

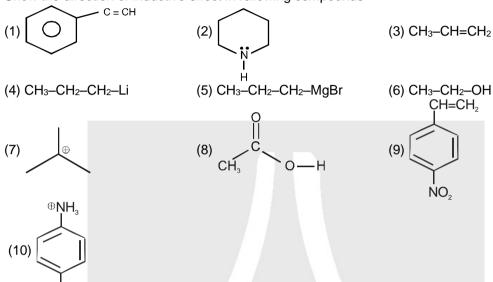
# **Exercise-1**

Marked guestions are recommended for Revision.

# **PART - I: SUBJECTIVE QUESTIONS**

#### Section (A): Inductive effect

A-1. Show the direction of inductive effect in following compounds



# Section (B): Resonance Concepts, Conditions, Resonating Structures & Conjugation

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

(P) 
$$CH_2 = CHCCH_3$$
 (Q) (R) (S)  $CH_3CH_2NHCH=CHCH_3$ 

B-2. Number of  $\pi$  electrons in resonance in the following structure is.

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

C-1. In the following sets of resonating structure, label the major and minor contributors towards resonance hybrid.

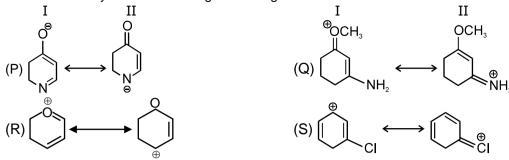
(P) 
$$CH_3$$
- $CH$ - $C\equiv N \leftrightarrow CH_3$ - $CH$ = $C=\stackrel{\bullet}{N}$ :
(I) (II)

(Q) 
$$CH_3 - \overrightarrow{C}H - CH = CH - NO_2 \leftrightarrow CH_3 - CH = CH - CH = \overrightarrow{N} - \overrightarrow{O}$$
(II)
(II)
 $O = O = O$ 

(R) 
$$CH_3-CH_2-\overset{\oplus}{C}-NH_2 \leftrightarrow \overset{CH_3-CH_2-C=NH_2}{I}$$
 $NH_2 \qquad \qquad NH_2$ 
(II) (II)



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



#### Section (D): Mesomeric Effect

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

(ii) 
$$-NH_2$$
,  $-OH$ ,  $-O^{\Theta}$ 

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

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

# Section (E): Steric Inhibition of Resonance (SIR Effect)

**E-1.** Compare the SIR effect between orthochloro benzoic acid, orthobromobenzoic acid and orthoiodo benzoic acid.

# Section (F): Hyperconjugation

- **F-1.** Define hyperconjugation by taking an example of propene.
- **F-2.** In which molecules or ions hyperconjugation effect is observed and write the number of hyperconjugable hydrogen atoms.

(A) 
$$C_6H_5$$
– $CH$ = $CH_2$ 

(C) 
$$CH_2=CH_2$$

(E) 
$$CH_3 - C - CH = CH_2$$
 (F)  $CH_3 - C - CH$   
 $CH_3 - C - CH = CH_2$  (F)  $CH_3 - C - CH$   
 $CH_3 - C - CH$ 

$$(G) C2H5 - C\oplus$$

## Section (G): Concept of Aromaticity

- **G-1.** What is aromaticity?
- **G-2.** Classify the following as aromatic, antiaromatic and nonaromatic compounds.























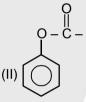


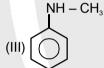
#### **G-3.** Why cyclooctatetraene is nonplanar.

#### Section (H): Applications of electronic effect

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



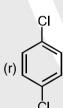




H-2. Correct dipole moment order is







# Section (I): Carbanions

I-1. Arrange the following in decreasing order of stability.

	9 9		
(a)	CH <sub>2</sub> -NO <sub>2</sub> ,	ÖH <sub>2</sub> –CHO	CH≡C 3
(b)	CH <sub>3</sub> - CH <sub>2</sub> - CH <sub>2</sub> - CH <sub>2</sub>	CH <sub>3</sub> – CH – CH <sub>2</sub> CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> C – CH <sub>2</sub> CH <sub>3</sub>

I-2. Arrange the following in decreasing order of stability











(c) CCI<sub>2</sub>







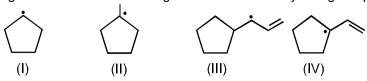
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#### Section (J): Carbon free radicals

J-1. Rank the following free radicals in increasing order of their stability and give appropriate reasons.



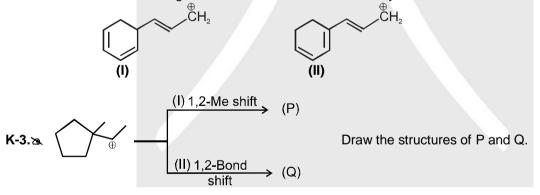
B-J. Arrange the following free radicals in decreasing order of stability:

#### Section (K): Carbocations

**K-1.** Arrange the following carbocations in decreasing order of their stability:

	(I)	(II)	(III)	(IV)
(P)	CH <sub>3</sub> —CH <sub>2</sub> — CH <sub>2</sub>	$CH_3 - CH - \overset{\oplus}{C}H_2$	$CH_3 - CH - \overset{\oplus}{C}H_2$ $H_2$ $H_3$	CH <sub>3</sub> — CH — CH H <sub>2</sub>
(Q)	CH <sub>3</sub> —CH—C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub> C—CH <sub>3</sub>	$CH_3$ $\downarrow$ $CH_3$ $\downarrow$ $CH_5$ $CDH_5$	Ph     Ph—C—C₂H₅
(R)	CH <sub>3</sub>	CH₃ ⊕	CH <sub>3</sub>	⊕ CH₂

