



III Semester M.Sc. Degree Examination, December 2014
(2010 – 11 Scheme) (NS)
CHEMISTRY
C – 304 : Spectroscopy – II (Common to AC/IC/OC/PC)

Time : 3 Hours

Max. Marks : 80

Instruction: Answer question 1 and **any five** of the remaining.

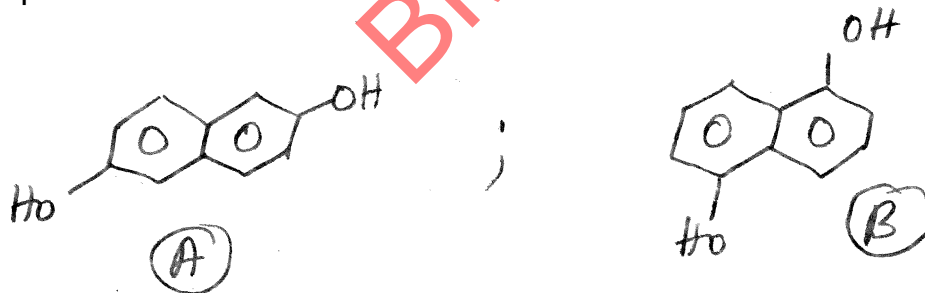
1. Answer **any ten** of the following :

(10×2=20)

a) Write the structure of a compound with the following data,

Molecular formula: C_4H_6 UV λ_{max} : 214 nm (EtoH);

IR : 3012, 1839, 1601, 1040 and 922 cm^{-1} .

b) Derive an expression for W_C in an ICR – MS instrument.c) How are the tautomers of methyl acetoacetate distinguished by 1H NMR ?d) Indicate the number of signals appearing in the broad-band decoupled ^{13}C NMR spectra of A and Be) The EI – MS of chlorobenzene gives base peak at 77, whereas benzyl chloride gives at $\frac{m}{e} > 91$. Why ?f) C_6H_8 may exist as two reactive intermediates : Cyclohexane and 1,2 – cyclohexadiene. Write the prominent Raman bands for the two structural isomers.



- g) Draw a diagram to show the anisotropic effects in C_6H_6 while recording 1H NMR.
- h) Justify the use of derivatives of cinnamic acid for matrix preparations in MALDI ionizations.
- i) Sketch the high resolution Pascal triangle for the coupling of protons in the isopropyl group.
- j) Molecular formula : C_8H_7N shows IR bands at 3097, 2247, 1579 and 1401 cm^{-1} . Deduce the structure of the compound and assign the values.
- k) The mass spectrum of benzene shows peaks at $\frac{m}{e}$, 78, 77, 51, 33.8 and 26. Account for the fragmentation.
- l) The protons attached to the nitrogen of profrionamide appear as a broad peak at δ 6.51 in its 1HNMR . Why ?
2. a) Outline Scott's rules to predict the λ_{max} of aromatic carbonyl compounds.
- b) Diamond, crystalline silicon and crystalline germanium show a strong line at 1332 , 520 and 300 cm^{-1} respectively in their Roman spectra. Explain the positions of the lines with respect to each other based on mass effect.
- c) Explain Nuclear Overhauser Effect (NOE) with suitable example. (4+4+4=12)
3. a) i) Mention the criteria required for a 1HNMR spectrum to be classified as first order.
- ii) Write and explain the first order splitting rules of 1H NMR.
- b) Sketch the Karplus curve and highlight its importance.
- c) Deduce the structure of an organic compound from the following data and assign the values :
- Mol. formula : $C_4H_6O_2$
- UV λ_{max} : 218 nm ($\epsilon = 10,000$)
- IR : $3400 - 2800$ (m, br), 1719 , 1641 and 1111 cm^{-1}
- $^{13}CNMR$: δ : 172.4 , 147.6 , 122.4 and 18.0 (6+3+3=12)

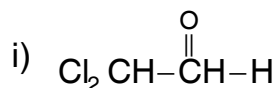


4. a) Discuss the factors effecting chemical shift in

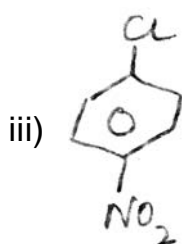
i) ^1H NMR and

ii) ^{13}C NMR

b) Predict the positions of the signals and designate the spin systems for



ii) $\text{CH}_3\text{CH}_2\text{Br}$ and



c) Illustrate McLafferty + 1 rearrangement with suitable example. **(6+3+3=12)**

5. a) Give an account of the instrumentation and working of a quadrupolar mass spectrometer.

b) A compound has molecular formula $\text{C}_5\text{H}_{12}\text{O}_4$. It exhibits a broad band between $3400 - 3100\text{ cm}^{-1}$ in its IR spectrum. The proton NMR showed two singlets at $\delta : 3.33$ and 3.29 with integral ratio $1 : 2$ respectively. Deduce the structure of the compound.

c) How are lanthanide shift reagents useful in simplifying complex proton NMR spectra ? **(5+4+3=12)**

6. a) State and explain :

i) Stevenson – Audier rule

ii) Nitrogen rule

b) Discuss the following :

i) Fermi resonance

ii) Usefulness of deuterium exchange in NMR

iii) FAB method for production of ions.

(3+9=12)



7. a) Deduce the structure of an organic compound from the following data and assign the values.

Molecular formula : $C_{13}H_{10}O_3$

UV λ_{max} : 276 nm

IR : 3192, 1682, 1595, 1487, 1406 and 1100 cm^{-1}

1H NMR : δ : 10.51, (s, 1H, D_2O exchangeable) 8.04
(d/d, 1H),

7.59 to 7.38 (m, 3 H),

7.34 to 7.18 (m, 3 H) and

7.04 to 6.90 (m, 2H)

^{13}C NMR : δ : 168.9, 162.3, 150.2, 136.4, 130.3, 129.6, 129.3,
121.6, 119.4, 117.8 and 111.9.

MS $\frac{m}{e}$ (rel. abundance) : 214 (13), 122 (8), 121(100), 93(9), 65(13) and 39(8).

- b) Write short notes on :

- Gas - sampling techniques for recording IR spectra.
- SFORD.

(6+6=12)
