# U.G. 1st Semester Examination - 2019

## CHEMISTRY

## [HONOURS]

**Course Code : CHEM(H)CC-02-T**

Full Marks : 40 Time : $2\frac{1}{2}$ Hours

*The figures in the right-hand margin indicate marks.*

*Candidates are required to give their answers in their own words as far as practicable.*

1. Answer any **five** questions : 2×5=10

a) Compare the stabilities of E- and Z-$HOCH_2CH{=}CHF$ in the vapour phase with reasons.

b) Tub-shaped cyclooctatetraene becomes planar on addition of two electrons to it. Explain.

c) Between cyclopropyl bromide and cyclopentyl bromide which one is expected to form carbocation more easily? Justify your choice.

b) Optical rotation of a compound is +50°. How can you establish that it is not –130° ?

e) Indicate the state of hybridization of the following carbanions with reasons.

$\overset{\ominus}{C}F_3$ $H_2\overset{\ominus}{C}-COMe$

f) 5-1-Phenyl ethyl chloride loses optical activity when distilled. Explain:

g) Compare the nucleophilicity of ammonia and hydrazine with reasons.

h) Boiling point of tert-butanol is lower than that of n-butanol. Explain.

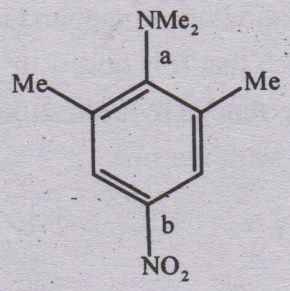
2. Answer any **two** questions: $5\times2=10$

a) i) Draw the $\pi$ M.O pictures of HOMO of pentadienyl cation and LUMO of allyl cation in the ground state.

ii) A stereogenic centre need not necessarily be a centre of chirality. Explain with suitable examples.

iii) How does inductive effect differ from field effect? 2+2+1

b) i) Which C-N bond between a and b in the following molecule is longer? Explain your answer.

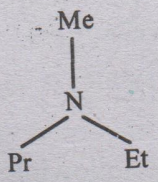


ii) Justify or contradict the following statements with reasons:

A. Specific rotation is more reliable than molecular rotation for the comparison of rotatory powers of chiral molecules of different molecular weights.

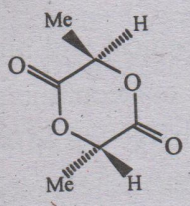
B. Rotation of the Fischer projection formula of R-2-bromobutane by an angle of 90° on the plane of the paper generates its enantiomer. 2+(2+1).

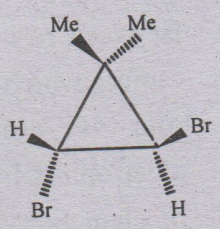
c) i) Comment on the chirality and resolvability of the following compound with reasons.




ii) Dipole moment of 4-nitro aniline is greater than the sum of dipole moments of aniline and nitrobenzene. Explain. $2\frac{1}{2} \times 2$

d) i) Indicate the element(s) of symmetry present in the following molecules.

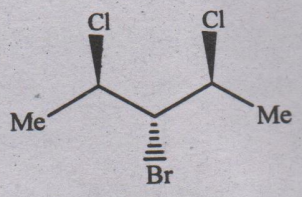


ii) Dichloro carbene reacts with isobutene but dimethoxy carbene fails to react with isobutene. Explain. 2+3

3. Answer any **two** questions : 10×2=20

a) i) Indicate asymmetric and pseudo asymmetric centres in the following molecule. Assign R/S configurational descriptors to the asymmetric centres. How does asymmetric centre differ from pseudoasymmetric centre? Is the molecule chiral? Explain




ii) Explain the following observations.