**K-2.** Which of the following carbocation is more stable and why?



#### PART - II: ONLY ONE OPTION CORRECT TYPE

#### Section (A): Inductive effect

- **A-1.** Inductive effect involves :
  - (A) Delocalisation of  $\sigma$ -electrons
- (B) Partial displacement of  $\sigma$ -electrons
- (C) Delocalisation of  $\pi$ -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  $\sigma$  bond electrons.
  - (C) I effect creates net charge in the molecule.
  - (D) I effect is distance independent.
- **A-3.** Which of the following group shows +I-effect:
  - (A) -Br (B) -COOH (C) -OR (D)  $-COO^{-}$



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- **A-4.** Which of the following alkyl group has the maximum +I effect?
  - (A) (CH<sub>3</sub>)<sub>2</sub>CH-
- (B) (CH<sub>3</sub>)<sub>3</sub>C-
- (C) CH<sub>3</sub>CH<sub>2</sub>-
- (D) CH<sub>3</sub>-

- A-5. Decreasing –I effect of given groups is :
  - (i) -CN
- (ii) NO<sub>2</sub>
- (iii) –NH<sub>2</sub>
- (iv) -F

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

- **A-6.** Which of the following is the strongest –I group:
  - $(A) \stackrel{+}{N} (CH_a)_a$
- (B) NH<sub>2</sub>
- $(C) \dot{S} (CH_3)_2$
- (D) F

## Section (B): Resonance Concepts, Conditions, Resonating Structures & Conjugation

- **B-1.** Resonance is delocalisation of :
  - (A)  $\pi$  electrons
- (B)  $\sigma$  electrons
- (C)  $\sigma$ – $\pi$  electrons
- (D) None

- B-2. Resonance involves:
  - (A) Delocalization of  $\pi$ -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. During delocalization, which statement is INCORRECT:
  - (A) Net charge remains same
  - (B) Number of paired electrons remain same
  - (C) Number of unpaired electrons remain same
  - (D) Energy of resonating structures always remains same
- **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.
- B-5.2 Which of the following species can not show resonance?









**B-6.** Resonance is not possible in :





(C) CH<sub>2</sub>=CH-Cl



- **B-7.** Which does not have conjugate system?
  - (A) CH<sub>2</sub>=CHCl
- (B) CH<sub>2</sub>=CHCHO
- (C) CH<sub>3</sub>CH=CH<sub>2</sub>
- (D) (\sqrt{})

B-8. ★ The compound which is not resonance stabilised

(A) CH<sub>2</sub>=CH-Cl



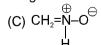
(C) CH<sub>2</sub>=CH–CH<sub>2</sub>Cl



**B-9.** Which of the following is not acceptable as resonating structure:

(A)  $\overset{\bigcirc}{CH_2}$  $\overset{\oplus}{-N}$ =C

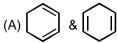




(D) None of these

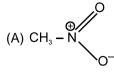


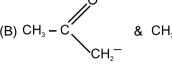
Which of the following pair is not pair of resonating structures?

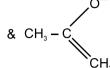


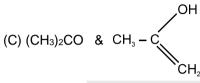
(B) 
$$CH_2 = CH - \overset{\Theta}{O} \& \overset{\Theta}{C}H_2 - CH = O$$

- (C) CH<sub>2</sub>=CH-O-CH<sub>3</sub> & CH<sub>2</sub>-CH=O-CH<sub>3</sub>
- (D)  $CH_3 C = O$  &  $CH_3 C \equiv O$
- B-11. Which of the following structures are resonance structures?









- (D) CH<sub>3</sub>-CH=CH-CH<sub>3</sub> & CH<sub>3</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>
- B-12. Among the given sets, which represents the resonating structure?

(A) 
$$H-C \equiv \stackrel{\oplus}{N}-\stackrel{\bigodot}{O}$$
: and  $H-O-C \equiv N$ .

(B) 
$$H - O = C = N$$
: and  $H - O - C = N$ :

(C) 
$$H-C \equiv \stackrel{\oplus}{N}- \stackrel{\odot}{O}$$
: and  $H-C-N$ :

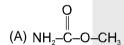
(D) 
$$H - O - C \equiv N$$
 and  $H - N = C = O$ :

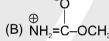
B-13. In which of the following resonance is not possible?

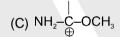
(A) 
$$CH_2=C=CH_2$$

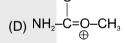
#### Section (C): Stability of Resonating Structures and different species

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





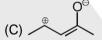


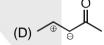


C-2. Which of the following resonating structure is the least contributing structure?









C-3. HNCO (isocyanic acid) has following resonating structures:

$$H-N=C=O\longleftrightarrow H-\overset{\odot}{N-C}=\overset{\oplus}{O}\longleftrightarrow H-\overset{\oplus}{N}=C-\overset{\odot}{O}$$

The order of stablity is:

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

(C) 
$$|| > ||| > 1$$

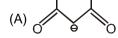
(D) 
$$|| > | > ||$$

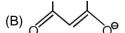
C-4. The correct stability order of the following resonanating structures is :

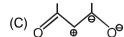
$$H_3\bar{C}-\bar{C}=0$$

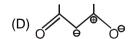
(A) 
$$(IV) > (I) > (III) > (II)$$

- (B) (II) > (IV) > (I) > (III) (D) (I) > (IV) > (III) > (II)
- C-5. Which is the most stable resonating structure?









## Section (D): Mesomeric Effect

Which of the following group show +M effect?



- (B) -O-NO
- (C) -CCI<sub>3</sub>

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(D) -CHO



D-2. Which of the following group show -M effect?



D-3. Which of the following group show +M and -I effect?







(D) -OH

D-4. Which of the following group show +M > -I effect?







(D) -COOH

D-5. Which of the following group show -M and -I effect?

(A) -NO<sub>2</sub>

(B) - NH<sub>2</sub>

(C) -OH

(D) -F

+M and +I both effects are shown by: D-6.

