

SEAT No. _____

No of Printed Pages: 06

[101 & A-59]

SARDAR PATEL UNIVERSITY
M.Sc. Organic Chemistry
Semester – IV, External Examination
April 10, 2018 Tuesday
Time: 02:00 pm - 05:00 pm
Spectroscopy-II [PS04CORC01]

[Total Marks – 70]

N.B. Figures to the right indicate full marks

Q.1 Answer the following multiple choice questions. [08]

- 1 A doublet observed in PMR recorded with 100 MHz instrument has coupling constant $J = 6$ Hz. The same doublet recorded with 400 MHz instrument will show the coupling constant $J =$ _____.
(a) 3 Hz (b) 6 Hz (c) 24 Hz (d) 32 Hz
- 2 In the intermediate portion of IR spectrum, _____ cm^{-1} region is usually called the fingerprint region.
(a) 4000-14000 (b) 200-400 (c) 500-1500 (d) 600-4000
- 3 The $-\text{CH}_2-$ protons in propionic acid are _____.
(a) Homotopic (b) Enantiotopic (c) Mesomeric (d) Diastereotopic
- 4 In ^{13}C NMR, Methanol- d_4 will give signal as _____.
(a) septet at 49 δ (b) quartet at 70 δ (c) triplet at 128 δ (d) triplet at 77 δ
- 5 In UV, the highest energy electronic transition is _____.
(a) $n \rightarrow \pi^*$ (b) $n \rightarrow \sigma^*$ (c) $\pi \rightarrow \pi^*$ (d) $\sigma \rightarrow \sigma^*$
- 6 In CI techniques for recording mass spectra, reagent gas used is generally _____.
(a) Argon (b) methane (c) helium (d) nitrogen
- 7 In ^{13}C -NMR, naphthalene will give _____ signals.
(a) 1 (b) 4 (c) 3 (d) 2
- 8 Number of Br atoms are _____ in a compound showing abundance pattern as 1:3:3:1 in mass spectrum.
(a) 1 (b) 2 (c) 4 (d) 3

Q.2 Answer the following questions. (ANY SEVEN) [14]

- 1 Dimethyl formamide, 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 $^\circ\text{C}$. Explain.

C.P.T. O.)

- 2 Give the structure and full form of TMS. Why it is used as the internal reference in PMR spectroscopy?
- 3 Sketch the ^1H - ^1H COSY spectrum of butanoic acid.
- 4 Explain McIlattferty rearrangement taking an example of ketone.
- 5 Write a short note on auxochromes and chromophores.
- 6 Explain Wagging and Rocking vibrations in IR spectroscopy.
- 7 Sketch the proton decoupled ^{13}C NMR spectrum of pentan-1-ol by taking approximate δ value for each signal.
- 8 Calculate stretching frequency of C-H bond.
- 9 Give the molecular formula for the compound having following molecular ion group peaks in its mass spectrum.

m/z:	94	95	96	97
Relative abundance:	100	6.1	96	1.1

Q.3

[A] Write general rules for predicting prominent peaks in EI spectra. [06]

[B] Do the mass fragmentation for the following molecules: [06]
 (a) benzamide (b) benzyl alcohol (c) 2-pentanone

OR

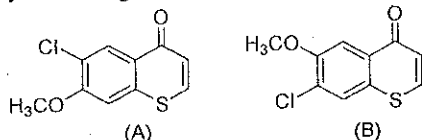
[B] Answer the following questions.

- I Predict the fragmentation pattern for diphenyl ether having molecular ion at m/z -170.
- II Write a note on CI method.

Q.4

[A] Answer the following questions. [06]

- I Define NOE. How can you distinguish following isomers using NOE-PMR spectra?



- II Define the coupling constant in PMR? Discuss vicinal and long range coupling.

