$NH_2$ 

# **HINTS & SOLUTIONS**

#### EXERCISE - 1 Single Choice



 $C_{3}H_{9}N \rightarrow$ 

amine  $CH_3-CH_2-CH_2-NH_2$  and  $CH_3-CH-CH_3$ amine  $CH_3-NH-CH_2-CH_3$ amine  $CH_3-N-CH_3$ 

ĊH

(6)

(7)

So C is correct option.

(1)

5. 
$$C_5H_{10} \rightarrow$$

1.

(2)  $CH_{3}-CH=CH-CH_{2}-CH_{3}$ 

 $CH_3 - CH_2 - CH_2 - CH = CH_2$ 

1° 2° 2°

$$\begin{array}{ccc} \text{(3)} & \text{CH}_{3}\text{-}\text{CH}\text{=}\text{C}\text{-}\text{CH}_{3} & \text{(8)} \\ & \text{CH}_{3} & \end{array}$$

(4) 
$$CH_{3}-CH_{2}-C=CH_{2}$$
 (9)  
(5)  $CH_{2}=CH-CH_{-}CH_{3}$  (10)  
 $CH_{3}$ 

9. Anthracene



Only three types of hydrogen so only three structural isomers possible.







11.	Ethene Propend Butene $CH_3 - C$	$ \rightarrow CH_2 = CH_2 $ Cannot show G.I. $ a \rightarrow CH_3 - CH = CH_2 $ Cannot show G.I. $ \rightarrow CH_3 - CH = CH - CH_3 $ Show G.I. and it also show positional isomerism. $ H_2 - CH = CH_2 $ and $CH_3 - CH = CH - CH_3 $		
13.	(A)	$CH_3 - CH_2 - CH_2 - CH_3$ exist in isomeric form.		
	<b>(B)</b>	$CH_3 - C - H \implies CH_2 = CH$ exist in tautomeric form.		
	(C)	$CH_2 = CH - Cl \longrightarrow H$ $C = C Cl$ no show G.I./or any isomers.		
14.	<b>(D</b> )	$\begin{array}{c} CH_2 - CH_2 \\ I & I \\ Cl & Cl \end{array} \rightarrow exists in conformational form$		
	$A \rightarrow$	$CH_3 - C = CH_2$ isobutene $CH_3$		
	$B \rightarrow$	$CH_3$ C=N-OH Acetone oxime		
	$C \rightarrow$	$CH_3$ C=N-OH Acetophenone oxime Show G.I.		
	$C \rightarrow$	Ph C=NOH Benzophenone Ph		
15.	$\mathbf{A} \rightarrow$	C1 C1 I I CH=CH $-$ CH $_2-$ CH $_3-$ CH $_3$ Show G.I.		
	$B \rightarrow$	$CI = CH_2 - CH_2 - CH_3 \text{ Show G.I.}$		
	$C \rightarrow$	$CI = CH - CH_2 - CH_2 - CH_3 - Not Show G.I.$		
	$D \rightarrow$	$H_1$ $H_2$ $-CH=CH-CH$ $-CH_3$ Show G.I.		
17.	CI CI  I I  CH3-CH-CH-CH3 total optical isomers = 3			
	$CH_3$ $CH_3$ $CH_3$ H $Cl$ $Cl$ $H$ $H$ $Cl$			
	H - CI H - CI CI - H			
	(II) and	$\begin{array}{ccc}  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & $		





 $1 \xrightarrow{3} 4 \xleftarrow{2} 4$ So option is (A)

27 Mirror imageof D-ribose is known as L-form.





#### **35.** Alkyl group is different.

 $\int_{-C-0}^{0} f_{-C-0}$  is bivalent group which has different alkyl groups in both compounds.

As we know that according to definitions off matamerism "When alkyl group is different around bivalent. or trivalent atom 1 group compounds termed as metamers.



Although in second compound trans from is present but structurel is also present so it will be metamers not geometrical isomers.



Ring will be Principle carbon chian so we assign numbering for ethylidene group ( $CH_3 - CH = C <$ ) which is E-in configuration.



