resonance structure.

(7) Resonance energy

(a) Resonance energy ∞ stability of molecules

(b) The P.E. difference between the most stable resonance structure and resonance hybrid is called resonance energy.



Resonance Energy of Benzene

(8) Conditions for resonance

- (a) System must be planar.
- (b) System must be in conjugation (i.e. parallel p orbitals are required)
- (c) Following type of conjugation may be present in a molecule :-

(A) $\pi \rightarrow \pi$ conjugation :

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

(i)
$$CH_2 = CH^{\bullet} - C - H \longleftrightarrow CH_2 - CH = C - H$$

(B) Lone pair $\rightarrow \pi$ conjugation :

If there is one lone pair conjugated with one π bond then electrons of lone pair are delocalised through π bond.

(i)
$$CH_2 = CH \stackrel{\frown}{=} CH \stackrel{\frown}{=} CH \stackrel{\frown}{=} CH \stackrel{\ominus}{=} CH = CH \stackrel{\oplus}{:} CH_2 - CH = CH \stackrel{\oplus}{:} CH \stackrel{O}{:} CH_2 - CH \stackrel{\oplus}{:} CH \stackrel{O}{:} CH_2 - CH \stackrel{O}{:} CH \stackrel{O}{:} CH_2 - CH \stackrel{O}{:} CH \stackrel{O}{:} CH_2 - CH \stackrel{O}{:} CH \stackrel{O}{$$

(ii)
$$\underset{CH_2=CH}{\overset{\frown}{\longrightarrow}}\underset{CH_2}{\overset{\ominus}{\longrightarrow}}\underset{CH_2}{\overset{\ominus}{\longrightarrow}}\underset{CH_2}{\overset{\ominus}{\longrightarrow}}\underset{CH_2-CH=CH_2}{\overset{\ominus}{\longrightarrow}}$$

- (iii) $CH_2 = CH \stackrel{\frown}{=} CH_3 \longleftrightarrow CH_2 CH = \stackrel{\oplus}{O} CH_3$ (iv) $CH_2 = CH \stackrel{\frown}{=} O \longleftrightarrow CH_2 CH = O$

(C) $\pi \rightarrow$ vacant orbital conjugation :

If there is one vacant orbital conjugated with one π bond then electrons of π bond are delocalised towards vacant orbital.

$$CH_2 \xrightarrow{\oplus} CH^{\oplus} \xrightarrow{\oplus} CH_2 \longleftrightarrow \xrightarrow{\oplus} CH_2 \xrightarrow{\oplus} CH_2 = CH_2$$

(D) $\pi \rightarrow$ unpaired e⁻ conjugation :

If there is one unpaired electron and one π bond are at alternate position.

(i) $\dot{CH_2} = CH - \dot{CH_2} \leftrightarrow \dot{CH_2} - CH = CH_2$

(ii) $CH_3 - \dot{CH} = \dot{CH} - \dot{CH}_2 \leftarrow \rightarrow CH_3 - \dot{CH} - CH = CH_2$

(E) Lone pair \rightarrow +ve charge conjugation :

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

$$\stackrel{\oplus}{\operatorname{CH}}_2 \xrightarrow{\bullet} \stackrel{\odot}{\operatorname{OH}} \longleftrightarrow \operatorname{CH}_2 \xrightarrow{\oplus} \stackrel{\oplus}{\operatorname{OH}}$$

Key points :

(1) If any group has more than one π bond in conjugation, then only one π bond will take part in delocalisation.

$$CH_2 = CH - C \equiv CH$$

Out of two π bonds only one π bond will take part in delocalisation.

(2) If any conjugate position has more than one lone pair then only one lone pair will take part in the delocalisation.

$$CH_2 = CH - OH_3$$

Out of two lone pairs only one will take part in delocalisation.

(3) If any conjugate position has π bond and any of the positive charge, negative charge, odd electron, lone pair electrons then only π bond will take part in delocalisation on priority.



Nitrogen has π bond as well as lone pair, but only π bond of nitrogen will take part in delocalisation.

(4) Electrons of negative charge or lone pair behave as 2π electrons if it is in conjugation with π bond.

 $CH_2=CH-NH_2$ Behaves as 2π e's ; $CH_2=CH-CH_2$ Behaves as 2π e's ;



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Examples of drawing resonating structures





5-Resonance structures

3. Determining stability of different resonance structures

Following sequence should be followed :

(a) Resonating structure with more π bonds will be more stable or structures in which all of the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are especially stable and make large contributions to the hybrid.



(ii)
$$CH_2 \stackrel{\frown}{=} \stackrel{\frown}{CH} - CH \stackrel{\frown}{=} \stackrel{\frown}{CH}_2 \longleftrightarrow \stackrel{\overleftarrow{}}{CH}_2 - CH = CH - \stackrel{\overleftarrow{C}}{CH}_2 \longleftrightarrow \stackrel{\overleftarrow{}}{CH}_2 - CH = CH - \stackrel{\overleftarrow{C}}{CH}_2 (II)$$

This structure is the most stable because it contains more covalent bonds.

(b) Charge separation decreases stability. Separating opposite charges requires energy. Therefore, structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation.

(iii)
$$\overrightarrow{CH_2} = CH \stackrel{f}{=} \overrightarrow{CH} : \longleftrightarrow : \overrightarrow{CH_2} - CH = \overrightarrow{CI}^{\oplus}(I \text{ is more stable than II})$$

(I) (II)

(c) Amongst the charged structures :

(1) Stability is more, if –ve charge is present on more electronegative atom and +ve charge is present on less electronegative atom.

(2) Stability \propto minimum distance between unlike charges (due to attraction).

(3) Stability ∞ maximum distance between the like charges.

4. Resonance /Mesomeric effect

Effects obtained in a molecule by an atoms or group due to delocalisation/transfer of π electrons is called resonance effect/mesomeric effect (R/M effects). It is of two types-

(a) Positive Mesomeric effect (+M effect)

When the group donates electron to the conjugated system it shows +M effect.

Relative order of +M strength of groups (usually followed) :

$$-\overset{\circ}{O} > -NH_{2} > -NHR > -NR_{2} > -OH > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -I$$
(i) $\overset{\circ}{X} \xrightarrow{1}_{I} CH \stackrel{\circ}{=} CH_{2} \longleftrightarrow \overset{\circ}{X} = CH \stackrel{\circ}{-} \overset{\circ}{C}H_{2}$
(ii) $\overset{\circ}{CH_{2}} \xrightarrow{=} CH \stackrel{\circ}{-} \overset{\circ}{O}H \longleftrightarrow \overset{\circ}{CH_{2}} - CH \stackrel{\otimes}{=} \overset{\circ}{O}H \equiv \overset{\circ}{CH_{2}} \xrightarrow{-} CH = \overset{\circ}{O}H$
(iii) $\overset{\circ}{CH_{2}} \xrightarrow{=} CH \stackrel{\circ}{-} \overset{\circ}{O}H \longleftrightarrow \overset{\circ}{CH_{2}} - CH \stackrel{\otimes}{=} \overset{\circ}{O}H$
(Resonance structure) (Hybrid structure)
(iii) $\overset{\circ}{CH_{2}} \xrightarrow{=} CH \stackrel{\circ}{-} \overset{\circ}{C}H_{2} \longleftrightarrow \overset{\circ}{C}H_{2} \xrightarrow{-} CH \xrightarrow{\circ}{C}H_{2}$
(Resonance structure) (Hybrid structure)
(iv) $H_{2}\overset{\circ}{C} = CH \stackrel{\circ}{-} CH \xrightarrow{-} CH \stackrel{\circ}{-} NH_{2} \longleftrightarrow H_{2}\overset{\circ}{C} - CH = CH - CH = \overset{\circ}{N}H_{2}$



(b) Negative Mesomeric effect (-M effect)

When the group withdraws electron from the conjugated system, it shows – M effect. Relative order of –M strength of groups (usually followed):



Note :

(1) When a +M group and –M group are at meta-positions with respect to each other then they are not in conjugation with each other, but conjugation with benzene ring exists.



