PG – 132

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)**

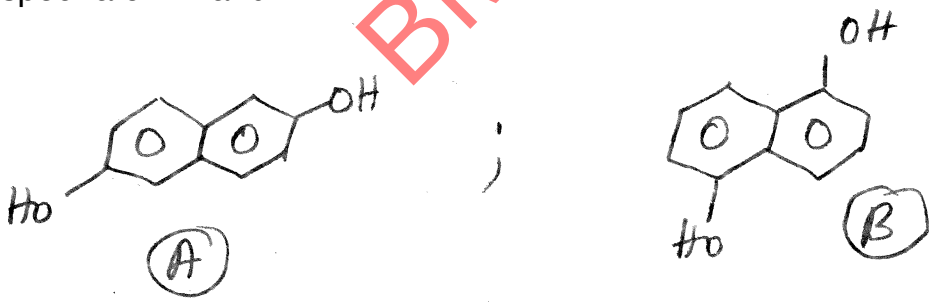
a) Write the structure of a compound with the following data,

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 toutomers 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 B



e) 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 ^{1}HNMR. 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 Overhouser Effect (NOE) with suitable example.

(4+4+4=12)

3. a) i) Mention the criteria required for a ^{1}HNMR 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 ($\in$ = 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) ^{1}H NMR and
   ii) ^{13}C NMR

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

   i) $Cl_2CH-\overset{\overset{O}{\|}}{C}H-H$

   ii) CH_3CH_2Br and

   iii) 

   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 $C_5H_{12}O_4$. It exhibits a broad band between 3400 – 3100 cm^{-1} in its IR spectrum. The proton NMR showed two singlets at δ : 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}

^{1}HNMR : 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}CNMR : 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 :

i) Gas - sampling techniques for recording IR spectra.

ii) SFORD. **(6+6=12)**