37. If terminal carbon have same group than it can show geometrical isomerism.

$$Cl$$
  $CH_2$   $CH_2$   $CH_3$   $CH$ 

In this compound there is not possibility to show geometrical isomerism because at first double bonded carbon 2same chlorine atom is attached.

**38.** Both will give n-Butane as a product.

Boiling point	cis-2-butene>Trans 2-butane
Dipole moment	cis-2-butene > Trans 2-butane
Heat of Hydrogenation	cis-2-butene > Trans 2-butane

Product same





same compounds

**39.** Higher Priority groups same side

= Z - form

Higher Priority groups oppsite side

= E - from

CH<sub>3</sub> – group name more Priority than H – atom



**40**.

Lone pair also counts as a different group.

For G.I. for ground attached to the terminal carbon or Nitrogen must be different.





41. In cyclo alkane minimum 2 group & carbon ring required.



43. Asymmetric carbon  $\equiv$  Chiral carbon.

$$\begin{array}{c} H & H \\ I \not \downarrow I \\ H - C - C - C - CH_3 \\ I & I \\ Br & OH \end{array}$$

42.

Telrahedral (Tetravalent carbon) having four different group is known as chiral/Asymmetric carbon.

44. Compound having single chiral carbon always optically active and gives two active compound

Active isomer = 
$$2^{n-1} = 2^{2-1} = 2$$

Where n = Number of chiral carbon









In tautomerism atom must ossilate in the compound. Geometrical isomerism shown by many compounds like, alkene, cycloalkanes, oximes, etc.





Lone pair and isotopes also counts as a different groups.



**22.** POS or COS may be present.

Meso are the compounds with was minimum 2-chiral carbon or more and having POS or COS or both.

Fro optical activity two necessary condition us compound must be asymmetric. It POS or COS present then it will super impose on its mirror image.



23. Check conformers of the compounds



24. Check R/S configuration

Fischer is in eclipse form so first we have to convert above compound into total eclipsed form.





25. Optially active compound will be resolvable. Resolution is a process by we separate entiopers and we know that entiopers are

Resolution is a process by we separate entiomers and we know that entiomers are individually active so check POS and COS.



**26.** Two different group - H and  $-CH_3$  is present.

When two groups (Bulky) are at 60° Dihedral angle is known as sancle form



- 3. Me C = N and Me N = C are functional isomers but H C = N and H N are Tautomer
- 4. The enol form of 5,5- dimethyl-1,3- cyclohexanedione is stable due to chelation, but same is not true in 2,2-dimethyl 1,3-cyclohexanedione dur to absence of  $\alpha$ -hydrogen because it is not having more acidic hydrogen.

#### EXERCISE - 3 Part # II : Comprehension

#### **Comprehension #4:**

1. [Specific rotation of (-) MSG]

$$C = \frac{169 \,\text{gm}}{845 \,\text{gm}} \quad l = 2 \,\text{dm}$$

$$[\theta^{\circ}] = \frac{\theta}{Cl} = \frac{9.6}{169/845 \times 2} = -24^{\circ}$$









1. If the bonds were localized, there would be 4 isomers ; actually there are only 3 of the following the first two are identical, because the bods are not localized.



- **3.** There are 7. 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, diethyl ether, methyl propyl ether, and methylisopropyl ether.
- 4. This is cis form. Two H atoms on the same side. To get trans, ring must be twisted.

Double bond becomes severely twisted-destablized. Effective overlap of P orbitals is missing, so does not exist.

5. The  $P_z$  orbitals forming  $\pi$ -bonds and the empty  $P_z$  orbital of the carbon with +ve charge are parallel. So the electrons may be delocalized. The +ve charge is effectively spread out over two carbons; delocalized.

 $\begin{array}{c} H & \bigcirc & \pi \text{-orbital} \\ H & \bigcirc & \bigcirc & C^+ - H \\ H & \bigcirc & \bigcirc & C^+ - H \\ H & \bigcirc & H \end{array}$ 

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

In n-propyl cation, + I effect of R increases the stability.

In alyl + M effect increases the stability. But + M effect in allyl cation is more effective. So allyl > propyl. A group with +M effect stabilized cation; destabilizes anion.