(2) +M group increases electron density in benzene ring, while –M group decreases electron density in the benzene ring.

Que. Write electron density order in the following compound.



5. SIR effect (Steric Inhibition of Resonance)

Restriction in exhibition of resonance due to steric hindrance is known as SIR effect.

In case of 1,2-disubstituted benzene if the substitutents are bulky then due to steric repulsion (vander waal repulsion) the group go out of plane with respect to benzene ring.

Due to this change in planarity the conjugation between the substituents on benzene is slightly diminished.

SIR effect ∞ Size of ortho substituent group

e.g. Arrange the following compounds in their decreasing SIR effect order.



SIR effect order = IV > III > II > I.

6. Hyperconjugation (No bond resonance)

(1) Like resonance it is also stablising phenomenon but less effective than resonance.

(2) **Condition of hyperconjugation** : If C–H bond of sp³ carbon will be in the conjugation with p-orbitals (alkene, alkyne, carbocation and free radical) then there will be transfer of C–H sigma electrons with p-orbitals i.e. atleast one α -hydrogen must be present with respect to p-orbitals.



(a) Hyperconjugation in alkene

In alkene there will be transfer of C–H σ electrons with $\pi^* \text{orbital}.$



These resonance structures only suggest that there is some ionic character between C - H bond. Carboncarbon double bond acquires some single bond character.

(b) Hyperconjugation in carbocation

In carbocation there will be transfer of C–H σ electrons with vacant p-orbitals



(c) Hyperconjugation in alkyl free radical

In free radicals there will be transfer of C–H σ electrons with p-orbital having unpaired electron.



(d) Hyperconjugation in toluene

Electron density of benzene nucleus is increased at ortho and para positions.



7. Applications of electronic effects (a) Stability of alkenes

More is the number of hyperconjugative structures more stable is the alkene.

"More alkylated alkenes are more stable".

Stability of alkenes ∞ delocalisation of π electrons

 ∞ no. of hyperconjugative structures



(b) Heat of hydrogenation

Greater number of α hydrogen atoms results greater stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation.

Stability of alkenes ∞ no. of hyperconjugative structures $\propto \frac{1}{\Delta H_{Hvdrogenation}}$

 $\mathsf{CH}_{_2} = \mathsf{CH}_{_2} > \mathsf{CH}_{_3} - \mathsf{CH} = \mathsf{CH}_{_2} > \mathsf{CH}_{_3} - \mathsf{CH} = \mathsf{CH} - \mathsf{CH}_{_3} \qquad (\Delta\mathsf{H}_{_{\mathsf{Hydrogenation}}})$

(c) Bond Length

Bond length is also affected by hyperconjugation and resonance.

$$H_{2}C \xrightarrow{H} HC \xrightarrow{e} CH_{2} \xrightarrow{H} HC \xrightarrow{e} CH_{2}$$

(i) Bond length of C(II) - C(III) bond is less than normal C–C bond in ethane.

(ii) Bond length of C(II) - C(I) bond is more than normal C=C bond in ethene.

(iii) C–H bond is longer than normal C–H bond in ethane.



(d) Stability of reaction intermediates

(i) Stability of carbocation ∞ +M, +H, +I effect groups.

(ii) Stability of carbon free radical ∞ resonance effect, +I effect groups.

(iii) Stability of carbanion \propto –M, –I effect groups.

Note: Resonance effect or delocalisation of electrons increases the stability of over all system. For example carbocation, carbon free radical, carbanion & alkenes.

(e) Dipole moment

Since hyperconjugation causes the development of charge, it also affects the dipole moment of the molecule.

(i) $CH_2 = CH_2 < CH_3 - CH = CH_2$ (Dipole moment) (ii) $H-CH=O < CH_3-CH=O < CH_3-CH=CH=CH=O$ (Dipole moment)



(f) Acidic & Basic strength of organic compounds

(i) Acidity (K_a) $\propto -M$, –I groups.

(ii) Basicity (K,) \propto + M, +H, +I groups and solvation effect in aqueous solution.

8. Electromeric effects

It is a temporary effect. The organic compound having a multiple bond (double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. It is represented by E and the shifting of the electrons is shown by a curved arrow. There are two types of eletromeric effect.

(i) +E effect : In this effect π -electron of the multiple bond are transferred to that atom to which the reagent gets attached.

$$CH_2 = CH_2 \xrightarrow{\oplus} CH_2 - CH_2 - E$$

(ii) – E effect : In this effect the π -electron of the multiple bond are transferred to that atom to which the attacking reagent does not get attached.

Note : When inductive and electromeric effects operate in opposite directions then the electromeric effect dominates.

9. Aromatic character [The Huckel 4n + 2 rule]

(i) **Definition:** Aromatic compounds are characterized by a special stability and that they undergo substitution reactions more easily than addition reactions.

- (ii) Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.
- (iii) Order of stability for prototype structure

Aromatic > Non Aromatic > Anti Aromatic

(iv) Antiaromatic compounds do not exist at room temperature.

	Conditions for Aromaticity	Conditions for Anti-aromaticity			
	Cyclic, planar, conjugated, (4n + 2) πe^{-} [Huckel's Rule]	Cyclic, planar, conjugated, 4nπe ⁻ [Huckel's Rule]			
(v)	n = integer	n = integer			
	2пе-, 6пе-, 10пе-, 14пе-	4πе-, 8πе-, 12πе-, 16πе-			

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Compound		Cyclic	Planar	Conjugated	πe-	Remarks
1.		\checkmark	×	×	2πe⁻	Non aromatic
2.	$\underbrace{\overset{\oplus}{\longrightarrow}}$	\checkmark	\checkmark	\checkmark	2πe⁻	Aromatic
3.		\checkmark	\checkmark	\checkmark	4πe⁻	Anti aromatic
4.		\checkmark	\checkmark	\checkmark	4πe⁻	Anti aromatic
5.	⊕	\checkmark	\checkmark	\checkmark	2πe⁻	Aromatic
6.		\checkmark	\checkmark	\checkmark	6πe⁻	Aromatic
7.		\checkmark	×	×	4πe⁻	Non Aromatic
8.	()	\checkmark	\checkmark	\checkmark	4πe⁻	Anti Aromatic
9.		\checkmark	\checkmark	\checkmark	6πe⁻	Aromatic
10.		\checkmark	\checkmark	\checkmark	6πe⁻	Aromatic
11.		\checkmark	\checkmark	\checkmark	6πe⁻	Aromatic
12.		\checkmark	\checkmark	\checkmark	10πe⁻	Aromatic

