ST JOSEPH'S UNIVERSITY, BENGALURU -27
M.Sc. (Chemistry) – II SEMESTER
SEMESTER EXAMINATION: APRIL 2024
(Examination conducted in May/June 2024)
CH 8422: Spectroscopy II
(for current batch students only)

Time: 2 Hours   **Max. Marks: 50**
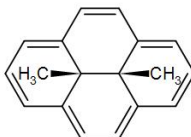### This question paper contains FIVE printed pages and THREE parts.
(Spectral data is given towards the end of this paper.)
Part A
Answer any EIGHT questions. Each question carries TWO marks.   (8 x 2= 16)

1. Explain why the two equivalent methyl groups in the ^{1}H-NMR spectrum of the following compound appear at -4.25 ppm far upfield of TMS.


2. Sketch a schematic diagram to represent the four general stages involved in any 2D NMR experiment.
3. Draw the ^{1}H-^{13}C correlation HETCOR spectrum of 2-nitropropane.
4. What information do you obtain from DEPT-135 data in ^{13}C-NMR spectroscopy?
5. How does conjugation affect the position of λ_{max} of compounds in UV-visible spectrum?
6. What is the 'fingerprint' region in an IR spectrum? What is its main application in the structural analysis of organic compounds?
7. Name the internal standard employed in EPR spectral analysis and provide reason for its selection.
8. Between CH_3^+ and $C_2H_5^+$, which ion would experience the highest deflection in a mass spectrometer? Provide reason for your selection.
9. Can you elaborate on why the base peak for *t*-butyl alcohol appears at m/z = 57?
10. Arrange the following compounds in increasing order of their isomer shift values. Provide appropriate justification.
$$Fe, Fe^{2+}, Fe^{3+}$$

Part B
Answer any TWO questions. Each question carries TWELVE marks.   (2 x 12= 24)

11. (a) Using a tree diagram construct the splitting pattern that would be observed for H_a and H_b in the following compound. J_{ab} = 2 Hz; J_{ac} = 15 Hz; J_{bc} = 7 Hz.

(b) How many ^{13}C signals (i.e. chemically distinct C atoms) would you expect for each of the following compounds?

(i) (ii) (iii) (iv)
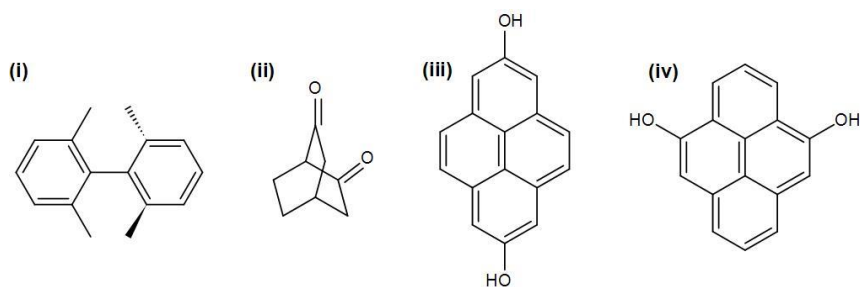
(c) A methine carbon gives an inverted peak in an attached proton test (APT) experiment. Explain the reason. (4+4+4)

12. (a) Give the number of chemically non-equivalent protons that are expected in ^1H-NMR spectra of the following compounds.

(i) (ii) (iii)
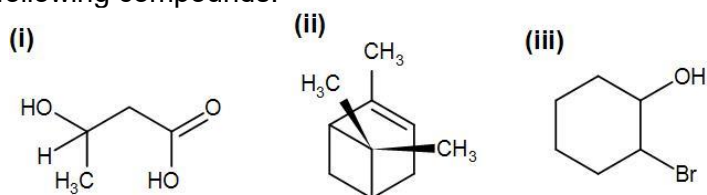
(b) Explain how polar solvents influence π-π^* and n-π^* transitions in organic molecules.

(c) Compare and contrast the advantages and limitations of ENDOR and ELDOR techniques in investigating paramagnetic species and molecular environments.

(d) In Mossbauer studies, a source emitting at 14.4 KeV (3.48×10^{18}Hz) had to be moved towards absorber at 2.2 mm/s for resonance. Calculate the shift of frequency between source and absorber. (3+3+3+3)

13. (a) Calculate the number of hyperfine lines observed for the radicals of the following molecules.

(I) (ii)
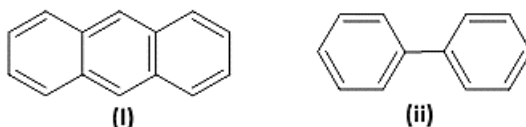
(b) Elucidate the mechanism to show why the presence of γ-hydrogen is crucial for facilitating the McLafferty rearrangement.

(c) The mass spectrum of the product formed in the following reaction exhibits M+, M+2 and M+4 peaks in the intensity of 1:2:1. Identify the HX and product 'P' in the following reaction with proper justification.

(Note: In the following reaction –OH is replaced by 'X')

(4+4+4)
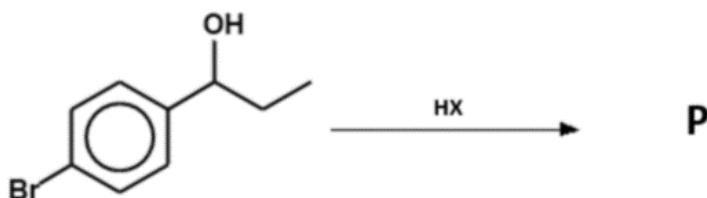
Answer any <u>TWO</u> questions. Each question carries <u>FIVE</u> marks.　　　　　(2 x 5= 10)

14. (a) Among the following isomers of C_4H_6 given below, the compound which exhibits an absorption band at 3300 cm^{-1} is

