Exam. Code : 210401
Subject Code : 3809

M.Sc. (Chemistry) 1st Semester

SPECTROSCOPY A : TECHNIQUES FOR STRUCTURE ELUCIDATION OF ORGANIC COMPOUNDS

Paper—Course-IV

Time Allowed—3 Hours] [Maximum Marks—75

Note :— The candidate is required to attempt **five** questions in all attempting at least **one** question from each Section. The fifth question may be attempted from any Section. All questions carry equal marks.

SECTION—A

1. (a) Giving suitable examples explain the terms chemical and magnetic equivalence.

   (b) Discuss the ^{1}HNMR spectra of acetyl acetone.

   (c) Giving suitable example describe the significance of nuclear magnetic double resonance.

   (d) What is the typical chemical shift of ethylenic protons ? Provide a suitable justification. 3+4+4+4

2. (a) Can we differentiate between axial and equatorial protons of 1-chlorocyclohexane using ^{1}HNMR. Justify your answer.

(b) What is coupling constant ? Describe the mechanism of coupling. Discuss the use of coupling constants in determining the o^-, m^-, and p^- substituents of aromatic ring.

(c) What are fluxional molecules ? Explain giving suitable examples.

(d) In a PMR spectrum, how will you verify that a particular signal arises from the proton of –NH ?

4+4+5+2

SECTION—B

3. (a) Discuss how mass spectrometry can be used to distinguish between 1-butanol,
2-butanol and 2-methyl-2 propanol.

(b) Describe various aspects used to identify the mass spectra of amines.

(c) Explain giving examples the Nitrogen rule.

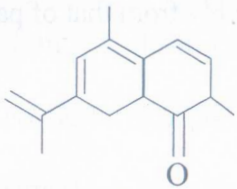
(d) Give the characteristic pattern observed in mass spectra of a compound having chlorine atoms.

6+3+3+3

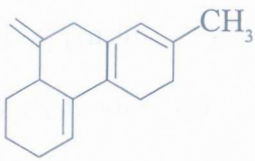
4. (a) Describe giving examples, the retro Diels Alder fragmentation pattern.

(b) How will you explain the formation of an ion at m/z 94 in the mass spectrum of $C_6H_5OCH_2CH_3$?

(c) Using Woodward — Fieser rules, calculate the values of absorption maxima for the following compounds :—



(i)



(ii)

(d) Define giving examples the terms hyperchromic and bathochromic shifts. 3+3+6+3

SECTION—C

5. (a) With the help of suitable example in each of the following explain their effect on characteristic IR stretching frequencies.

(i) Steric effect

(ii) H-bonding

(iii) Resonance.

(b) Taking a suitable example discuss why β-diketones frequently exists as mixtures of enolic and ketonic forms ? Mention the various stretching and bending vibrations encountered in both these forms.

(c) Give the equation for calculating the frequency of vibration of a diatomic molecule. 9+4+2

6. (a) Explain why some of the fundamental vibrations are infrared active while others are not ?

(b) Does carbonyl absorption frequency of the carboxylate anion differs considerably from that of parent acid ? Justify your answer.

(c) Giving reasons :—

(i) Arrange Acetic acid, acetamide, acetyl chloride, ethylacetate and acetic anhydride in order of their decreasing carbonyl frequencies.

(ii) Arrange nitrobenzene, p-nitroacetophenone and p-methoxynitrobenzene in order of their decreasing nitro frequencies. 3+2+10

SECTION—D

7. (a) Giving suitable justification, deduce the structure of a compound with molecular formula $C_5H_8O_2$ having following spectral data :—

UV, λ_{max} : shows no intense UV absorption above 200 nm

IR (cm^{-1}) : 1740 (important band)

^{1}HNMR δ : 4.0 (2H, t), 2.35(1H, m), 2.20 (2H, m), 1.15 (3H, d)

(b) A compound with molecular formula $C_6H_{12}O_2$ gives the following spectral data :—

UV, λ_{max} : Transparent above 200 nm

IR (cm^{-1}) : 1740 (s), 1160(s)

^{1}HNMR δ : 3.6 (3H, s), 1.2(9H, s)

MS[m/z] : 116, 85, 59, 31

Giving suitable explanation, assign the structure to the compound. 7.5+7.5

8. (a) An organic compound containing carbon, hydrogen and oxygen only showed abundant mass spectral peaks at M^+ (m/z 136), base peak (m/z 91) and fragment ion peak at (m/z 45). Other spectral data are given below :

UV, λ_{max} : 229 nm and 257 nm

IR (cm^{-1}) : 1710 (s), 3000 – 2500 (br)

^{1}HNMR δ : 7.2 (5H, s), 3.5(2H, s), 11.6 (1H, s) (exchangeable with D_2O)

Giving proper explanation, deduce the structure of the compound.

(b) Deduce the structure of the compound with M.F. $C_{10}H_{13}NO_2$ having the following spectral data :

UV, λ_{max} : K-band in ethanol appears at 290 nm

IR (cm^{-1}) : 3402, 3318, 3025, 1695, 1602, 1580

^{1}HNMR δ : 7.9 (2H, d, J = 8 Hz), 6.7(2H, d, J = 8Hz), 4.75 (1H, septet), 4.2 (2H, Br), 1.25(6H, d)

Justify your answer. Write down important peaks observed in mass spectrum. 7.5+7.5