(A) - OH

(B) - NHCH<sub>3</sub>

(C) - O<sub>□</sub>

 $(D) - C (CH_3)_3$ 

The weakest +M group of the given species is : D-7.

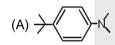
(A) - OCH<sub>3</sub>

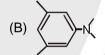
(B) - F

 $(D) - N (CH_3)_2$ 

#### Section (E): Steric Inhibition of Resonance (SIR Effect)

E-1. Maximum extent of steric inhibition of resonance can be expected in









# Section (F): Hyperconjugation

F-1. In hyperconjugation there is overlap between:

(A) p- and  $\pi$ -orbitals

- (B)  $2\pi$ -orbitals
- (C) d- and  $\pi$ -orbtial
- (D) σ- and p-orbitals
- F-2. Which of the following cannot exhibit hyperconjugation -

(A) CH<sub>3</sub>CH<sub>2</sub>

(B) CH<sub>3</sub> CH

(C)  $CH_3CH = CH_2$ 

(D)  $(CH_3)_3C-\bar{C}H_2$ 

F-3. Which of the following alkenes will show maximum number of hyperconjugation forms?

(A)  $CH_2 = CH_2$ 

(B) CH<sub>3</sub>-CH=CH<sub>2</sub>

(C) CH<sub>3</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub> (D) CH<sub>3</sub>

F-4. Which one of the following has inductive, mesomeric and hyperconjugation effect?

(A) CH<sub>3</sub>CI

(B) CH<sub>3</sub>-CH=CH<sub>2</sub>

(C) CH<sub>3</sub>CH= CH-C-CH<sub>3</sub>

(D) CH<sub>2</sub>=CH-CH=CH<sub>2</sub>

F-5. Which of the following group has the maximum hyperconjugation effect when attached to bezene ring?

(A) CH<sub>3</sub>−

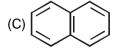
(B) CH<sub>3</sub>CH<sub>2</sub>–

(C) (CH<sub>3</sub>)<sub>2</sub>CH-

(D) (CH<sub>3</sub>)<sub>3</sub>C-

# Section (G): Concept of Aromaticity

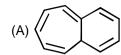
G-1. Which out of the following is aromatic hydrocarbon?



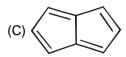




G-2. Identify the aromatic compound?





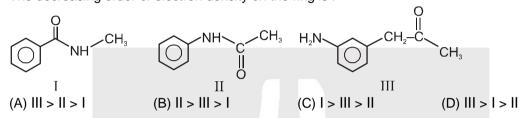




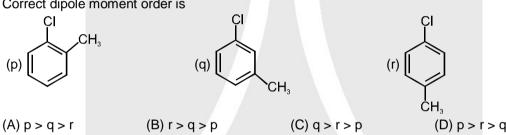
- G-3. Aromatic compounds burn with sooty flame because:
  - (A) They have a ring structure of carbon atoms.
  - (B) They have a relatively high percentage of hydrogen.
  - (C) They resist reaction with oxygen of air.
  - (D) They have a relatively high percentage of carbon.

#### Section (H): Applications of electronic effect

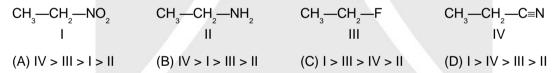
H-1. The decreasing order of electron density on the ring is:



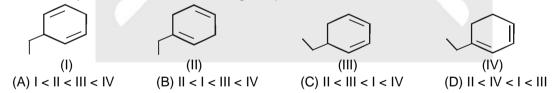
H-2. Correct dipole moment order is



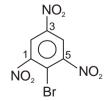
H-3. Arrange following compounds in decreasing order of their dipole moment.



H-4. The stability order of alkene in following compounds is:



H-5. 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.



H-6. Arrange the stability of following:









(D) II < III < I

#### Section (I): Carbanions

- I-1. Which of the following is the least stable carbanion?
  - (A)  $HC \equiv \overline{C}$
- (B)  $(C_6H_5)_3\overline{C}$
- $(C)(CH_3)_3\overline{C}$
- (D) CH<sub>2</sub>

I-2. The most stable anion is:







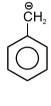
I-3. In which of the following pairs of carbanion the first one is more stable than second.

(A) 
$$\overset{\circ}{\mathsf{C}}\mathsf{F}_3$$
,  $\overset{\circ}{\mathsf{C}}\mathsf{C}\mathsf{I}_3$ 

(B) 
$$HC \equiv \overset{\Theta}{C}$$
,  $H_2C = \overset{\Theta}{C}H$ 

(D) 
$$(CH_3)_3C^{\Theta}$$
,  $H_3C - CH_2$ 

Arrange the following carbanions in decreasing order of stability: I-4.



(A) III > I > IV > II



(B) III > II > I > IV



(C) I > III > II > IV



(D) |I| > I > I > IV

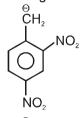
The most stable anion is: I-5.≿

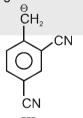






I-6.≿ Arrange the following carbanions in increasing order of stability: ČH<sub>2</sub>





CN NO. IV

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

#### Section (J): Carbon free radicals

- Among the following, the paramagnetic species is: J-1.
  - (A) Free radical
- (B) Carbocation
- (C) Carbanion
- (D) All the three
- J-2. The stability of given free radicals in decreasing order is:
  - (i) CH<sub>3</sub>-CH<sub>2</sub>
- (ii) CH<sub>3</sub>-CH-CH<sub>3</sub>
- (iv) CH<sub>3</sub>

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

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- J-3. Which of the following is the correct order of stability of free radicals?
  - (A) benzyl > allyl >  $2^{\circ}$  >  $1^{\circ}$

(B) allyl > benzyl >  $2^{0} > 1^{0}$ 

(C) allyl >  $2^{\circ}$  >  $1^{\circ}$  >benzyl

- (D) benzyl >  $2^{\circ}$  >  $1^{\circ}$  > allyl
- **J-4.** Most stable radical among the following is :