A. Cyclopentadiene reacts with base much faster than cyclopropene.

B. Boiling point of neopentane is lower than that of n-pentane but reverse is true for their melting points. $5\frac{1}{2}+(2+2\frac{1}{2})$

b) i) Between *tert*-butyl radical and nitro methyl radical which one is nucleophilic and which one is electrophilic? Explain their electrophilicity and nucleophilicity in terms of elementary molecular orbital theory.

ii) $H\text{-}C_2\text{-}H$ Bond angle in propane is smaller than H-C-H bond angle in dichloromethane. Explain.

iii) Compare the polarity and polarisability of C-Cl and C-I bonds with reasons.

iv) Find out the point groups to which the following molecules belong.

*o*-dichlorobenzene, BrCH=C=CHBr, $CHCl_3$.

3+2+2+3

c) i) Indicate whether the following statement is true or false. Justify with suitable examples:

"Aehiral molecules can never have stereogenic centres(s) but chiral molecules will always have all centres stereogenic".

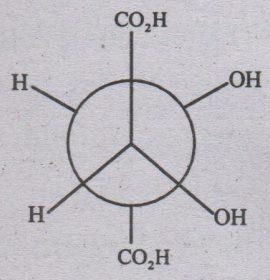
ii) The following molecule has very barrier to rotation as compared to simple ethylene. Explain.

$$(NC)_2C=C(SMe)_2$$

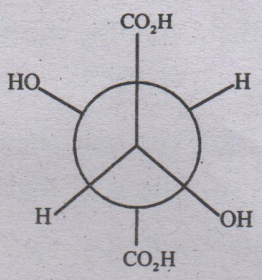
iii) What do you mean by homochirality with respect to absolute stereochemistry? Explain with an example.

iv) From the Newman projections as mentioned below point out which are identical,

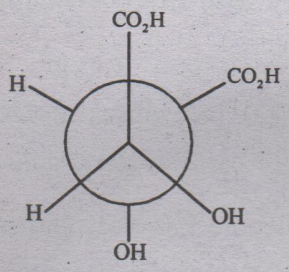
enantiomers, or diastereomers?



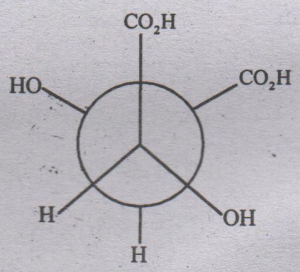

(I)




(II)



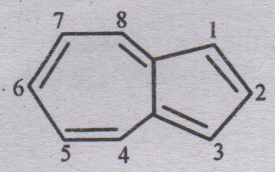

(III)



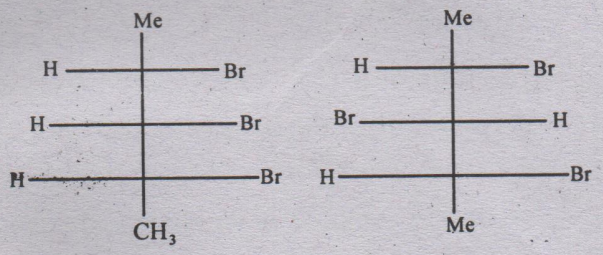

(IV)

3+2+2+3=10

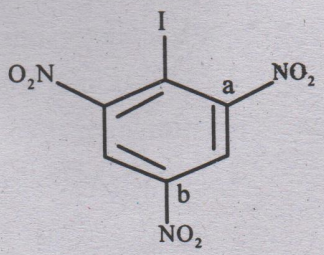
d) i) Azulene is polar and it undergoes electrophilic substitution at C-1 carbon centre. Explain.




ii) Point out the psudoasymmetric centre(s) in the following molecules and designate their pseudoasymmetricity at those points.




iii) The bond lengths 'a' and 'b' are different in the following molecule. Explain.



iv) $Ph_3CCl \xrightarrow[Ether]{Na\,Hg} A \xrightarrow[EtOH]{H_2O\ or} B$

(Solution is deep red) (Color of the solution is discharged)

Explain the above observation and identify A and B. 3+2+3+2=10