13.		\checkmark	✓	\checkmark	6πe⁻	Aromatic
14.	N N	\checkmark	\checkmark	\checkmark	6πе⁻	Aromatic
15.	B H H	\checkmark	\checkmark	\checkmark	4πe⁻	Anti Aromatic
16.	N	\checkmark	\checkmark	\checkmark	6πe⁻	Aromatic
17.	N N H H	√	\checkmark	\checkmark	6πe⁻	Aromatic
18.		\checkmark	\checkmark	\checkmark	6πe⁻	Aromatic
19.		\checkmark	×	×	6πe⁻	Non Aromatic
20.	\bigcirc	\checkmark	\checkmark	\checkmark	6πе⁻	Aromatic



Section (B) : Resonance concepts

B-1. Which of the following compounds have delocalized electrons?

 $(P) CH_2 = CH - C = CH \qquad (Q) CH_2 = C = CH_2 \qquad (R) \checkmark (S) CH_3 - COOH$

- B-2. In which of the following lone-pair indicated is not involved in resonance?
 - (a) $CH_2 = CH \dot{N}H CH_3$ (b) $CH_2 = CH - CH = \dot{O}$ (c) $CH_2 = CH - \dot{O} - CH = CH_2$ (d) $CH_2 = CH - C = N$ (e) \dot{O} \dot{O} \dot{O} (f) \dot{O} \dot{O}

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- B-3. Draw the resonating structures to show the delocalization of electrons in the following compounds/ions.
 - (a) $CH_2 = CH CH_2$ (b) Aniline (c) Phenol (e) R-COOH (f) Nitrobenzene

(d) Chlorobenzene

Section (C) : Stability of Resonance Structures and different species

C-1. In each of the following pairs of resonating structures which resonating structure is more stable?

(a)
$$\begin{bmatrix} CH_3 - \overline{C}H - C \equiv N : \leftrightarrow CH_3 - CH = C = \overline{N} : - \end{bmatrix}$$

(b) $\begin{bmatrix} O & O & O \\ CH_3 - \overline{C} - \overline{C}H - \overline{C} - CH_3 \leftrightarrow CH_3 - \overline{C} = CH - \overline{C} - CH_3 \end{bmatrix}$

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

C-2. Write the stability order of following resonating structures :



C-3. Identify less stable canonical structure in each of the following pairs :



C-4. In the given pair of compounds select the one in each pair having higher resonance energy :

(a)
$$CH_2 = CH - \overset{\Theta}{N}H$$
 and $HN = CH - \overset{\Theta}{N}H$
(b) $\overset{\bullet}{\bigcirc}CH_2$ and $CH_2 = CH - \overset{\bullet}{C}H_2$



C-5. Draw all the significantly contributing resonance structures of pyrrole.



C-6. The guanidinium ion resulting from protonation on the guanidine group is stabilized by the existence of the resonance. Draw two resonance structures B and C.



Section (D) : Mesomeric & SIR Effect

D-1. Arrange the following groups in the increasing order of + M :

(i)
$$- I_{2} - CI_{2} - F_{2} - Br$$
 (ii) $-NH_{2}, -OH, -O^{\Theta}$

D-2. Arrange the following groups in the increasing order of –M :

D-3. How many of the following groups (attached with benzene ring) show + M effect?



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- **D-4.** How many of the following are electron donating groups through resonance when attached with benzene nucleus?
- **D-5.** How many of the following are electron withdrawing groups through resonance when attached with benzene nucleus?

(a)–COOH	(b) – CONHCH ₃	(c) – COCI	(d) – CN
$(e) - O - CH = CH_2$	(f) – CHO	$(g) - SO_2CH_3$	(h)–COO⁻

D-6. Compare the SIR effect between orthochloro benzoic acid, orthobromobenzoic acid and orthoiodo benzoic acid.

Section (E) : Hyperconjugation

- E-1. Define hyperconjugation by taking an example of propene.
- E-2. In which molecule or ion hyperconjugation effect is observed and write the number of hyperconjugable hydrogen atoms?



E-3. Write decreasing order of stability of following alkene.



Section (F) : Concept of Aromaticity

- F-1. What is aromaticity?
- F-2. Why cyclooctatetraene is nonplanar?

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F-3 Write down the number of π -electrons in each of the compounds shown below.







Section (G) : Applications of electronic effect

G-1. The correct decreasing order of electron density in aromatic ring of following compounds is :



G-2. Correct dipole moment order is



G-3. Compare the C–N bond-length in the following species:



G-4 Which of the following two compounds would you expect to have a greater dipole moment ? Support your answer by writing the corresponding (plausible) resonance structures.



PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Inductive effect

- A-1. Inductive effect involves : (A) Delocalisation of σ -electrons.
 - (C) Delocalisation of π -electrons.
- (B) Partial displacement of σ -electrons.
- (D) Displacement of lone pair electrons.
- A-2. Select correct statement about I- effect?
 - (A) I effect transfers electrons from one carbon atom to another.
 - (B) I effect is the polarisation of σ bond electrons.
 - (C) I effect creates net charge in the molecule.
 - (D) I effect is distance independent.

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- A-3. Which of the following is false order of - I effect?
 - (A) -F > -CI > -Br > -I
 - (C) $-F > -OH > -NH_{2}$

A-5. Which of the following is the strongest - I group?

$$(A) - \overset{+}{N}(CH_3)_3$$
 $(B) - \overset{+}{N}H_3$ $(C) - \overset{+}{S}(CH_3)_2$ $(D) - F$

A-6. Which of the following orbital overlaps is involved in the formation of the carbon-carbon single bond in the molecule $HC \equiv C - CH = CH_2$? (B) $sp^2 - sp^3$

(A)
$$sp^3 - sp^3$$

(C) sp - sp^2

- (D) sp³ sp
- A-7. Which of the following has incorrect direction of Inductive effect?





$$(D) CH_{3} \stackrel{\bullet}{\leftarrow} CH_{2} \stackrel{\bullet}{\rightarrow} CH_{2} \stackrel{\bullet}{\rightarrow} CH_{3}$$

Section (B) : Resonance Concepts

B-1. Resonance effect is delocalisation of ? (A) π electrons (B) σ electrons

(C) $\sigma - \pi$ electrons

(B) $-NR_3 > -NH_3 > -NO_2$

> --C = CH > --H

(D) None

- B-2. Resonance involves :
 - (A) Delocalization of π -electrons along a conjugated system.
 - (B) Delocalization of lone pair along a conjugated system.
 - (C) Delocalization of negative charge along a conjugated system.
 - (D) All are correct.
- B-3. Which of the following statement is incorrect?
 - (A) Resonating structures 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.
- B-4. Resonance structure of the molecule does not have
 - (A) higher energy than their hybrid structure.
 - (B) identical arrangement of atoms.
 - (C) the same number of paired electrons.
 - (D) always equal contribution to the resonance hybrid.
- In which of the following delocalisation of π -electron is possible? B-5. (A) CH = CH - CHപ്പറ (B)CH = CH CH = O

(C)
$$CH_3 - CH - CH_3$$

 $H_3 - CH - CH_3$
 $H_3 -$

B-6. Which of the following compounds have delocalisation of π -electrons?