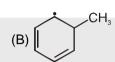


- J-5. Arrange the following radicals in decreasing order of their stability.
  - (I) **ċ**H<sub>2</sub>
- (II) CH<sub>3</sub> CH<sub>3</sub>
- (IV) (T) ĊH-(T)

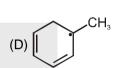
- (A) IV > I > III > II
- (B) IV > III > II > I
- (C) I > II > III > IV
- (D) IV > III > I > II

**J-6.** Least stable radical among the following is:









#### Section (K): Carbocations

- K-1. The most unstable carbocation is:
  - (A) CH<sub>3</sub>  $\overset{\oplus}{\text{CH}}_2$
- (B) Cl − CH<sub>2</sub> − CH<sub>2</sub>
- (C) CH₂ CHO
- (D)  $\overset{\oplus}{C}H_2 O CH_3$

**K-2.** The most stable carbocation is :

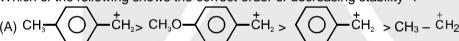








K-3.≥ Which of the following shows the correct order of decreasing stability?



(B) 
$$CH_3O - CH_2 > CH_3 - CH_3 - CH_2 > CH_3 - CH_3 - CH_2$$

(C) 
$$CH_2 > CH_3O - CH_2 > CH_3 - CH$$

(D) 
$$CH_3O - CH_2 > CH_2 > CH_3 - CH_2 > CH_3 - CH_3 - CH_3 = CH_3 - CH$$

**K-4.** Which of the following is the rearranged more stable carbocation of the given species?

$$\begin{array}{c} \mathsf{CH_3} \\ \mid \ \oplus \\ \mathsf{CH_3} - \mathsf{C} - \mathsf{CH} - \mathsf{CH_3} \end{array} \longrightarrow \\ \begin{matrix} \mathsf{CH_3} \\ \mid \\ \mathsf{CH_3} \end{matrix}$$

CH<sub>3</sub>
(B) CH<sub>3</sub>-C-CH<sub>2</sub>-
$$\overset{\oplus}{\text{CH}}_2$$

(D) 
$$CH_3$$
  $\stackrel{\oplus}{\mid}$   $CH_2$ 



**K-5.** Most stable rearranged form of given carbocations is :

$$(A) \xrightarrow{\mathbb{C}} C + CH_3$$

$$CH_3$$

# PART - III : MATCH THE COLUMN

**1.** Match the following:

	Coulmn-I (Compounds)		Coulmn-II (Characteristics)
(A)	\/\/\ <sup>0</sup>	(p)	Mesomeric effect / resonance
(B)	Ph-CH=CH-CH <sub>3</sub>	(q)	Inductive effect.
(C)	CH <sub>3</sub>	(r)	Hyperconjugative effect
(D)	CI	(s)	Nonpolar
_		(t)	Polar

# **Exercise-2**

Marked questions are recommended for Revision.

#### PART - I: ONLY ONE OPTION CORRECT TYPE

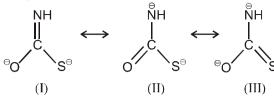
**1.** The most unlikely representation of resonance structures of p-nitrophenoxide ion is:

2. In which delocalisation of positive charge is possible?

3. Decreasing order of potential energy of the following cations is :



4. Stability order of the following species?



- III < II < I
- (B) III > I > II
- (C) III > II > I
- (D) I > III > II
- 5. In which of the following first resonating structure is more stable than the second?
  - (A)  $CH_2$ -CH=O  $\longleftrightarrow$   $CH_2$ =CH-O
- (B)  $CH_2$ -O- $CH_3 \longleftrightarrow CH_2$ =O- $CH_3$
- (C)  $CH_2=CH-NH_2 \longleftrightarrow CH_2-CH=NH_2$
- (D)  $\overset{\oplus}{O}$ -CH=CH<sub>2</sub>  $\longleftrightarrow$  O=CH- $\overset{\oplus}{C}$ H<sub>3</sub>
- Which of the following is incorrect for stability of structures. 6.

- (C)  $CH_2 = CH \overset{\oplus}{C}H_2 > CH_3 CH_2 \overset{\oplus}{C}H_3$
- (D)  $CH_2 = CH CH = CH CH_2 > CH_2 CH_2 CH = CH_2$
- 7. Least contributing resonating structure of nitroethene is :
  - (A)  $CH_2 = CH N = O$

(B)  $\dot{C}H_2 - \bar{C}H - \dot{N} = 0$ 

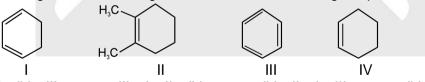
(C)  $\overline{C}H_2 - \overline{C}H - \overline{N} = 0$ 

- (D)  $\dot{C}H_2 CH = \dot{N} = 0$
- 8. Which of the following statement is correct?
  - (A) In the dianion

, 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
- The decreasing order of bond length of C=C bond in the following compounds is: 9.



