

Class : II PG
Major : Chemistry

Max. Marks: 60
Time: 3 Hours

12MCHC12 Spectroscopy I

Part - A
Answer the following

10 x ½ = 5

Choose the correct answer

- In which of the following compounds $n-\pi^*$ transition takes place
a) CH_4 b) CH_3Cl c) $\text{H}_2\text{C}=\text{O}$ d) Cl_2
- Number of conjugated double bonds in β -Carotene is
a) 10 b) 11 c) 12 d) 9
- Coupling constant (J) is zero for
a) Vicinal coupling b) germinal coupling c) virtual coupling d) ortho coupling
- How many different types of protons are in allyl bromide
a) 3 b) 4 c) 2 d) 5
- The order of ^{13}C - chemical shifts for the following functional groups
a) $\text{C}=\text{O} > \text{C}=\text{C} > \text{C}-\text{X} > \text{alkanes}$ b) $\text{C}=\text{C} > \text{C}=\text{O} > \text{C}-\text{X} > \text{alkanes}$
c) $\text{alkanes} > \text{C}-\text{X} > \text{C}=\text{C} > \text{C}=\text{O}$ d) $\text{C}-\text{X} > \text{C}=\text{O} > \text{C}=\text{C} > \text{alkanes}$
- The nuclear spin of ^{13}C and ^{12}C atoms are
a) $+1/2, -1/2$ b) $-1/2, +1/2$ c) $+1/2, 0$ d) $0, +1/2$
- Which of the following molecule is ESR active?
a) N_2 b) O_2 c) CO d) H_2
- Magnetic dipole selection rule for ESR spectra is
a) $\Delta m_j = +1$ b) $\Delta m_j = -1$ c) $\Delta m_j = \pm 1$ d) $\Delta m_j = \pm 2$
- Which of the following metal is not used as anode metal in X-ray diffraction?
a) Cu b) Mo c) Co d) Fe
- Total number of bravias lattices for crystal system is
a) 7 b) 14 c) 13 d) 23

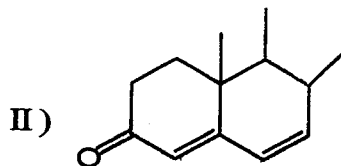
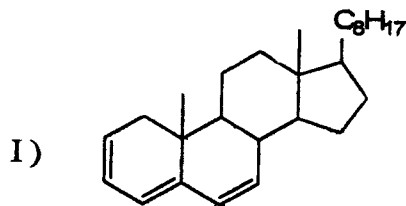
Part - B

5 x 4 = 20

Answer ALL questions

Each answer should not exceed 200 words or one page

11. (a) Calculate the λ_{\max} for the following compounds



(OR)

(b) Describe the various absorption bands exhibited by benzene.

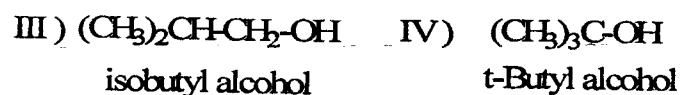
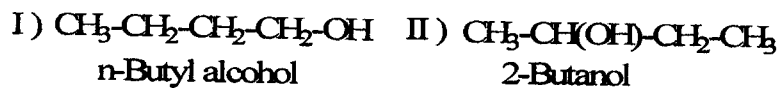
12. (a) i) Explain why the aromatic protons are more deshielded than the ethylenic protons although both the types of protons are attached to sp^2 hybridised carbons.

ii) How would you distinguish cyclohexanol from chlorocyclohexane on the basis of PMR spectroscopy?

(OR)

(b) Explain the terms (i) spin - spin coupling and (ii) double resonance.

13. (a) How the number and position of ^{13}C nmr signals can help in the identification of the following four isomeric alcohols. $C_4H_{10}O$.



(OR)

(b) Describe the theory of COSY .

14. (a) Write the significance of g-value in ESR spectrum.

(OR)

(b) Write notes on Kramers degeneracy and Zero field splitting

15. (a) Derive Braggs equation.

(OR)

(b) Differentiate between X-ray diffraction and Neutron diffraction.

