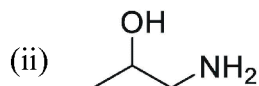


3. (a) How is UV-Visible spectroscopy helpful in detection of functional group in organic compounds ? **3**
- (b) Discuss the different ionisation techniques being used in mass spectrometry, highlighting the advantages and disadvantages of each. **6**

Section B

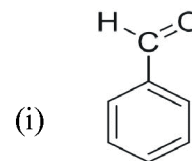
4. (a) [18] Annulene shows two signals in its $^1\text{H-NMR}$ spectrum, one at 9.25 ppm and other upfield at -2.88 ppm. What hydrogens are responsible for each of the signals ? Also discuss about the factor responsible for these chemical shift values. **3**
- (b) How the $^1\text{H-NMR}$ spectra of four isomeric forms of compounds with molecular formula $\text{C}_3\text{H}_6\text{Br}_2$ differ ? **3**
- (c) How many signals will you get in the $^1\text{H-NMR}$ of the following compounds and mention the expected multiplicity for each proton ? **3**

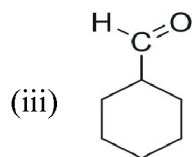
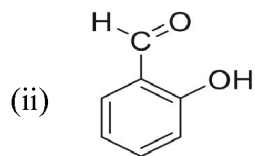


Note : Attempt *Five* questions in all, selecting at least *one* question from each Section. Q. No. **1** is compulsory. All questions carry equal marks.

(Compulsory Question)

1. (a) Why is an O-H stretch more intense than N-H stretch in IR ? **1**
- (b) How an increase in solvent polarity shift $n-\pi^*$ and $\pi-\sigma^*$ absorption bands ? **1**
- (c) Arrange the following compounds in order of decreasing frequency of carbonyl absorption in their IR spectra : **1**



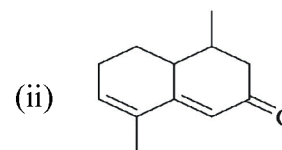
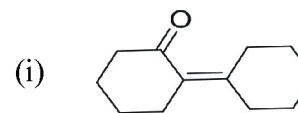


- (d) Primary alcohols have a strong peak at $m/z = 31$.
What fragment is responsible for this peak ? **1**
- (e) What m/z value would you predict for the base peak in the mass spectrum of 3-methyl pentane ?
1
- (f) A signal has been reported to occur at 120 Hz downfield from TMS in an NMR spectrometer with a 300-MHz operating frequency. Then : **2**
- What is its chemical shift ?
 - What would its chemical shift be in an instrument operating at 100 MHz ?
 - How many Hz downfield from TMS would the signal be in an 100 MHz spectrometer ?

- (g) Compound A, with molecular formula C_4H_9Cl , shows two signals in its ^{13}C -NMR spectrum. Compound B, an isomer of compound A, shows four signals and in the spin coupled mode, the signal most downfield is doublet. Identify compounds A and B. **2**

Section A

2. (a) Using Woodward and Fisher's rule, calculate the expected λ_{max} for the given compounds : **3**



- (b) Discuss the fragmentation pattern of 4-n-butyltoluene involving (i) benzylic fission, (ii) the McLafferty rearrangement. Label the ions formed as cations or radical cations along with their masses. **3**
- (c) What identifying characteristics would be present in the mass spectrum of a compound having single halogen atom or more halogens of same kind or different kinds ? **3**

7. (a) Briefly introduce the terms (i) Fermi resonance and (ii) Overtones, used in IR spectroscopy with suitable examples. **3**
- (b) Deduce the structure of a compound of molecular formula C_3H_7NO with the following spectral data : **6**
 M.F. C_3H_7NO
 UV : λ_{max} 238 nm, ϵ_{max} 10500
 IR : ν_{max} cm^{-1} 3428, 2941-2857, 1681 and 1452
 1H NMR : δ 1.9 (3H, s), 2.7(3H, s) and 8.13 (1H, s)
 ^{13}C -NMR (off resonance decoupled) : Two quartets and one singlet.
 The singlet at δ 176.

5. Briefly discuss the following :

- (a) Virtual coupling **3**
- (b) Nuclear Overhauser effect **3**
- (c) Simplification of complex NMR spectra through chemical methods. **3**

Section C

6. (a) How proton noise decoupled ^{13}C -NMR spectroscopy be used to distinguish the following : **3**
- (i) 1,2-, 1,3-, and 1,4-dinitrobenzenes
- (ii) 1-Methylcyclohexene and 1-Methylenecyclohexane
- (iii) Acetone and Methylacetate
- (b) Compare the sensitivity and chemical shifts values of 1H and ^{13}C -NMR spectroscopy. **3**
- (c) How is IR spectroscopy used to differentiate the following : **3**