- (A) |I| > I > |V| > |I|
- (B) III > I > II > IV
- (C) IV > II > I > III
- (D) |V > I > I| > |I|
- 10. Which of the following is correct about the following compound

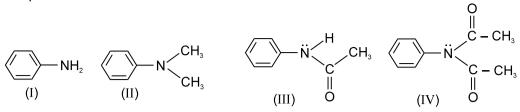


(Naphthalene)

- (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<sub>1</sub>–C<sub>2</sub> bond length is greater than C<sub>2</sub>–C<sub>3</sub> bond length
- (D) All the C-C bond length are equal to C-C bond length of benzene



11. The correct order of +M effect of 'N' containing functional group on benzene ring, amongst the given compounds is



- (A) I > II > IV > III
- (B) |I| > I > |I| > |V|
- (C) I > II > III > IV
- (D) |V > |I| > |I| > 1
- 12. In which case the  $\sigma$ -bond pair and  $\pi$ -bond pair of electrons both are attracted in the same direction, (towards same atom.) :
  - (A) H<sub>2</sub>C=CH-Cl
- (B) CH<sub>3</sub>-CH<sub>2</sub>-NH<sub>2</sub>
- (C) H<sub>2</sub>C=CH-CH=O
- (D) H<sub>2</sub>C=CH-OCH<sub>3</sub>
- 13. The correct stability order of given resonating structures is :

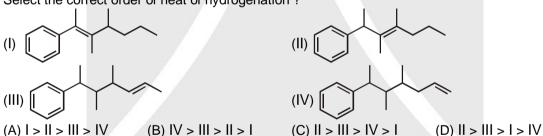
$$(I) \qquad (III) \qquad (III) \qquad (IV)$$

$$(A) \mid S \mid I \mid S$$

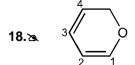
**14.** The longest C–N bond length in the given compound is:

(A) x (B) y (CH<sub>3</sub> 
$$CH_3$$
  $N \stackrel{\times}{=} C$   $N \stackrel{\times}{=} CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

15. Select the correct order of heat of hydrogenation?



- **16.**  $H_3C-CH-CH=CH_2$  does not involve :
  - (A) σ–p overlap
- (B)  $\sigma \pi^*$  overlap
- (C) pπ-pπ overlap
- (D)  $p\pi$ – $d\pi$  overlap
- 17. Stability of  $\pi$ -bond in following alkenes in the increasing order is :



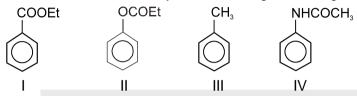
In this molecules,  $\pi$ -electron density is more on :

- (A) C<sub>1</sub> and C<sub>3</sub>
- (B) C<sub>2</sub> and C<sub>4</sub>
- (C) C<sub>2</sub> and C<sub>3</sub>
- (D) C<sub>1</sub> and C<sub>4</sub>

**19.** If the given compound is planar. Select the correct statement.



- (A) The boron is sp<sup>2</sup> hybridized and the p-orbital contains an unshared pair of electron
- (B) The boron is sp<sup>2</sup> hybridized and a hybrid orbital contains an unshared pair of electron.
- (C) The boron in sp<sup>2</sup> hybridized and hybrid orbital is vacant
- (D) The boron is sp<sup>2</sup> hybridized and the p-orbital is vacant
- 20. The correct order of electron density in aromatic ring of following compounds is:



- (A) IV > III > II > I
- (B) I > II > III > IV
- (C) IV > II > I > III
- (D) |V > |I > |I| > |I|
- **21.** Arrange the following carbanions in decreasing order of stability:

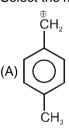
$$^{\Theta}$$
CH<sub>2</sub> $-$ CI (I)

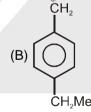
$$^{\Theta}$$
CH<sub>2</sub>-NO<sub>2</sub> (III)

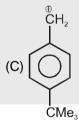
- (A) III > II > IV > I
- (B) III > II > I > IV
- (C) III > I > II > IV
- (D) |I| > |I| > |I| > |I|
- 22. Correct decreasing stability order of following carbanions :

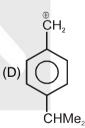
- (A) ||| > |V > || > |
- (B) IV > II > III > I
- (C) IV > III > II > I
- (D) III > II > I > IV

**23.** Select the most stable intermediates :



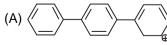


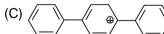


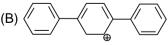


- **24.** Which of the following is most stable carbocation?
  - (A) CH<sub>3</sub> CH<sub>2</sub>
- (B)  $CH_3 \overset{\oplus}{C} = O$
- (C)  $CH_3 \overset{\oplus}{C} = NH$
- (D)  $CH_2 = \overset{\oplus}{C}H$

25. The most stable carbocation is:







(D) (D)

26.8 The following carbocation rearranges to

CH<sub>3</sub> CH<sub>3</sub>

$$CH_{3} \quad CH_{3} \\ | \quad \oplus \quad |$$

$$CH_{2} = C - C - CH - CH - CH_{3} \\ | \quad | \quad |$$

$$CH_{3} CH_{2} = C - C - CH - CH - CH_{3} \\ | \quad | \quad | \quad |$$

$$CH_{3} CH_{3} \\ | \quad | \quad | \quad |$$

$$CH_{3} CH_{3} \\ | \quad |$$

# **PART - II: NUMERICAL VALUE QUESTIONS**

1.b Among the given sets, how many of the following not represents the resonating structure:

(v) 
$$\overset{\ominus}{C}H_2$$
–CH=O

$$\Theta$$
 CH<sub>2</sub> = CH – O (vi) CH<sub>2</sub>=CH–NH<sub>2</sub>

and

CH<sub>3</sub> CH<sub>3</sub>

$$2 = C - CH_3$$

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











CH<sub>2</sub>=CH-CI,

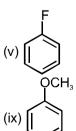


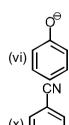


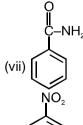
How many groups (attached with benzene ring) can show +M effect ? 3.3











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













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













(ix) 
$$CH_3 - CH_2 - CH - N O$$

- $(x) \stackrel{\ominus}{C}H_2 F$
- 6. In how many of the following compounds Hyperconjugation effect is observed -
  - (A) C<sub>6</sub>H<sub>5</sub>-CH=CH<sub>2</sub>
- (B) Ph-CH<sub>3</sub>

(C) C<sub>2</sub>H<sub>5</sub>-C-CH



- (I) CH<sub>3</sub>-C-CH<sub>2</sub>
- 7.> How many of the following compounds is/are aromatic?















