2019

M.Sc.

4th Semester Examination

CHEMISTRY

Paper - CEM 403

Full Marks : 40 Time : 2 Hours

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

1. Answer any *four* questions from the following : 2×4=8

(a) Draw the diagram of the components of a NMR instrument.

(b) What is spin-spin coupling ? What is Karplus equation ?

(c) What are the full forms of DEPT, HMBC and HMQC ?

(d) What is the temperature at which the magnet of a high field (e.g., 400 MHz) NMR is kept ?

[Turn Over]

(e) Give examples of two NMR active and two NMR inactive nuclei and explain why.

(f) What is the difference between a base peak and a molecular ion peak in Mass spectroscopy ?

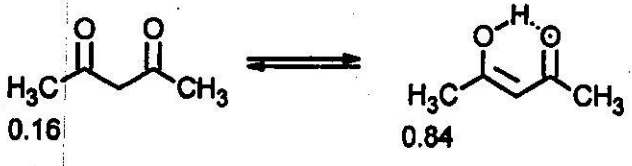
(g) What is NMR shift reagent ? Give an example and explain the mechanism of its activity.

(h) Which reference compound is used for NMR in D_2O. ? Write its structure.

2. Answer any *four* questions from the following : 4×4=16

(a) A Compound $C_9H_{10}O_2$ has strong infrared absorption at 1695 cm^{-1}. The ^1H *NMR* spectrum has five sets of line : a triplet at $\delta 1.3(3H)$, a quartet at $\delta 4.1(2H)$, a doublet at $\delta 7.0(2H)$, a doublet at $\delta 7.8(2H)$ and a singlet at $\delta 9.8(1H)$ ppm. Suggest a structure for this compound.

(b) What is chemical exchange ? Calculate the percentage of keto and enol forms of acetyl acetone from the integral data given below ?



(c) A and B are two isomer having molecular formula $C_9H_{10}O_2$, deduced the structure of the isomers (A & B) with the help of given FTIR and ^1H *NNR* data :

For isomer A : FTIR : 1680 cm^{-1}; ^1H *MNR* (δ):7.6 (2*H*, *d*), 6.9 (2*H*, *d*), 3.9 (3*H*, *s*) 2.0 (3*H*, *s*)

For isomer B : FTIR 1740cm^{-1}; ^1H *MNR* (δ):7.2 (5*H*, *s*), 5.0 (2*H*, *s*,), 1.98 (3*H*, *s*)

(d) Isomeric esters D and E have the composition $C_{11}H_{12}O_4$. Spectral data are summarized below : Deduce the structure of D and E and rationalize your answer.

[Turn Over]

Compound D :

$\delta\, 2.46\,(s, 3H), 3.94(s, 6H),$

$8.05\,(d, J = 2\,Hz, 2H), 8.49\,(t, J = 2Hz, 1H)$

Compound E :

$\delta\, 2.63\,(s, 3H), 3.91\,(s, 6H),$

$7.28\,(d, J = 8Hz, 1H),$

$8.00(dd, J = 8, 8\,Hz, 1H),$

$8.52\,(d, J = 2Hz, 1H)$

(e) An organic compound having molecular formula $C_9H_8O_2$ shows following spectral data $^1H\ NMR$

$\delta(12.7, 1H, brs); \delta(7.8, 1H, d, J = 18Hz);$

$\delta(7.56, 5H, m); \delta(6.45, 1H, d, J = 18Hz),$

IR - $1680cm^{-1}$, $2520 - 3070cm^{-1}$ (broad). Draw the structure of the compound.

(f) An organic compound having molecular formula $C_{10}H_{12}O_2$ shows following spectral data $^1H\ NMR$ - $\delta(8.0, 2H, m); \delta(7.2, 3H, m);$ $\delta(5.2, 1H, m); \delta(1.3, 6H, d)$, *IR*- $1730cm^{-1}$, $3050cm^{-1}$ and $2950cm^{-1}$. Draw the structure of the compound.

(g) An organic compound having molecular formula C_5H_8O shows following spectral data

$^1H\ NMR$ - $\delta(6.2, 1H, d, J = 18Hz)$;

$\delta(5.4, 1H, m, J = 17Hz)$;

$\delta(2.3, 3H, s)$; $\delta(1.9, 3H, d)$, IR - $1685cm^{-1}$, $3020cm^{-1}$,

UV-VIS $\lambda_{max}\ (EtOH) = 277$nm, ε max $= 4600$.

Draw the structure of the compound.

(h) What characteristics bands are observed for A-DNA and B-DNA conformation in CD spectrophotometry ?

3. Answer any *two* questions from the following : 8×2

(a) (i) Explain why recoilless emission and absorption of γ-ray is essential for Mössbauer spectroscopic study.

(ii) Showing all possible transitions explain the Mössbauer spectrum of $Fe(CO)_5$. 4+4

(b) (i) What characteristics bands are observed for Random coil, β-Sheet and α-helix conformation of protein structure in CD spectrophotometry.

[Turn Over]

(ii) Write down the solvent ethanol effect on the strucutre of the CD band. 4+4

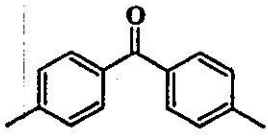
(c) (i) An organic compound having molecular formula $C_{15}H_{14}O$ exhibited the following ^1H *NMR* and ^{13}C *NMR* spectral data.

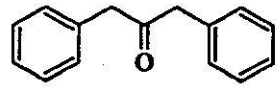
^1H NMR : δ 7.3-7.7 (*m*, 6*s*), 6.85 (*d*, 1*H*, *J* = 7 *Hz*), 2.95 (Septet, 1*H*, *J* = 6 *Hz*), 1.2 (*d*, 6*H*, *J* = 7 *Hz*) ^{13}C *NMR* : δ : 203, 142, 134, 130, 128.8, 128.2, 124.3, 39, 18

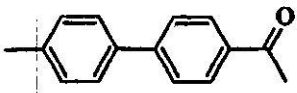
(ii) An organic compound having molecular formula $C_{15}H_{14}O$ exhibited the following ^1H *NMR* and ^{13}C *NMR* spectral data.

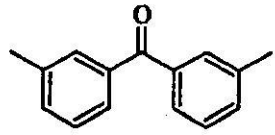
^1H *NMR* : *d* 2.4 (s), 7.2 (*d*, *J* = 8 *Hz*), 7.7 (*d*, *J* = 8 *Hz*)

^{13}C *NMR* : *d* 21.0, 129.0, 130.0, 136.0, 141.0, 190.0 4+4

1 

2 

3 

4 

(d) (i) Explain the appearance of six lines in the Mössbauer spectrum of soft iron with a gamma ray source of ^{57}Co.

(ii) Calculate the recoil velocity and recoil energy of the free Mössbauer nucleus ^{119}Sn when emitting a γ-ray of frequency 5.76×10^{18} *Hz*. What is the Doppler shift of the γ-ray frequency to an outside observed ? 4+4