B-13. In which of the following resonance is not possible? (A) $CH_2 = C = CH_2$ (B) $CH_2 = C = CH^{\odot}$ (C) $CH_2 = C = CH^{\odot}$ (D) $CH_2 = C = CH^{\odot}$

General Organic Chemistry-1

Section (C) : Stability of Resonating Structures and different species

C-1. Which one of the following is least stable resonating structure ?

C-2. Which of the following resonating structure is the least contributing structure ?

$$(A) \xrightarrow{O^{\ominus}} (B) \xrightarrow{\ominus} (C) \xrightarrow{\oplus} (D) \xrightarrow{O^{\ominus}} (D) \xrightarrow{\oplus} (D)$$

C-3. Arrange the following resonating structure according to their contribution towards resonance hybrid?

(a)
$$CH_2 = \overset{\oplus}{N} = \overset{\Theta}{N}$$
 (b) $\overset{\Theta}{CH}_2 - N = \overset{\oplus}{N}$ (c) $\overset{\oplus}{CH}_2 - \overset{\Theta}{N} = \overset{\Theta}{N}$ (d) $\overset{\Theta}{CH}_2 - \overset{\oplus}{N} = \overset{\bullet}{N}$
(A) $a > d > c > b$ (B) $b > a > c > d$ (C) $a > c > b > d$ (D) $d > a > b > c$

C-4. Formic acid is considered as a hybrid of the four structures.

C-5. HNCO (isocyanic acid) has following resonating structures :

$$\begin{array}{cccc} H-N=C=O & \longleftrightarrow & H-\overset{\odot}{N}-C=\overset{\odot}{O} & \longleftrightarrow & H-\overset{\odot}{N}=C-\overset{\odot}{O} \\ II & III & III \end{array}$$
The order of stability is :
$$(A) \ | > |I| > |I| & (B) \ | > |I| > |I| & (C) \ |I > |I| > | (D) \ |I > | > |I| \end{array}$$

C-6. The correct stability order of the following resonating structures is :

$$\begin{array}{cccc} CH_2 = C = O & H_2\bar{C} - \bar{C} = O & H_2C = \bar{C} - \bar{O} & H_2\bar{C} - C \equiv \bar{O} \\ (I) & (II) & (III) & (IV) \\ (A) (IV) > (I) > (III) > (II) & (B) (II) > (IV) > (I) > (III) \\ (C) (III) > (IV) > (I) & (D) (I) > (IV) > (III) > (III) \\ \end{array}$$

C-7. Which is the most stable resonating structure ?

C-8. Which of the following is incorrect for stability of structures?

General Organic Chemistry-1



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(D) σ -and p - orbitals

D-9. A Maximum extent of steric inhibition of resonance can be expected in



D-10. Select the correct statement about this compound.



(A) All three C–N bond length are same.

- (B) C_1 -N and C_3 -N bonds length are same but shorter than C_5 -N bond length.
- (C) $C_1 N$ and $C_5 N$ bonds length are same but longer than $C_3 N$ bond length.
- (D) C_1 -N and C_3 -N bonds length are different but both are longer than C_5 -N bond length.

Section (E) : Hyperconjugation

- **E-1.** In hyperconjugation there is overlap between : (A) p- and π -orbitals (B) 2π -orbitals (C) d-and- π -orbital
- **E-2.** Which of the following group has the maximum hyperconjugation effect when attached to be energine ring? (A) CH_3 - (B) CH_3CH_2 - (C) $(CH_3)_2CH$ - (D) $(CH_3)_3C$ -
- E-3. Which of the following cannot exhibit hyperconjugation?

(A)
$$CH_3 CH_2$$
 (B) $CH_3 CH_3 CH_3 CH_3$ (C) $CH_3 CH = CH_2$ (D) $(CH_3)_3 C - CH_2$

E-4. Arrange the stability of following alkenes.



E-5. Which one of the following dienes would you expect to be the most stable?







E-6. Which of the following has the most negative heat of hydrogenation?







E-7. Which one of the following has inductive, mesomeric and hyperconjugation effect?

(A)
$$CH_{3}CI$$
 (B) $CH_{3} - CH = CH_{2}$ (C) $CH_{3}CH = CH - C - CH_{3}$ (D) $CH_{2} = CH - CH = CH_{2}$

F-3.

Section (F) : Concept of Aromaticity

F-1. Which out of the following is an aromatic hydrocarbon?









F-2. Which species is not an aromatic ?



Which of the following is non-aromatic?





(A) (B)





F-4. Identify the aromatic compound?



- **F-5.** Aromatic compounds burn with sooty flame because :
 - (A) They have a ring structure of carbon atoms.
 - (B) They have a relatively high percentage of hydrogen.
 - (C) They resist reaction with oxygen of air.
 - (D) They have a relatively high percentage of carbon.

Section (G) : Applications of electronic effect

G-1. The decreasing order of electron density in the ring is :



G-2. In which of the following molecules π – electron density in ring is minimum ?



(D) |V > | > || > |||

G-3. Correct dipole moment order is



G-8. Stability of π -bond in following alkenes in the increasing order is :

(B) ||| > | > || > |V

(A) || > | > |V > |||

(C) |V > || > | > ||

G-9.If Heat of hydrogenation of 1-butene is 30 Kcal/mol then heat of hydrogenation of 1,3-butadiene is ?(A) < 60</td>(B) 60(C) > 60(D) < 30</td>

PART - III : MATCH THE COLUMN

1. Match the column I with column II.

Column-I

(Group attached with benzene ring)

- (B) —O
- (C) __O__CH₃
- (D) $-C \equiv N$
- 2. Match the following Coulmn - I

(C)

(D)

(Compounds)



ŇΟ,

Cl

Column-II

(Effect shown by the group)

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

Coulmn - II (Characteristics)

- (p) Mesomeric effect / resonance
- (q) Inductive effect.
- (r) Hyperconjugative effect
- (s) Nonpolar
- (t) Polar
- 3. Alkenes and alkynes are collectively referred to as unsaturated compounds, as they contain less hydrogen atoms compared to the corresponding alkanes. Alkenes are also called olefins. a term derived from oleflant gas, meaning oil forming gas. This term originated due to the oily appearance of alkene derivatives. Compared to alkenes, alkynes are not so common in nature, but some plants use alkynes to protect themselves against diseases or predators.

Heats of Hydrogenation indicates the relative stability of alkenes match the list of compounds given in column A with the corresponding heats of hydrogenation listed in column-B.