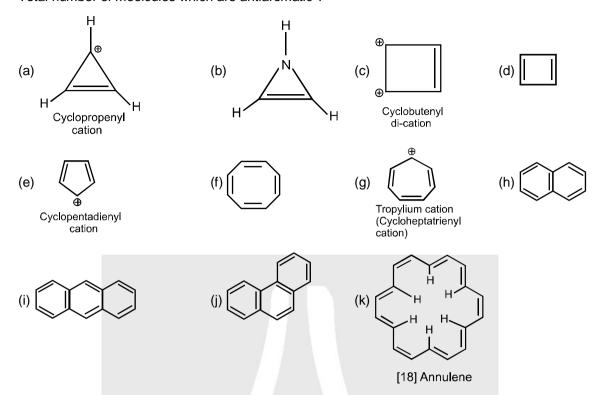








#### 8. Total number of moelcules which are antiaromatic?



**9.** Find the number of carbon atoms including the given structure which can have negative change in resonating structures. (The structure with charge reperating are not accepted)

$$HC \equiv C - \stackrel{\Theta}{C} - CH = C = CH_2$$
 $C \equiv N$ 
 $CH_3$ 

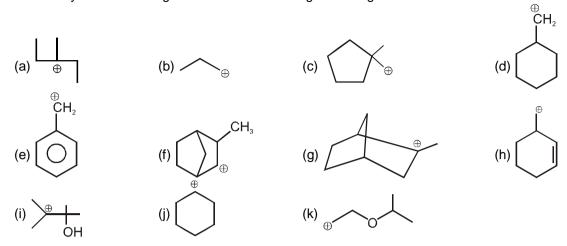
10. Observe the following compound and write the number of hydrogen atom involved in hyperconjugation?

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

$$CH_2$$
 $CH_3-CH-CH=CH-C-$ 
(Excluding the given position)

人

12. How many of the following carbocation can undergo rearrangement:

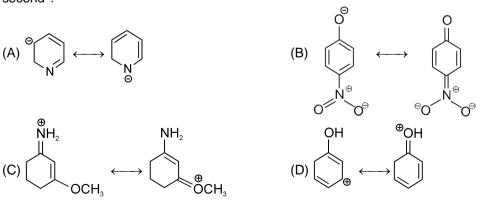


# PART - III: ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

- 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 resonating structure.
  - (D) Resonanting structures can not be isolated at any temperature
- 2. Which of the following statement is incorrect about resonance?
  - (A) The most stable resonance 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, will second structure have more contribution to resonance hybrid than first?

(A) 
$$\bigcirc$$
 &  $\bigcirc$  (B)  $\bigcirc$  &  $\bigcirc$  (B)  $\bigcirc$  A  $\bigcirc$  (B)  $\bigcirc$  A  $\bigcirc$  (C) F-C-OH & F=C-OH  $\bigcirc$  (D)  $\bigcirc$  &  $\bigcirc$  (D)  $\bigcirc$  &  $\bigcirc$  (D)  $\bigcirc$  &  $\bigcirc$  (D)  $\bigcirc$  (D)  $\bigcirc$  (E)  $\bigcirc$  (E)  $\bigcirc$  (D)  $\bigcirc$  (E)  $\bigcirc$  (E)  $\bigcirc$  (D)  $\bigcirc$  (E)  $\bigcirc$  (E)

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





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**5.** In which of the following compounds delocalisation of electrons and shifting of electron in the same direction?



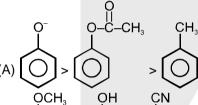
(B) CH<sub>3</sub>-NH-NO<sub>2</sub>

(C) CH<sub>2</sub>=CH–CH=CH–NO<sub>2</sub>

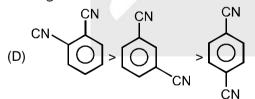
- (D) H<sub>2</sub>N C = CH<sub>2</sub>
- **6.** Which of the following groups cannot participate in resonance with benzene :
  - (A) COOH
- (B) COO<sup>®</sup>
- (C) −NH<sub>3</sub>
- (D) COCI

- 7. > Which of the following is/are correct:
  - (A) is antiaromatic

- (B) is aromatic
- (C) is aromatic
- (D) is aromatic
- **8.** Which of the following is/are correct statement :



- e<sup>-</sup> density
- (B) > > >
- e<sup>-</sup> density
- all are aromatic



Dipole moment

**9.** The correct orders for bond length are :

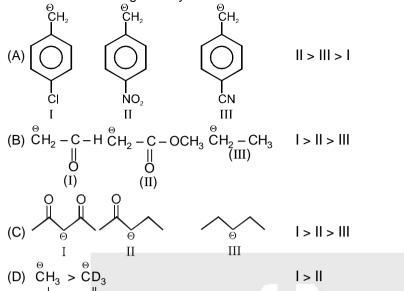
(B) 
$$CH_3 - C - NH_2$$
 (b' = b)

(C) 
$$CH_3-C^{C}-ONa$$
 (c > c')

(D) 
$$\frac{d}{d}$$
 (d > d')



10. Which of the following stability order of anions is/are correct:



#### **PART - IV : COMPREHENSION**

#### Read the following passage carefully and answer the questions.

#### Comprehension #1

Hydrogenation of unsaturated hydrocarbons is an exothermic reaction. Due to hyperconjugation and resonance the stability of unsaturated hydrocarbons increases and the increase in stability is more due to resonance. Compound with same number of  $\pi$ -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

(q) 1,3-Butadiene

(r) 2,3-Dimethyl-1,3-butadiene

(s) Propadiene

(A) p > q > r > s

(B) s > q > p > r (C) q > s > p > r

(D) s > p > q > r

**2.** The order of heat of formation of the following molecules is :

#### Comprehension # 2

Answer Q.3, Q.4 and Q.5 by appropriately matching the information given in the three columns of the following table.

