

Exam. Code : 210401
Subject Code : 4927

M.Sc. Chemistry 1st Semester (Batch 2021-23)
SPECTROSCOPY A : TECHNIQUES IN
STRUCTURE ELUCIDATION OF ORGANIC
COMPOUNDS

Paper : Course-IV

Time Allowed—3 Hours]

[Maximum Marks—75

Note :— Attempt FIVE questions in all, selecting at least ONE question from each section. The fifth question may be attempted from any section. All questions carry equal marks.

SECTION—A

- (a) Giving examples, discuss how coupling constant is related to dihedral angle.
(b) Describe ring current and anisotropic effect.
(c) Discuss the NMR spectra of cinnamaldehyde. 5×3
- Discuss the following giving examples :
 - Fluxional molecule
 - Lanthanide Shift reagents
 - How can the -NH/-OH protons can be identified using ¹H NMR technique. 5×3

SECTION—B

3. (a) How will you distinguish between the following on the basis of mass spectrometry :

(i) Three isomeric butanols i.e. 1-butanol, 2-butanol and 2-methyl-2-propanol

(ii) 3-methyl and 4-methylcyclohexene.

(b) Which neutral fragment is responsible for the following mass losses from the molecular ion :

17, 18, 20, 26, 27, 30. 10+5

4. (a) How would you distinguish among ethylamine, diethylamine and triethylamine on the basis of their mass spectral studies ?

(b) Explain the following patterns in mass spectra :

(i) Alkylanilines exhibit the base peak at m/z 106.

(ii) Difference of $m/z = 28$ in the mass spectral peaks of pent-2-one and 1-butanoic acid.

(c) Discuss giving example retro-diels alder reaction.

5×3

SECTION—C

5. (a) Giving suitable examples describe hyperchromic and hypochromic shift.

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(b) Explain Beer-Lambert law. Also define Molar extinction coefficient.

(c) Discuss, citing suitable example, the role of IR spectroscopy in determining the inter-molecular and intra-molecular hydrogen bonding.

(d) What is the difference between carbonyl stretching frequencies in IR spectra of the following pair ?

$\text{CH}_3\text{CH}_2\text{CO-OC}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{CO-OCH}_2\text{CH}_3$

4+4+4+3

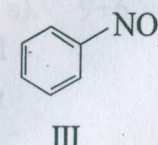
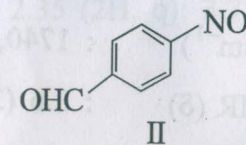
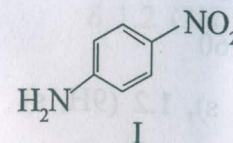
6. (a) Giving suitable examples discuss the effect of following on ultraviolet and visible spectra :

(i) Solvent.

(ii) Steric hinderance.

(b) With the help of suitable examples discuss how IR spectroscopy is helpful in studying reaction Kinetics.

(c) Giving justification, arrange the following compounds in ascending order of the Nitro-stretching absorptions.



5×3

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SECTION—D

7. (a) An organic compound containing C, H, N and a halogen gave the following spectral analysis :

UV, λ_{\max} : 240 (ϵ 8000); 300 (ϵ 100) nm

IR (ν cm^{-1}) : 3400, 3300, 3200 (w), 2900, 1620, 1600, 1500, 1380, 880, 820

^1H NMR (δ) : 7.2 (1H, d, $J = 9$ Hz); 6.5 (1H, d, 3.5 Hz); 6.3 (1H, dd, $J = 9$ and 3.5 Hz); 3.4 (2H, broad s, removed on D_2O shaking) and 2.30 (3H, s)

Mass, m/z (RA) : 187 (90), 185 (90), 186 (20), 184 (20), 160 (10), 158 (10), 106 (100)

Assign the structure to the compound and explain the spectral data.

- (b) 2, 2-Dimethylcyclopropanone undergoes ring opening when attacked by methoxide ion, the product obtained possess the following spectral properties :

IR (ν cm^{-1}) : 1740, 1160

^1H NMR (δ) : 3.6 (3H, s), 1.2 (9H, s)

Mass, m/z : 116, 85, 59, 31

Deduce the structure of the product and explain its formation. Also write the structure of the other possible product. 9+6

8. (a) Elucidate and explain the structure of a compound with the following spectral characteristics and explain the spectral data :

UV : λ_{\max} 245 nm

IR (ν cm^{-1}) : 1710, 1725

Mass (m/z) : 130, 87, 85, 43 (base peak), 29

^1H NMR (δ) : 4.20 (2H, s); 3.5 (2H, q); 2.3 (3H, s); 1.3 (3H, t)

In addition, the compound exhibits tiny peaks at 5.0 and 12.0.

- (b) Three isomeric compounds A, B and C have molecular formula $\text{C}_4\text{H}_8\text{O}_2$. All of them show a strong absorption at 1730 cm^{-1} in their IR spectra. Write down the structure of the compound with following ^1H NMR spectral data :

δ 1.2 (3H, t); 2.35 (2H, q); 3.7 (3H, s). 9+6