Column-A	Column-B (kcal mol⁻¹)
(A) CH ₂ = CHCH ₂ CH= CH ₂	(p)-226
(B) CH ₃ -CH=C=ČH-CH ₃	(q)—119
(C) CH_3 $H_2=C-CH_2-CH_3$	(r) <i>—</i> 295
ĊН³	
(D) I CH ₃ -C=CH-CH ₃	(s) –252
(E) CH ₂ =CH–CH=CH–CH ₃	(t) – 113



2. The most stable canonical structure of the given molecule is

(B)



(A)





3. The most unlikely representation of resonance structures of p-nitrophenoxide ion is:



4. In which of the following delocalisation of positive charge is possible?



General Organic Chemistry-1

5. The Decreasing order of potential energy of the following cations is :



6. Stability order of the following species is ?



7. In which of the following first resonating structure is more stable than the second ?

(A)
$$\overrightarrow{CH}_2 - CH = O \leftrightarrow CH_2 = CH - O^{\ominus}$$

(B) $\overrightarrow{CH}_2 - O - CH_3 \leftrightarrow CH_2 = O - CH_3$
(C) $CH_2 = CH - NH_2 \leftrightarrow \overrightarrow{CH}_2 - CH = NH_2$
(D) $\overrightarrow{O} - CH = CH_2 \leftrightarrow O = CH - CH_2$

8. Which of the following statement is correct?

(A) In the dianion (A), all the C–C bonds are of same length but C–O bonds are of different length.

- (B) In the dianion, all C–C bonds are of same length and also all C–O bonds are of same lengths.
- (C) In the dianion, all C–C bond lengths are not of same length.
- (D) None of the above.
- 9. Which of the following is correct about the following compound?



(Naphthalene)

(A) All the C-C bond length are same

- (B) $C_1 C_2$ bond length is shorter than $C_2 C_3$ bond length
- (C) $C_1 C_2$ bond length is greater than $C_2 C_3$ bond length
- (D) All the C-C bond length are equal to C-C bond length of benzene
- 10. The correct order of +M effect of 'N' containing functional group on benzene ring, amongst the given compounds is



General Organic Chemistry-1

- 11. In which case the σ -bond pair and π bond pair of electrons both are attracted in the same direction, (towards same atom.)? (B) CH₃-CH₂-H-CH=O
 - $(A) H_2C=CH-CI$

$$-NH_2$$
 (C) $H_2C=C$

$$(D) H_2C = CH - OCH_3$$

(D) w

12. The longest C - N bond length in the given compound is :

(B) y



(C) z

(A) x

13. A Select the correct order of heat of hydrogenation?



14. If the given compound is planar then select the correct statement.



- (A) The boron is sp² hybridized and the p-orbital contains an unshared pair of electron
- (B) The boron is sp² hybridized and a hybrid orbital contains an unshared pair of electron.
- (C) The boron in sp² hybridized and hybrid orbital is vacant
- (D) The boron is sp² hybridized and the p-orbital is vacant

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1.2 Among the given pairs, how many of the following do not represent the canonical structures?

(i)
$$H-C=\overset{\oplus}{N}-\overset{\ominus}{O}$$
 and $H-O-C=N$
(ii) $H-\overset{\oplus}{O}=C=\overset{\oplus}{N}$ and $H-O-C=N$
(iii) $H-\overset{\oplus}{O}=C=\overset{\oplus}{N}$ and $H-O-C=N$
(iii) $H-C=\overset{\oplus}{N}-\overset{\ominus}{O}$ and $H-N=C=O$
(iv) $H-O-C=N$ and $H-N=C=O$
(v) $\overset{\oplus}{C}H_2-CH=O$ and $CH_2=CH-\overset{\oplus}{O}$
(vi) $CH_2=CH-NH_2$ and $\overset{\ominus}{C}H_2-CH=\overset{\oplus}{N}H_2$
(vii) $CH_3-\overset{\ominus}{C}-CH_3$ and $\overset{OH}{L}_{L_2=C-CH_3}$

General Organic Chemistry-1

2. How many of the following species can show resonance?



3. How many groups (attached with benzene ring) can show +M effect?



4. Identify the number of compounds in which positive charge is delocalised ?



5. In how many of the following cases, the negative charge is delocalised?



General Organic Chemistry-1

6. In how many of the following compounds hyperconjugation effect is observed ?



8. Find the number of carbon atoms including the given structure which have negative charge due to resonance effect. (The structure with charge separation is not accepted)

$$HC \equiv C - C - CH = C = CH_2$$

9. Find the total number of positions where positive charge can be delocalized by true resonance?

$$\begin{array}{c} CH_2 \\ \oplus \\ CH_3 - CH - CH = CH - C - \end{array}$$
 (Excluding the given position)

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

- 1. Which statement is/are true about resonance?
 - (A) It decreases the energy of system.
 - (B) The hybridisation of atoms do not change due to resonance.
 - (C) Resonance hybrid is more stable than any other resonance structure.
 - (D) Resonance structures can not be isolated at any temperature.
- 2. Which of the following statement is incorrect about resonance?
 - (A) The most stable structure explains all the characteristics of a species.
 - (B) All resonating structures remain in equilibrium.
 - (C) Resonance hybrid has maximum similarity with most stable resonating structure.
 - (D) Resonance hybrid is real.
- **3.** In which of the following pairs of compounds, second structure have more contribution to resonance hybrid than first ?



4. In which of the following pairs of resonating structures first resonating structure is more stable than second?

⊕.









General Organic Chemistry-1



(D) s > p > q > r

PART - IV : COMPREHENSION

Comprehension # 1

Hydrogenation of unsaturated hydrocarbons is an exothermic reaction. Due to hyperconjugation and resonance the stability of unsaturated hydrocarbon increases and the increase in stability is more due to resonance. Compound with same number of π -bonds and more stability has lower heat of hydrogenation. Heat of formation is defined as the energy evolved when a molecule is formed from its atoms. For isomers the more stable compound has higher heat of formation.

1. The correct heat of hydrogenation order is :

(p) 1, 3-Pentadiene		(a) 1, 3-Butadiene
(r) 2, 3-Dimethyl-1, 3-	butadiene	(s) Propadiene
(A) p > q > r > s	(B) s > q > p > r	(Ć) q > s > p > r

2. The order of heat of formation of the following molecules is ?



Comprehension # 2

Cyclooctatetraene and Aromaticity : The chemists in the early 1900s believed that the only requirement of aromaticity was the presence of a cyclic conjugated system. Cyclooctatetraene. **(A)** defied this assumption. It was first prepared by German chemist Richard Willstater in 1911 and found to resemble an open chain polyene !

Aromatic compounds

In 1825, Michael Faraday isolated benzene for the first time from the oily mixture that condensed from illuminating gas (the fuel burnt in gas lights) Subsequently many compounds related to benzene were discovered. These compounds had typical odours (aroma) and hence this group of compounds was called aromatic.

As per Hukel's rule of aromaticity, a cyclic compound is aromatic if it is conjugated, planar and has $(4n+2)\pi$ electrons, where , n is a positive integer, including zero. Similar compounds possessing $(4n)\pi$ electrons are highly unstable are called antiaromatic compounds. It is interesting that compounds adjust their 3D and electronic structures to lower energies.