	Column-I	Column-II	Column-III
(P)	Z	(i) lone pair is present in hybrid orbital	(I) delocalised lone pair
(Q)	H-Z:	(ii) Charge is present in hybrid orbital	(II) localised lone pair
(R)	<b>(</b>	(iii) lone pair is present in p-orbital	(III) localised charge



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(S)	©H <sub>2</sub> (iv) charge is present	n p-orbital (IV) delocalised charge
-----	--	-------------------------------------

- 3. The only correct combination for pyridine is -
  - (A) (Q) (i), (II)
- (B) (P) (i) (II)
- (C) (R) (iv) (III)
- (D) (Q) (ii) (II)

- The only correct combination for benzyl cation is-4.
  - (A) (P) (ii), (II)
- (B) (R) (iv) (IV)
- (C) (S) (iv) (IV)
- (D) Q (i) (II)

- The only correct combination for pyrrole is 5.
  - (A) (P) (ii), (II)
- (B) (R) (iv) (IV)
- (C) (S) (iv) (IV)
- (D) Q (iii) (I)

#### Comprehension #3

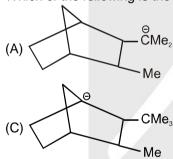
Reaction intermediates: Reaction intermediates are short lived species and are highly reactive. They are formed by heterolytic and homolytic bond fission. There are various types of reaction intermediates in which the most important are carbocation, carbanion and free radical.

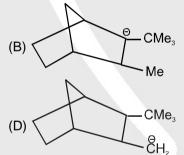
Carbocation is an organic species in which carbon have positive charge and six electrons in its outermost shell. The stability of carbocation can be increased by positive inductive effect, hyperconjugation and delocalisation. If  $\alpha$ -atom with respect to carbocation has one or more lone pair of electrons then lone pair of electron strongly stabilises the carbocation due to octet completion.

Species in which carbon have negative charge is called carbanion. Carbanion carries three bond pairs and one lone pair. The stability of carbanion can be increased by negative inductive effect, negative mesomeric effect and delocalisation.

Free radical is a species which have seven electrons in its outermost shell. The stability of free radical can be increased by hyperconjugation and delocalisation.

Which of the following is the most stable carbanion intermediate? 6.





- 7. The stability order of following free radicals is:
  - C<sub>k</sub>H<sub>s</sub>CH<sub>s</sub>CH<sub>s</sub>

CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>

C<sub>6</sub>H<sub>6</sub>ČH<sub>2</sub> CH.

(A) I > II > III > IV

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

(C) I > III > II > IV

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

The stability order of following carbocations is 8.



(B) |I| > I > |I|(C) |I| > I > I|

(D) |I| > |I| > I

(A) I > II > III



# **Exercise-3**

\* Marked Questions may have more than one correct option.

# PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

Write resonating structure of the compound 1.

[JEE-03(S), 2/60]

2. Explain the following observations



[JEE-05, 2/84]

3. Which will be the least stable resonating structure:

(A)  $CH_2 = CH - \overset{\oplus}{C}H - \overset{\ominus}{C}H - O - CH_3$ 

- (C) CH-CH=CH-CH=O-CH<sub>3</sub>
- (D)  $CH_2=CH-CH-CH=O-CH_3$

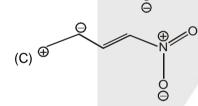
but not

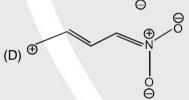
Among the following, the least stable resonating structure is: 4.

[JEE-07, 3/162]









Hyperconjugation involves overlap of the following orbitals: 5.

(A) 
$$\sigma$$
– $\sigma$  (B)  $\sigma$ –p

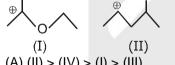
$$(C) p - p$$

(D) 
$$\pi - \pi$$

The correct stability order for the following species is: 6.

[JEE-08, 3/163]

[JEE-08, 3/163]



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

- (D) (I) > (III) > (IV)
- 7. In the following carbocation; H/CH<sub>3</sub> that is most likely to migrate to the positively charged carbon is [JEE-09, 3/160]

- (A) CH<sub>3</sub> at C-4
- (B) H at C-4
- (C) CH<sub>3</sub> at C-2
- (D) H at C-2
- The correct stability order of the following resonating structures is: 8.  $H_2 \stackrel{+}{C} = N = \overline{N}$ H<sub>2</sub>C−N≡N
- [JEE-09, 3/160]

- H<sub>2</sub>C=N=N
- (II)
- (III)
- H<sub>2</sub>C-N=N

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

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



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]







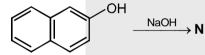


- 11. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to
  - (A)  $\sigma \rightarrow p$  (empty) and  $\sigma \rightarrow \pi^*$  electron delocalisations.

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

- (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]



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

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













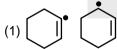


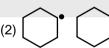




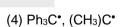
# PART - II: JEE (MAIN) ONLINE PROBLEMS (PREVIOUS YEARS)

1. In which of the following pairs A is more stable than B? [JEE(Main) 2014 Online (09-04-14), 4/120]

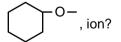








2. Which one of the following substituents at para-position is most effective in stabilizing the phenoixde



[JEE(Main) 2014 Online (19-04-14), 4/120]

- (1) -CH<sub>3</sub>
- (2) -OCH<sub>3</sub>
- (3) -COCH<sub>3</sub>
- (4) -CH<sub>2</sub>OH

**3.** Which of the following compounds is not aromatic?

[JEE(Main) 2019 Online (09-01-19), 4/120]









**4.** Which compound(s) out of the following is/are not aromatic?

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









- (1) (B)
- (2) (B), (C) and (D)
- (3) (C) & (D)
- (4) (A) & (C)
- 5. Which of the following compounds will produce a precipitate with AgNO<sub>3</sub>?

