U.G. 2nd Semester Examination - 2025

CHEMISTRY

[MAJOR]

Course Code : CHEM-MAT-2

[NEP-2020]

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.

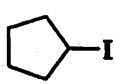
1. Answer any **five** questions: 2×5=10

a) Arrange the following in increasing order of bond energies with reasons.

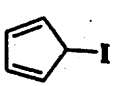
C=O, C=C, C–I, C≡N

b) Represent meso –3, 4-dibromohexane in Newman and Flying Wedge formulas.

c) Compound I undergoes solvolysis when treated with silver perchlorate in propionic acid, whereas compound II does not. Explain.



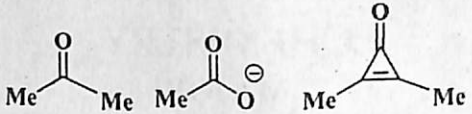
I



II

d) S-2-bromobutane undergoes racemization when treated with chlorine in the presence of sunlight. Explain.

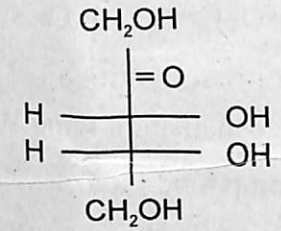
e) Compare the C=O bond distance in the following molecules.



f) What is meant by alternating axis of Symmetry (S_n)? Indicate the point group of hexafluorobenzene.

g) Boiling point of n-pentane is higher than neopentane, but reverse is true for their melting points. Explain.

h) What are the absolute configurations at the two chiral centres in D-ribulose?



2. Answer any **two** questions: 5×2=10

a) i) What do you mean by internal compensation in optical activity? Give an example of internally compensated optically inactive molecule.

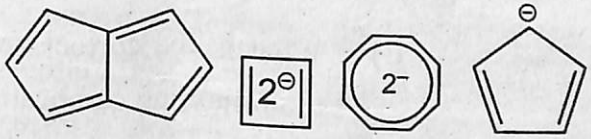
ii) Draw all the possible stereoisomers of the following compound and comment on their optical activity.

MeCHBr – CH = CHMe 2+3

b) i) What is resonance energy? Calculate the resonance energy of 1,3-butadiene if its heat of hydrogenation is 57 kcal/mole and that of 1-butene is 30.3 kcal/mole.

ii) Optically pure sample of R-2-butanol show the specific rotation of +13.6°. What realtive molar proportion of S-2-butanol and R-2-butanol would give a specific rotation of +6.8°? What is the optical purity of the above mixture? 3+2

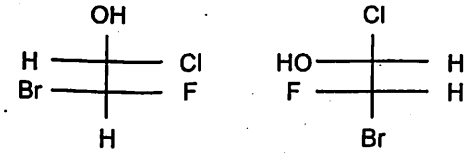
c) i) Justify with reasons, the following compounds as aromatic, antiaromatic or non-aromatic.



ii) Draw the π-MO diagram indicating the HOMO and LUMO of allyl cation and 1,3-butadiene. 2+3

d) i) How a carbene is formed? What is the shape, bond angle and state of hybridization of triplet carbene?

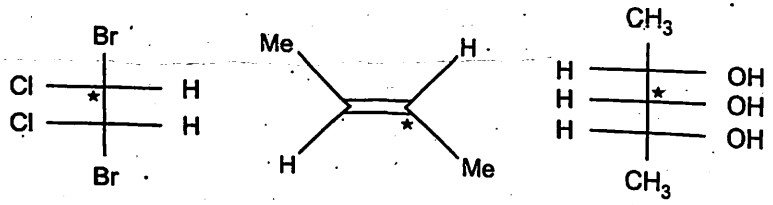
ii) Are the following molecules enantiomers, diastereomers or the same?



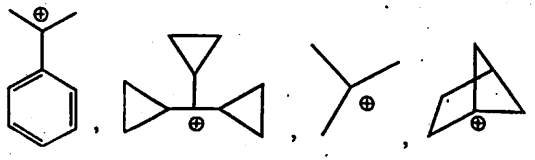
3+2

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

a) i) Outline the differences between stereogenecity and chirotopicity. Comment on the stereogenecity and chirotopicity of the labelled carbons in the following molecules.

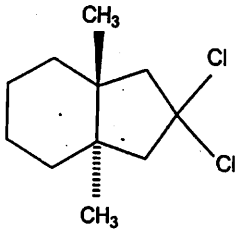


ii) What is the correct order of stability of the following carbocations and why?



iii) α-hydrogen atom of (S)-α-chloropropionic acid is replaced with bromine with retention of configuration. Write the structure of the product.

iv) Indicate the number of stereogenic centres in



(2+3)+2+2+1=10

b) i) Which one of the following pair has the higher dipole moment and why?

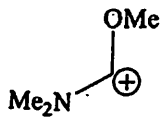
p-Diacetylbenzene and p-dicyanobenzene.

ii) Specific rotation is more reliable than molecular rotation for the comparison of rotatory powers of chiral molecules of different molecular weights. Justify or contradict.

iii) Compare with proper justification the stability of Z-2-butene and E-2-butene.

iv) Write a short note on Baeyer's Strain theory.

v) Write down all the canonical forms of the following carbocation and indicate the most contributing one with reason.



2+2+2+2+2=10

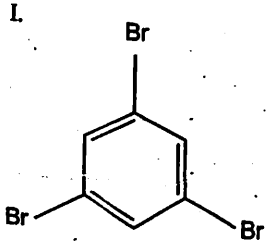
c) i) Dipole moment of 4-nitroaniline is greater than the sum of dipole moments of aniline and nitrobenzene. Explain.

ii) Explain invertomerism with proper example. Outline the chemical method or resolution of a racemic mixture of 1-phenyl-2-propanamine.

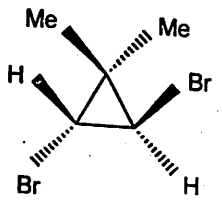
iii) Though NO_2 group is more powerful electron withdrawing group than CN, trinitromethyl carbanion is less stable than tricyanomethyl carbanion. Give explanation. 2+(2+3)+3=10

d) i) Indicate the type of symmetry elements in the following molecules:

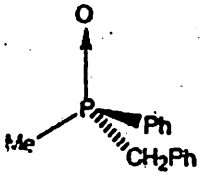
I.

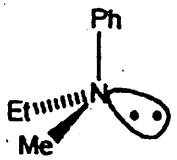


II.



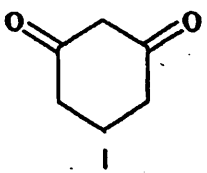
ii) Justify whether the following compounds are resolvable or not.



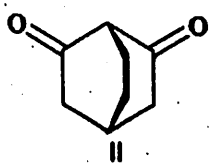


iii) Between *tert*-butyl radical and nitro methyl radical, which one is electrophilic and which is nucleophilic? Explain their electrophilicity and nucleophilicity in terms of elementary molecular orbital theory.

iv) Explain the fact why compound I is readily soluble in alkali but compound II is not.



I



II

3+2+3+2=10