B

6. Only CHBr = CHCl can exist as geometric Isomers :

$$\begin{array}{c} Br \\ H \end{array} C = C \begin{pmatrix} Cl \\ H \end{pmatrix} and \quad \begin{array}{c} Br \\ H \end{pmatrix} C = C \begin{pmatrix} H \\ Cl \end{pmatrix} \\ Cl \end{pmatrix}$$

In  $CH_2Cl - CH_2Cl$  and  $CH_2Cl - CH_2Br$ , the carbon atoms are connected by a single bond about which the groups can rotate relatively freely. Thus any conformation of the halogen atoms may be converted into any other simply by rotation about the single bond. In  $CH_2Cl_2$ , the configuration of the molecule is tetrahedral and all interchanges of atoms yield exactly equivalent configurations.

7. Maleic acid forms an anhydride where as fumaric acid does not.



8. Lone pair -  $p\pi$  conjugation between fluorine and carbon will be more effective than between chlorine and carbon.

9. 
$$III > IV > I > II$$

11. (A)  $-Br > -CH_2CH_2OH > -CH_2CH_3 > -H$ , (B)  $-OH > -COOCH_3 > -COOH > -CH_2OH$ (C)  $-NH_2 > -CN > -CH_2NHCH_3 > -CH_2NH_2$ (D)  $-Br > -Cl > -CH_2Br > -CH_2Cl$ 

12. Tertiary amines have pyramideal geometry with sp<sup>3</sup> hybridization at nitrogen.

It should be a chiral molecule (assuming lone pair to be a substituent).

Thus, tertiary amines exist as racemic mixture but they cannot be resolved.



This is due to the reason that the energy difference between the isomer is very small (25 kJ mol<sup>-1</sup>). Hence, reapid nitrogen or amine inversin takes palce.



Enantiomers

Tertiary amine N-oxide has four group hence nitrogen inversion is not possible, thus tertiary amine -N-oxide can be resolved.

CH, = CH ≠ NH-CH,

13.

 $\breve{C}H_2 - \breve{C}H = \breve{N}H - CH_3$  (this shows Geometrical isomerism)



15. a & b are tautomers and a & c are resonating structures. 16. Le x is the % of (+) 2-butanol. 13.9 x - 13.9 (100 - x) = -300.x = 39.2, % of d form = 39.2, % of 1 form = 60.8. Hydroxyl bearing carbon is stereogenic centre, 17. **(i)** (ii) 5=2H OH It has no stereogenic cetre. (iii)  $CH_3 - CH_2 - CH_2 - CH_3$  bromine bearing carbon is stereogenic centre. (iv)  $CH_3 - CH_2 - CH - CH_2 - CH_3$  It has no stereogenic centre. 18. (i) 2R, 3R (ii) 2S, 3R 19. Clumer (C) Metamerism (D) Positional 21. (A) Positional (B) Functional (E) Functional (F) Tautomerism 22. Z - I, II, III, VI, VII; E – IV, V, VIII, IX, X, XI, XII 23. (A) 2; (B) 2 24. (A) Tightly on stable keto dur to repulsion between  $\alpha$  – CO groups has 100% enol. > (B) Active 'H' atom/Acidic 'H' atom so has more enolic content (enol stabilise by resonance & Intra molecular H-bonding) >(C) Enolic contents decreases with introduction of  $e^-$  donator group which causes repulsion in enolic form.

- (D) Due to ester group acidic structure of active H decreases & C=C of enol undergoes cross resonance >
- (E) Lowest enolic content because  $\sum C=O$  is more stable than  $\sum C=C \le D$  bond ]























#### EXERCISE - 5 Part # I : AIEEE/JEE-MAIN

17.  $H_3C - HC = CH - CH_2 - Ph$ Both double bonded carbon are differently disubstituted.

Part # II : IIT-JEE ADVANCED

**18.** Molecule is unsymmetrical

n = 2



Total stereoisomers  $= 2^n = 2^2 = 4$ 



Only three stereocentre are present.  $\therefore$  Total isomer =  $2^3 = 8$ But one is optically inactive. (Meso compound)



So optically active = 8 - 1 = 7