Non-Benzoid aromatic system :

Since the discovery of benzene, a lot of compounds have been identified that behave similarly. They all have some common features. According to Huckel's rule, an aromatic system must have the following properties: * cvclic

- * fully conjugated
- * planar

4.

5.

- * (4n + 2) π electrons
- 3. Which of the following is/are an aromatic compound?





9. The total number of contributing structures showing hyperconjugation (involving C–H bonds) for the following carbocation is [JEE-11, 4/180]



10.* Which of the following molecules, in pure form, is (are) unstable at room temperature? [JEE-12, 4/136]



11. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to

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

(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.

12. The number of resonance structures for N is

[JEE(Advanced)-2015, 4/168]

[JEE(Advanced)-2013, 4/120]

OH NaOH N

13. Among the following, the number of aromatic compound(s) is

[JEE(Advanced)-2017, 3/122]



PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. In the following benzyl/allyl system

$$R - CH = CH_2$$
 and $\swarrow R$

(R is alkyl group)

The decreasing order of inductive effect is :

 $(1) (CH_3)_3 C \longrightarrow (CH_3)_2 CH \longrightarrow CH_3 CH_2 \longrightarrow (2) CH_3 CH_2 \longrightarrow (CH_3)_2 CH \longrightarrow (CH_3)_3 CH_2 \longrightarrow (CH_3)_2 CH_2 \longrightarrow (CH_3)_3 CH_2 \longrightarrow (CH_3)_3 CH_2 \longrightarrow (CH_3)_2 \longrightarrow (CH_3)_2 CH_2 \longrightarrow (CH_3)_2 \longrightarrow (CH_3)_2 \longrightarrow (CH_3)_2 \longrightarrow (CH_3)_2 \longrightarrow (CH_3)_2 \longrightarrow$

- In HCOO⁻, the two carbon-oxygen bonds are found to be of equal length. What is the reason for this ? 2_. (1) The anion is obtained by the removal of a proton from the acid molecule. [AIEEE-2003, 3/105]
 - (2) Electronic orbitals of carbon atoms are hybridised.
 - (3) The C=O bond is weaker than C-O bond.
 - (4) The anion HCOO⁻ has two equally stable resonating structures.
- 3. For which of the following molecule singnificant $\mu \neq 0$?



4. Which of the following molecules is least resonance stabilized?

(1)



5. Wheih of the following compound is not aromatic ? [JEE (Main)- 2019 Online (09-01-19), 4/120]



6. Whcih compound(s) out of the following is/are not aromatic?

[JEE (Main)- 2019 Online (11-01-19), 4/120]



[AIEEE-2002]

[JEE (Main)- 2014, 4/120]

[JEE (Main)- 2017, 4/120]



(S) || > |

- **C-1.** (a) II ; (b) II ; (c) II
- **C-2.** (P) I > II ; (Q) II > I ;
- C-3. a-I, b-II, c-II, d-I, e-I, f-I, g-II
- **C-4.** (a)-II, (b)-I, (c)-II, (d)-I



- **D-3**. 6
- **D-4.** c, f, g, h
- **D-5.** a, b, c, d, f, g, h

D-6. SIR effect increases with the size of ortho group. The order of SIR effect is o-iodo benzoic acid > o-bromo benzoic acid > o-chloro benzoic acid.

E-1. It is delocalisation of sigma electron with p-orbital. It may take place in alkenes, alkynes, carbocations, free radicals, alkyl benzene.

Necessary Condition : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, benzene nucleus.

(R) | > ||;

	H Propene H ₂ C III	$\stackrel{\text{\tiny \widehat{H}}}{\underset{\text{\tiny Π}}{\overset{\text{\tiny \widehat{H}}}{\underset{\text{\tiny Π}}{\overset{\text{\tiny \widehat{H}}}{\underset{\text{\tiny Π}}{\overset{\text{\tiny \widehat{H}}}{\underset{\text{\tiny Π}}{\overset{\text{\tiny }}}{\overset{\text{\tiny Π}}{\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{\tiny Π}}{\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{\tiny Π}}{\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{\tiny }}{\overset{\text{\tiny }}}\overset{\text{\tiny }}{\overset{\text{\tiny }}}\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{\tiny }}}{\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{\tiny }}}{\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{\tiny }}}{\overset{\text{\tiny }}}{\overset{\text{\tiny }}}{\overset{\text{\tiny }}}{\overset{ }}}\overset{\text{\tiny }}}{\overset{\text{\tiny }}}\overset{\text{ }}}{\overset{ }}}\overset{\text{ }}}{\overset{ }}\overset{\text{\tiny }}}{\overset{ }}\overset{ }}}\overset{\text{ }}}{\overset{ }}\overset{ }}}\overset{ &}\overset{ }}}\overset{ &}}\overset{ &}}\overset{ &}\overset{ }}&\overset{ &}\overset{ &}}\overset{ &}}\overset{ &}}\overset{&}}\overset{&}}\overset{&}}\overset{&}}\overset{&}\overset{&}}\overset{&}}\overset{&}}\overset{&}&$	$C=CH - CH_2$ II I	
E-2.	(a)0	(b) 2	(c) 0	(d) No hyperconjugation
	(e)0	(f) 0	(g) 6	(h) 9
	(i) 3	(j) 10	(k) 0	(I) 10

- **E-3.** (i) a > b (ii) a > b ; (iii) b > a
- F-1. Those molecules are aromatic which have very high resonance energy. Only those molecules has sufficiently high amount of resonance energy to become aromatic which
 - (a) are cyclic
 - (b) are planar
 - (c) contains (4n +2) number of π -electrons in ring.
 - (d) must have cyclic resonance between (4n + 2) number of π-electrons Where n = 0,1,2,3,4
- F-2. Cyclooctatetraene is nonplanar to avoid its anti aromaticity and it becomes tub-shaped structure.



Charge separation is more favourable in compound (b), because there is one mesomeric resonance structure in which both rings are formally aromatic according to Hucke's rule. In all other resonance structures at least one of the rings is formally antiaromatic ($4n \pi$ -electrons). Hence, compound (b) resemble electronically a cycloheptatrienyl cation fused to a cyclopentadiene anion and therefore possesses a large dipole moment.