　　　　(i) 1,3 butadiene (ii) 1-Butyne (iii) 2-Butyne (iv) Cyclobutene

(b) Match the following three compounds to the corresponding stretching frequencies at 1750, 1770, and 1800 cm^{-1}. Justify your answer.
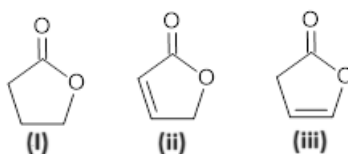
　　(I)　　　　　(ii)　　　　　(iii)　　　　　　　　　(2+3)

15. Deduce the structure of an organic compound with the molecular formula $C_{10}H_9NO_2$. The given spectral data is

　　IR:　　　　2210, 1724 cm^{-1}

　　^{1}H NMR:　1.4 (triplet, 3H, J = 7.1 Hz)

　　　　　　　　4.4 (quartet, 2H, J = 7.1 Hz)

　　　　　　　　7.7 (doublet, 2H, J = 7.0 Hz)

　　　　　　　　8.2 (doublet, 2H, J = 7.0 Hz) ppm

　　^{13}C NMR:　16, 62, 118, 119, 125, 126, 127 and 168 ppm.

16. Determine the structure of a compound with formula $C_6H_5Br_2N$. The proton NMR spectrum is shown. The infrared spectrum has medium bands at 3420 and 3315 cm^{-1} and a strong band at 1612 cm^{-1}. The normal carbon, DEPT-135, and DEPT-90 spectra data are tabulated. Show all logical steps in analysing the spectral data and propose possible structure of the compound.

Normal carbon (ppm)	DEPT-135	DEPT-90
109	No peak	No peak
119	Positive	Positive
132	Positive	Positive
142	No peak	No peak
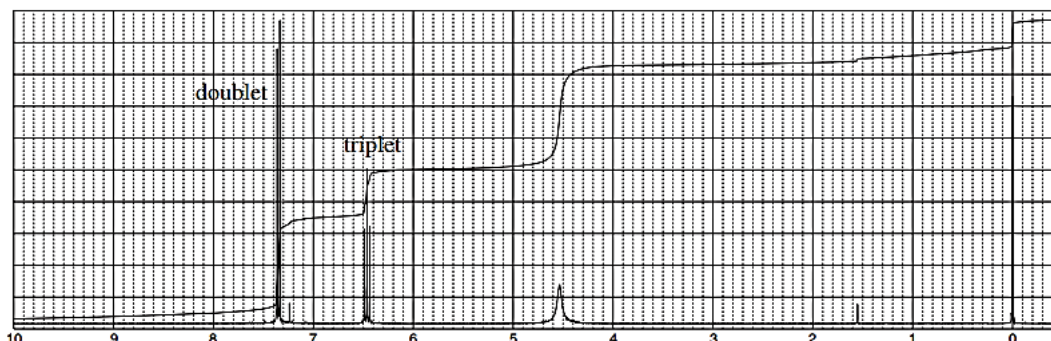
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Approximate IR Absorption Frequencies

Bond	Frequency (cm^{-1})	Intensity
O–H (alcohol)	3650–3200	Strong, broad
O–H (carboxylic acid)	3300–2500	Strong, very broad
N–H	3500–3300	Medium, broad
C–H	3300–2700	Medium
C≡N	2260–2220	Medium
C≡C	2260–2100	Medium to weak
C=O	1780–1650	Strong
C–O	1250–1050	Strong

Approximate ^{1}H NMR Chemical Shifts

Hydrogen	δ (ppm)
CH$_3$	0.8–1.0
CH$_2$	1.2–1.5
CH	1.4–1.7
C=C–CH$_x$	1.7–2.3
O=C–CH$_x$	2.0–2.7
Ph–CH$_x$	2.3–3.0
≡C–H	2.5
R$_2$N–CH$_x$	2.0–2.7
I–CH$_x$	3.2
Br–CH$_x$	3.4
Cl–CH$_x$	3.5
F–CH$_x$	4.4
O–CH$_x$	3.2–3.8
C=CH	4.5–7.5
Ar–H	6.8–8.5
O=CH	9.0–10.0
ROH	1.0–5.5
ArOH	4.0–12.0
RNH$_x$	0.5–5.0
CONH$_x$	5.0–10.0
RCOOH	10–13

Approximate ^{13}C NMR Chemical Shifts

Carbon	δ (ppm)
Alkanes	
Methyl	0–30
Methylene	15–55
Methine	25–55
Quaternary	30–40
Alkenes	
C=C	80–145
Alkynes	
C≡C	70–90
Aromatics	110–170
Benzene	128.7
Alcohols, Ethers	
C–O	50–90
Amines	
C–N	40–60
Halogens	
C–F	70–80
C–Cl	25–50
C–Br	10–40
C–I	−20–10
Carbonyls, C=O	
R$_2$C=O	190–220
RXC=O (X = O or N)	150–180

Empirical Rules for Dienes

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	253 nm	214 nm
Increments for		
Double bond for extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar grouping		
-OCOCH$_3$	0	0
-OR	6	6
-Cl, -Br	5	5
-NR$_2$	60	60

Empirical Rues for Enones

Base values:	
Six-membered ring or acyclic parent enone	215 nm
Five-membered ring	202 nm
Acyclic dienone	245 nm
Increments for:	
Double-bond-extending conjugation	30
Alkyl group or ring residue	α 10
	γ and higher 18
Polar grouping:	
-OH	α 35
	β 30
	δ 50
-OCOCH$_3$	α, β, δ = 6
-OCH$_3$	α 35
	β 30
	γ 17
	δ 31
-Cl	α 15
	β 30
-Br	α 25
	β 30
-NH$_2$	β 95
Exocyclic double bond	5
Homocyclic diene component	39