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No. of Printed Pages: $4 + 6$

(63)   SARDAR PATEL UNIVERSITY
M.Sc. Semester – IV (Industrial Polymer Chemistry) Examination
Thursday, 29ᵗʰ November 2012

PS04(?)PC01: Spectroscopy-II

Time: 10:30 am to 01:30 pm   Total Marks: 70

Note: Right hand figures indicate marks.

Q. 1   Select the correct answer in the following.   08

1. In IR, the C-H stretching absorption of alkyne is observed at

    a. ~2150 cm^{-1} c. ~1000cm^{-1}
    b. ~3300cm^{-1} d. ~1300cm^{-1}

2. In UV spectra the $n \longrightarrow \sigma^*$ transition is shown by

    a. Ketones   c. Alcohols
    b. Alkanes   d. Olefins

3. In the instrument with 1.4 Tesla magnetic field the proton will resonate at

    a. 60 MHz   c. 100 MHz
    b. 90 MHz   d. 300 MHz

4. In the PMR spectrum, mesitylene(1,3,5-trimethyl benzene) will give

    a. 2 signals   c. 4 signals
    b. 3 signals   d. 6 signals

5. In ^{13}C NMR, phenanthrene will give

    a. 14 signals   c. 5 signals
    b. 6 signals   d. 7 signals

6. The solvent CDCl₃ in ^{13}C NMR spectrum will give

    a. a doublet at 100 δ   c. a singlet at 180 δ
    b. a triplet at 77 δ   d. a singlet at 40 δ

7. In mass spectra, the metastable ion peak is observed

    a. as diffused peak at non integral m/z value   c. as two lines with equal intensity
    b. at heighest m/z value   d. at M-15 position

8. In HETCOR spectra, the connectivity observed between ^1H and ^{13}C is

a. ^2J
b. ^3J

c. ^2J and ^3J
d. ^1J

Q. 2 Answer the following (Any Seven).

14

1. Explain Fermi resonance observed in IR spectroscopy.

2. With suitable example explain the terms chromophores and auxochromes.

3. The symmetrical stretching vibration in H_2O is IR active whereas the same is inactive in CO_2. Explain.

4. Sketch the expected PMR spectrum for ethyl acetate by taking approximate δ value for each signal.

5. Assign the spin systems (Pople notations) for 1-nitropropane and p-chloro nitrobenzene.

6. How will you differentiate o-, m- and p- xylenes on the basis of proton decoupled ^{13}C NMR spectra.

7. Write the important characteristic properties of DEPT-90 and DEPT-135 spectra.

8. With suitable example explain Mclafferty rearrangement observed in mass spectroscopy.

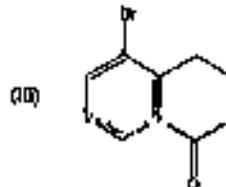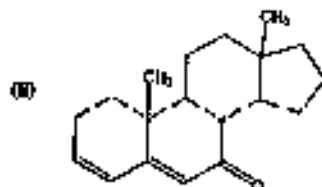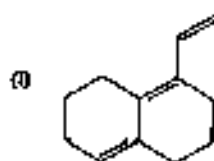9. Sketch the ^1H-^1H COSY spectrum for ethyl benzene by taking approximate δ value for each signal.

Q. 3 A. Answer the following.
(i) State and explain the Beer-Lambert law.
(ii) Discuss in detail the characteristic IR absorptions in aldehydes and esters.

06

B. Calculate λ_{max} for the following molecules.

06

OR

B. Answer the following.

06

(i) How can you differentiate o-hydroxy acetophenone and p-hydroxy acetophenone on the basis of their IR sprctra?
(ii) In IR, s-trans benzal acetone absorbs at 1674 cm^{-1} while s-cis benzal acetone absorbs at 1699 cm^{-1}. Explain.
(iii) Draw the relative energy level diagram for the following electronic transitions. $\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$

Q. 4 A. (i) What is coupling constant in PMR? Explain vicinal and germinal couplings in detail.　03

(ii) List the important methods for the simplifications of PMR spectra. Discuss the use of shift reagents in detail.　03

B. (i) A compound with molecular formula $C_6H_{12}O_2$ shows the following signals in PMR spectrum. Assign the structure.　03
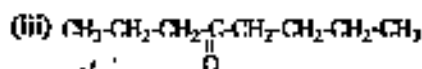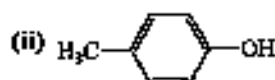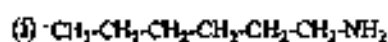
Signal position(δ)	Multiplicity	Protons
0.9	Doublet	6H
1.9	Multiplet	1H
2.1	Singlet	3H
3.85	Doublet	2H

(ii) What is nuclear overhauser effect? How will you distinguish following compounds using NOE-PMR spectra?　03

(I)　　(II)

OR
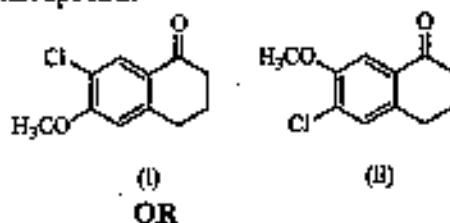
B. (i) Sketch the expected PMR spectrum for 3-methyl-2-pentanone by taking approximate δ value for each signal.　03

(ii) What is chemical shift equivalent? Dimethylformamide, in its PMR spectrum shows two separate signals for two methyl groups at room temperature but it shows only one signal for two methyl groups at 123 °C. Explain.　03

Q. 5 A. Do the ^{13}C NMR chemical shift calculations for the following molecules.　06

(i) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

(ii)

(iii) $CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{\text{O}}{\underset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

B. (i) Sketch the proton coupled and proton decoupled ^{13}C NMR spectra for p-methoxy benzaldehyde by taking approximate chemical shift value for each signal.　03

(ii) Indicate the position and multiplicity of the signals for the following solvents in ^{13}C NMR.　03

(a) Acetone-d_6　(b) DMSO-d_6　(c) Benzene-d_6

OR

B. (i) A bicyclic hydrocarbon with molecular formula C_8H_{14} shows only two peaks in proton decoupled ^{13}C spectrum. The DEPT spectra indicated that those signals are for CH and CH_2. Assign the structure to the compound.   03

(ii) Sketch the ^1H-^{13}C HETCOR spectrum for 2-butanol by taking approximate δ value for each signal.   03

Q. 6 A. Do the mass fragmentation for the following molecules.   06
(a) 2-methyl-2-pentanol (b) 2-pentanone (c) 3-pentanone

B. (i) Discuss FAB and MALDI techniques used in mass spectroscopy.   03
(ii) What is metastable ion peak in mass spectroscopy? A parent ion with mass 91, results a daughter ion of mass 65, calculate the position of the meta stable ion peak.   03

OR

B. A compound has molecular formula $C_{10}H_{12}O_2$. It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound.   06

IR (cm^{-1}) : 1711, 3000, 2950, 1500, 1600 and 820.

PMR :

δ	Multiplicity	No. of protons
2.1	Singlet	3H
3.6	Singlet	2H
3.8	Singlet	3H
6.9	Doublet	2H
7.1	Doublet	2H

^{13}C NMR :

^{13}C (δ)	DEPT-90	DEPT-135
30.0	-	positive
50.0	-	Negative
55.0	-	positive
114.0	positive	positive
127.0	-	-
130.0	positive	positive
159.0	-	-
207.0	-	-

Mass:
m/e : 164(M^+), 149, 133, 121, 107, 43

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