PART - II

A-1. B-1. B-8.	(B) (A) (C)	A-2. B-2. B-9.	(B) (D) (B)	A-3. B-3. B-10.	(D) (A) (A)	A-4. B-4. B-11.	(B) (D) (D)	A-5. B-5. B-12.	(A) (B) (B)	A-6. B-6. B-13.	(C) (B) (A)	A-7. B-7. C-1.	(D) (D) (C)
C-2.	(B)	C-3.	(A)	C-4.	(A)	C-5.	(A)	C-6.	(D)	C-7.	(B)	C-8.	(A)
C-9.	(C)	C-10.	(D)	D-1.	(C)	D-2.	(A)	D-3.	(D)	D-4.	(B)	D-5.	(B)
D-6.	(D)	D-7.	(D)	D-8.	(D)	D-9.	(C)	D-10.	(C)	E-1.	(D)	E-2.	(A)
E-3.	(D)	E-4.	(C)	E-5.	(C)	E-6.	(A)	E-7.	(C)	F-1.	(C)	F-2.	(B)
F-3.	(A)	F-4.	(B)	F-5.	(D)	G-1.	(A)	G-2.	(D)	G-3.	(B)	G-4.	(D)
G-5.	(C)	G-6.	(D)	G-7.	(B)	G-8.	(A)	G-9.	(A)				

PART - III

- 1. (A)–P,S ; (B)–Q,R ; (C)–Q,S ; (D)–P,S
- **2.** (A) p,q,r,t ; (B) p,q,r,t ; (C) p,q,r,t ; (D) p,q,s
- **3.** (A s); (B r); (C p); (D q); (E t)

EXERCISE # 2													
PART - I													
1. 8.	(D) (B)	2. 9.	(B) (B)	3. 10.	(C) (C)	4. 11.	(D) (C)	5. 12.	(A) (D)	6. 13.	(A) (B)	7. 14.	(C) (D)
	()					PAF	RT - II						()
1.	5 (i, iii,	iv, v, vii)		2.	8 (ii, iii	, iv, vi, v	ii, viii, ix,	xi)		3.	5 (i, ii,	v, vi, ix)	1
4. 7.	5 (i, iii, 6 (i, iv,	v, vi, vii) v, vi, vii,	x)	5. 8.	5 (i, ii, 6	iv, vi, ix)			6. 9.	3 (B, 0 2	C & G).	
						PAF	RT - III						
1. 6.	(ABCD (ABD))	2. 7.	(AB) (ABC)		3. 8.	(ABC) (BD)		4. 9.	(BC) (AD)		5.	(BC)
	PART - IV												
1.	(B)		2.	(C)		3.	(A)		4.	(B)		5.	(C)
	EXERCISE # 3												
						PA	RT - I						
	СН⊳	~ ~	CH₂										
1.	َ ۳	рн ОН											
									æ				
2.	7-brom	10-1, 3, 5	-cyclohe	eptatrien	e on ioni	sation g	ives tropy	ylium io	on 🚺	which is	aromat	ic & high	ly stable,
											€		
	but ioni	sation of	5-brom	o-1, 3-cyc	lopenta	diene giv	ves 1, 3-c	yclope	ntadienyl	cation \\	_// whi	ch is anti	aromatic
_	& UNSta	able. (no	nexiste	nt)							.		
3.	(A) In the is finished stable.	ne forma ned and	tion of fi the proc	rst produ luct becc	ct the an omes mo	itiaroma ore stabl	e.While i	to the p in 2nd (case the p	of three " product is	s thermo	ngs of the odynami	e reactant cally less
4. 9.	(A) 6		5. 10.	(A) (BC)		6. 11.	(B) (A)		7. 12.	(B) 9	8. 13.	(D) 5 (1,3	,6,8,9)
				·		ΡΔΓ	ЯТ - II					-	
1.	(1)	2.	(4)		3.	(4)		4.	(4)		5.	(1)	
6.	(2)												

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART-1: PAPER JEE (MAIN) PATTERN

SECTION-I: (Maximum Marks: 80)

- This section contains **TWENTY** questions.
- Each question has FOUR options (A), (B), (C) and (D). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in <u>one of the following categories</u>:
 Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
 Zero Marks : 0 If none of the bubbles is darkened.
 Negative Marks : -1 In all other cases
- 1_. Select the correct statement regarding the following compounds :



(A) II has a greater dipole moment than I (C) I is more soluble in polar solvent than II

(B) Covalent character of II is less than I (D) None of these

2. Select the correct option related to stability of following structures.









3_. The minimum magnitude of heat of hydrogenation per mole of molecule is -



4. The decreasing order of electron density on the ring is :



General Organic Chemistry-1

11_. Resonance stabilized cation is :









Squaric acid dianion has :

(A) 4-identical resonating structures

- (B) C-C bond length is equal to C-O bond length
- (C) 3 nonidentical resonating structures
- (D) Localised negative charged on oxygen
- 13_. Which of the following benzene ring has greater electron density than toluene?



14_. Compare C-N bond length in the following



(C) ||| > || > |

(C



(D)

(D)

Among the following aromatic compound is 15.





16_. Which is not stable at room temperature ?



All the carbon-carbon bond lengths are equal in 17.

 $(A) CH_2 = C = C = CH_2$





- 18_. The kind of delocalization involving sigma bond orbitals is called (A) Inductive effect (B) Hyperconjugation effect (C) Electromeric effect (D) Mesomeric effect

19. Which of the following compound(s) is/are an aromatic compounds?



• For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, -0.33, -.30, 30.27, - 127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

For Example : If answer is -77.25, 5.2 then fill the bubbles as follows.

- Answer to each question will be evaluated according to the following marking scheme:
 Full Marks : +4 If ONLY the correct numerical value is entered as answer.
- **21.** Total number of α -hydrogen atoms in given compound is :



- 22. How many resonance structures are there for anthracene?
- 23. Use the following data to answer the question below.



Calculate the resonance energy of anthracene :

- In the molecule CH₃C=CCH=CH₂, the maximum number of carbon atoms arranged linearly is? 24.
- 25. Observe the following compound and write the number of hydrogen atom involved in hyperconjugation.



PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains FOUR questions.
- Each question has FOUR options (A), (B), (C) and (D). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories : If only the bubble corresponding to the correct option is darkened. Full Marks +3 Zero Marks 0 If none of the bubbles is darkened. Negative Marks : -1 In all other cases
- 1._ Which of the following resonating structure of 1-Methoxy-1,3-butadiene is most stable?

(A)
$$\overset{\Theta}{C}H_2 - CH = CH - CH = \overset{\Theta}{O} - CH_3$$

(B)
$$CH_2 = CH - \overset{\Theta}{C}H - CH = \overset{\Theta}{O} - CH_3$$

(C)
$$CH_2 = CH - CH - CH - CH - O - CH_3$$

(D)
$$CH_2 = CH - \overset{\Theta}{C}H - \overset{\Theta}{C}H - O - CH_3$$

2._ Which of the following has shortest C-Cl bond?

(A) CH₃-Cl

(D) CH₂=CH–CH=CH–CI

3.

The most stable canonical structure of this molecule is :



4._

SECTION-II: (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has FOUR options for correct answer(s). ONE OR MORE THAN ONE of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	:	+4	If only (all) the correct option(s) is (are) chosen.
Partial Marks	:	+3	If all the four options are correct but ONLY three options are chosen.
Partial Marks	:	+2	If three or more options are correct but ONLY two options are chosen,
		both of	which are correct options.
Partial Marks	:	+1	If two or more options are correct but ONLY one option is chosen
		and it	is a correct option.
Zero Marks	:	0	If none of the options is chosen (i.e. the question is unanswered).

- *Negative Marks* : -1 In all other cases.
- For Example : If first, third and fourth are the ONLY three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), with result in +1 marks. Selecting any incorrect option(s) (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in −1 marks.
- 5._ In which of the following pairs both have same dipole moment?