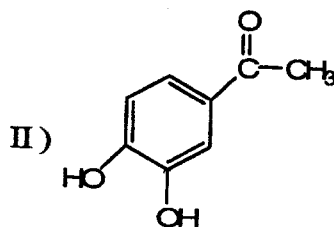
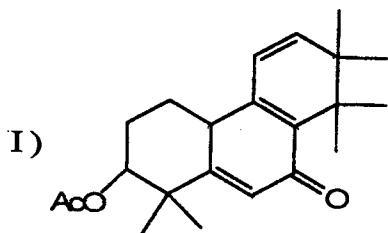
Part - C

5 x 7 = 35

Answer ALL questions

Each answer should not exceed 600 words or three pages

16. (a) i) Calculate the absorption maximum for the following compounds.



ii) Explain why 1-acetylcyclohexene absorbs at 233 nm (ϵ_{\max} 13000), while 2-methyl-1-acetyl cyclohexene absorbs at 249 nm (ϵ_{\max} 6890) with much reduced intensity.

(OR)

(b) i) Draw the structural formulae that are consistent with the following observation

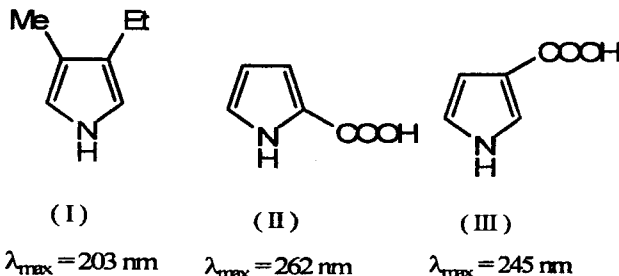
I) an acid $C_7H_4O_2Cl_2$ shows a UV maximum at 242 nm

II) a ketone $C_8H_{14}O$ shows a UV maximum at 248 nm

III) an aldehyde $C_8H_{12}O$ absorbs in the UV with λ_{max} of 244 nm

ii) The pyrrole derivatives (I-III) show the indicated wavelength of absorption.

Explain.



17. (a) Discuss the relationship between dihedral angle and coupling constant making use of Karplus equation.

(OR)

(b) i) The PMR spectrum of ethyl 2-butenoate $CH_3CH=CHCO_2CH_2CH_3$, shows the following signals $\delta = 6.95$ (d, $J = 16, 6.8 \text{ Hz}$, 1H), 5.81 (d, $J = 16, 1.7 \text{ Hz}$, 1H), 4.13 (q, $J = 7 \text{ Hz}$, 2H), 1.88 (d, $J = 6.8, 1.7 \text{ Hz}$, 3H) and 1.24 (t, $J = 7 \text{ Hz}$, 3H) ppm. Assign these δ values to various hydrogens and tell if the double bond is cis or trans substituted.

ii) What are shift reagents? Explain its uses with specific examples.

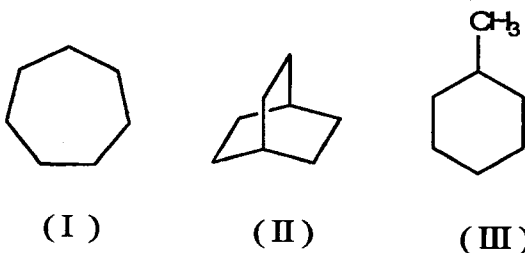
18. (a) i) Predict the chemical shift positions for the carbons in sec-butyl acetate and isobutyl acetate.

ii) Explain the significant effect of hybridization of carbon atom on chemical shifts.

(OR)

(b) i) Explain briefly the α , β and γ effect in ^{13}C nmr spectroscopy with suitable examples.

ii) How many peaks you expect in the proton decoupled ^{13}C nmr of I – II?



19. (a) Discuss the applications of ESR spectroscopy.

(OR)

(b) What is hyperfine splitting? Discuss the factors affecting the intensity, position and multiplet structure of hyperfine splitting.

20. (a) Discuss the experimental methods used for the determination of structure of crystals.

(OR)

(b) Explain the basic principles and applications of Neutron diffraction.