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









- 6. Which of the following has the shortest C-Cl bond? [JEE(Main) 2020 Online (09-01-20)S2, 4/120]
  - (1) CI-CH=CH-NO<sub>2</sub>
- (2) CI-CH=CH-CH<sub>3</sub>
- (3) CI-CH=CH<sub>2</sub>
- (4) CI-CH=CH-OCH<sub>3</sub>

# **Answers**

# **EXERCISE - 1**

#### PART - I

# **A-1.** (1) C ≡ CH

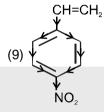


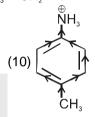
- (4)  $CH_3 \leftarrow CH_2 \leftarrow CH_2 \leftarrow Li$
- (5)  $CH_3 \stackrel{\sqcap}{\longleftarrow} CH_2 \stackrel{\longleftarrow}{\longleftarrow} CH_2 \stackrel{\longleftarrow}{\longleftarrow} MgBr$
- (6) CH<sub>3</sub>→ CH<sub>2</sub>→ OH



(R) I - minor

(8) CH₃→COOH





- **B-1.** (P), (R), (S)
- **B-2.** 8
- **C-1.** (P) I minor
- II major II – major
- (Q) I minor (S) I – minor
- II major II – major

- **C-2.** (P) I > II;
- (Q) || > | ;
- (R) I > II;

– CH<sub>2</sub>

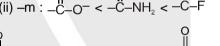
(S) II > I

D-1.

(i) 
$$+m: -l < -Br < -Cl < -F$$

(ii) +m : 
$$-OH < -NH_2 < -O^{\Theta}$$







N(CH<sub>3</sub>)<sub>2</sub> SH have +M group.



NHC — CH<sub>3</sub>





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

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

Propene 
$$H_2C \stackrel{\leftarrow}{-} HC = \stackrel{\leftarrow}{C}H_2 \longrightarrow H_2C = CH - CH_2$$

$$III II I II II II II$$

- F-2.
- (A) 0
- (B) 2
- (C) 0
- (D) No hyperconjugation

- (E) 0 (I) 3
- (F) 0 (J) 10
- (G) 6 (K) 0
- (H) 9 (L) 10
- **G-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  $\pi$  -electrons in ring.
- (d) must have cyclic resonance between (4n + 2) number of  $\pi$ -electrons Where n = 0, 1, 2, 3, 4 .......



- G-2. Aromatic: (a), (b), (c), (d), (e), (f), (h), (l); Antiaromatic: (g), (i), (j), (m); Nonaromatic: (k)
- G-3. Cyclooctatetraene is nonplanar to avoid its anti aromaticity and it becomes tub-shaped structure.



- H-1. (III) > (II) > (IV) > (I)+m group increases electron density and -m group decreases electron density in aromatic ring.
- H-2.
- I-1. (a) 2 > 1 > 3 > 4; (b) 1 > 2 > 3; (c) 1 > 2(a) 1 > 2 > 3; (b) 1 > 2 > 3I-2.
- J-1. Stability order: I < II < III < IV IV is most stable being 3° and delocalised but III is 2° and delocalised.
- (P) I > III > IV > II; (Q) IV > III > II > I; (R) III > II > IV > IJ-2. ||| > || > | > |VK-1.
- K-2. (II) is more stable carbocation due to extented conjugation
- K-3. (P) =; (Q) =

#### PART - II

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

(A)

(D)

D-1. (B) D-6. (C) F-3. (B) G-3. (D) H-5. (C) I-4. (D) J-3. (A) K-2. (B)

A-5.

B-4.

B-9.

C-1.

(D)

(D)

(B)

(C)

- PART III
- (A) p,q,r,t; (B) p,q,r,t; (C) p,q,r,t; (D) p,q,s1.

# **EXERCISE - 2**

# PART - I

- 1. (C) 2. (D) 3. (A) 4. (A) 5. (C) 6. 7. (A) (C) 8. (B) 9. (B) 10. (B) (D) 11. 12. (C) 13. 14. (D) 15. (B) (C)
- 16. 17. (A) 18. 20. (D) (B) 19. (D) (D) 21. 22. (C) (B) 23. (A) 24. (C) 25. (A)
- 26. (D)

I-5.

J-4.

K-3.

(B)

(C)

(B)

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#### PART - II

- **1.** 4 (i, iii, iv, vii)
- **2.** 8 (ii, iii, iv, vi, vii, viii, ix, xi)
- **3.** 5 (i, ii, v, vi, ix)

- **4.** 5 (i, iii, v, vi, vii)
- **5.** 5 (i, ii, iv, vi, ix)
- **6.** 3 (B, C & G).

- **7.** 6 (i, iv, v, vi, vii, x)
- 8.
  - Aromatic a, c, g, h, i, j, k.
- Antiaromatic b, d, e ;
- Nonaromatic f

- **9.** 6
- **10.** 9
- **11.** 2

**12.** 7

#### PART - III

- **1.** (ABCD)
- 2.
- (AB)
- **3.** (ABC)
- **4.** (BC)
- **5.** (BC)

- **6.** (C)
- **7.** (BD)
- **8.** (AD)
- **9.** (ABD)
- **10.** (ABCD)

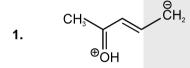
#### PART - IV

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

- **6.** (D)
- 7.
- 8.
  - (A)

# **EXERCISE - 3**

#### PART - I



- 2. (A) In the formation of first product the antiaromaticity due to the presence of three " | | | | | " rings of the reactant is finished and the product becomes more stable. While in 2nd case the product is thermodynamically less stable.
- **3.** (A)
- 4.
- (A)
- **5.** (B)
- **6.** (D)
- **7.** (D)

- **8.** (B)
- **9.** 6
- **10.**\* (BC)
- **11.** (A)
- **12.** 9

**13.** 5

#### PART - II

**1.** (4)

(1)

6.

- **2.** (3)
- **3.** (1)
- 4.

(2)

**5.** (2)