6._ Which is/are the correct order of electron density in aromatic ring?

7._ In which cases delocalisation of charge is possible?

(A)
$$\overset{\Theta}{O} - \overset{\oplus}{N} \overset{CH_3}{\underset{CH_3}{\leftarrow}}$$
 (B) $\overset{\Theta}{O} - P(CH_3)_2$ (C) $\overset{\Theta}{O} - P(CH_3)_3$ (D) $\overset{\Theta}{O} - B(CH_3)_2$

8._ The acceptable resonating structure(s) of the following molecule is/are :

Among these canonical structures of pyridine, the correct order of stability is/are :

(A) (II = IV) > (I = V)(B) (I = V) > (II = IV) $(C) \parallel l \geq (l = l \vee)$ (D)(II = IV) > III

10._ Which of the following statement is/are correct?

(A) Contributing structures contributing to the resonance hybrid is directly proportional of their energies.

- (B) Equivalent contributing structures make the resonance very important.
- (C) Contributing structures represent hypothetical molecules having no real existance.
- (D) Contributing structures are less stable than the resonance hybrid.
- 11. In which of the following pairs first one is having less resonance energy than the second one ?

12. The correct orders for bond length are?

SECTION-III : (Maximum Marks: 18)

- This section contains SIX questions.
- The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the second decimal place; e.g. 6.25, 7.00, -0.33, -.30, 30.27, -127.30, if answer is 11.36777.... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.
 For Example : If answer is -77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:
 Full Marks : +3 If ONLY the correct numerical value is entered as answer.
 Zero Marks : 0 In all other cases.
- 13. Find total number of the atoms where positive charge can be delocalized by true resonance?

(Excluding the given position)

14. Find the number of carbon atoms including the given structure which can have negative charge in resonating structures. (The structures with charge separation are not accptable)

15. How many species out of the following are aromatic?

How many of the following molecules are antiaromatic? 16.2

17. Number of π electrons in resonance in the following structure is?

(m)

How many of the following are antiaromatic compounds? 18.๖

JEE (Adv.)-Chemistry **General Organic Chemistry-1** 8. Identity the aromatic compound from the following. [NSEC-2005] (B) (D) [9. Which of the following species is aromatic? [NSEC-2006] (B) (C)(D) 10. Following is an example of [NSEC-2006] $CH_{2} = CH - CH \leftrightarrow CH_{2} - CH = C - H \leftrightarrow CH_{2} = CH - CH - CH = C - H$ (A) hyperconjugation (B) tautomerism (C) resonance (D) inductive effect. 11. The number of π electrons required for a planar cyclic conjugated system to exhibit aromatic behaviour is $(4n + 2)\pi$. Here n is [NSEC-2006] (A) number of C atoms in the system (B) number of π bonds (C) a non negative integer (D) number of bonds in the system 12. The carbonation $(CH_3)_3C^+$ is stabilized primarily by : [NSEC-2007] (A) hyperconjugation (B) tautomerism (C) resonance (D) conjugation 13. Identify the odd species out (Which of the species among the following is different from others ?) [NSEC-2007] (A) (B) (C (D) 14. The correct order of dipole moment for the following molecules is [NSEC-2011] OН CH. NO₂ CI CH₃ (III)(I) (II)(B) I < II < III (A) I = II = III(C) I > II > III(D) II < III < I 15. The order of decreasing stability is : [NSEC-2011] (II)(III) (IV)(I)

(A) |V > | > || > |||

(B) | > IV > III > II

(C) | > || > |V > |||

 $(\mathsf{D}) |\mathsf{V} > \mathsf{I} > \mathsf{I} > \mathsf{II}$

General Organic Chemistry-1

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1.	(C)	2.	(C)	3.	(D)	4.	(C)	5.	(D)	6.	(B)	7.	(B)
8.	(A)	9.	(C)	10.	(B)	11.	(C)	12.	(A)	13.	(C)	14.	(A)
15.	(C)	16.	(C)	17.	(B)	18.	(B)	19.	(D)	20.	(B)		
						SEC	ΓΙΟΝ-	П					
21.	6	22.	4	23.	84 kca	ıl / mol		24.	5		25.	9	
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SECTION- I													
						♥		-					
1.	(B)	2.	(C)	3.	(C)	4.	(C)						
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5. 12.	(ACD) (ABD)	6.	(ABC)	7.	(BCD)	8.	(AB)	9.	(BD)	10.	(BCD)	11.	(ABD)
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13.	10		14.	7		15.	5 (i, ii,	iv, vii, vi	iii)				
16.	3												
	Aroma	tic – a,	c, g, h, i	, j, k.	,	Antiar	omatic -	- b, d, e	;	Nona	romatic –	f	
17.	8		18.	4									
						PAF	रT - 3						
1.	(D)	2.	(B)	3.	(A)	4.	(C)	5.	(A)	6.	(C)	7.	(B)
8.	(A)	9.	(B)	10.	(C)	11.	(C)	12.	(A)	13.	(B)	14.	(C)
15.	(A)	16.	(B)	17.	(A)	18.	(D)	19.	(D)	20.	(D)	21.	(B)

RRP SOLUTIONS

PART-1

SECTION-I

both rings are aromatic so, it will be polar in nature.

8.

 $N \rightarrow sp^{3}$

sp³, N-atom, nonpolar molecule so, it will be non-aromatic.

10. Heat of hydrogenation $\propto \frac{1}{\text{stabilityof alkene}}$.

(III & IV have both resonance and hyperconjugation where as I and II have only hyperconjugation.)

- 14. C–N bond length \downarrow by increasing extent of delocalisation of π -electrons.
- 16. Anti aromatic compounds are unstable at room temperature.

SECTION-II

PART 2

SECTION- I

3.

 $\stackrel{\oplus}{\cdot N} \equiv N$ is aromatic and has complete octet of all atoms.

SECTION-II

- 8. A & B are proper resonating structures while C & D violate octet rule.
- 12. Due to hyperconjugation, bond length decreases for a single bond and increases for a double bonds.

SECTION-III

The negative charge is delocalised on the marked carbon atoms (1 - 7).

15. Aromatic species are :

- **16.** Aromatic \rightarrow cyclic, planar, conjugated system having $(4n + 2) \pi$ electrons. Antiaromatic \rightarrow cyclic, planar, conjugated system having $4n \pi$ electrons.
- **18.** Aromatic : (a), (b), (c), (d), (e), (f), (h), (l), (n) Antiaromatic : (g), (i), (j), (m) Nonaromatic : (k)

PART - 3

14. High dipole moment of (I) is due to ionic structure of resonating form.

- 15. Benzene is most stable as it is aromatic, I and II are more stable than III because of conjugation.
- 16. Only I follows Huckel's rule and aromatic.
- 17. It has more alpha H, hence more stabilized by hyperconjugation.
- **18.** (D)
- 19. -ve charge is never delocalized on the meta positon.

20.

It is non aromatic since in tub shape it is non-planar

21.
$$F = 2.42$$
; $F = 0$; $F = 0$; $F = 1.3$