[B] Answer the following questions. [06]

- I Enlist the methods used for the simplification of NMR spectra. Explain the use of shift reagent in detail.
- II Sketch the expected PMR spectrum of furfuraldehyde by taking approximate δ value for each signal and show that it is an AMX system having three coupling constants.

OR

[B] Answer the following questions.

- I In PMR, the acetylene protons give signal at 1.80 δ which is shielded compared to the ethylene protons (5.5 δ). Similarly, benzene protons give signal at 7.27 δ which is deshielded signal compared to ethylene protons. Explain this on the basis of circulation of π -electrons and ring current effect.

II Sketch the PMR spectra of pure ethanol and ethanol with acidic impurity by taking approximate δ value for each signal.

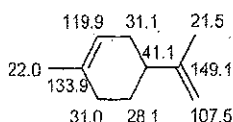
Q.5

[A] Calculate the ^{13}C NMR shift for the following molecules. [06]

(1) 3-methyl phenol (2) pentan-3-ol (3) 3-methyl pentane

[B] Answer the following questions. [06]

I Sketch the proton decoupled ^{13}C NMR, DEPT-90° and DEPT-135° spectra of Limonene.



II Sketch the ^1H - ^1H COSY spectrum of 4-amino ethylbenzoate.

OR

[B] Answer the following questions.

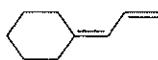
I Sketch the expected HETCOR spectrum of butan-2-ol.

II Write the full form of DEPT. Explain its importance and characteristic properties for the interpretation of signals in ^{13}C NMR spectrum.

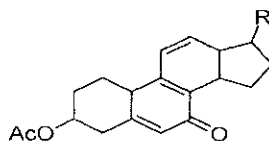
Q.6

[A] Calculate λ_{max} for the following compounds [06]

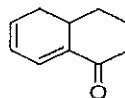
(1)



(2)



(3)



[B] Answer the following questions. [06]

I An organic compound $\text{C}_8\text{H}_8\text{O}_2$ gives following stretching and bending vibrations. Deduce the structure of the compound.

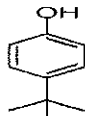
IR : 3000, 1690, 1600, 1500, 1400 and 735 cm^{-1}

II Esters of o-chloro benzoic acid shows $\text{C}=\text{O}$ stretching at two different frequencies, Explain.

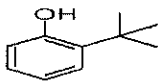
OR

[B] Answer the following questions.

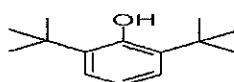
I In the following substituted phenols, the O-H stretching is observed at 3608 cm^{-1} in A, at 3605 and 3643 cm^{-1} in B and at 3643 cm^{-1} in C. Explain.



A



B



C

II Drawing figures, explain all types of stretching vibrations observed in IR Spectrum.

—————X—————

(P.T.O.)

Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm^{-1}
C-H	Alkanes	2850-2960
		1350-1470
C-H	Alkenes	3020-3080 (m)
		675-1000
C-H	Aromatic rings	3000-3100 (m)
		675-870
C-H	Alkynes	3300
C=C	Alkenes	1640-1680 (v)
C=C	Alkynes	2100-2260 (v)
C=C	Aromatic rings	1500, 1600 (v)
C-O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
O-H	Monomeric alcohols, phenols	3610-3640 (v)
	Hydrogen bonded alcohols, phenols	3200-3600 (broad)
	Carboxylic acids	2500-3000 (broad)
N-H	Amines	3300-3500 (m)
C-N	Amines	1180-1360
C=N	Nitriles	2210-2260 (v)
-NO ₂	Nitro compounds	1515-1560
		1345-1385

TABLE 5.1

Shifts of the ¹³C NMR Parameters in Some Alkyl and Aryl Groups (Hydrocarbon)

¹³ C Atoms	Shift (ppm) (Δ)
α	+9.1
β	+9.4
γ	-2.5
δ	+0.3
ε	+0.1
1° (3°)*	-1.1
1° (4°)*	-3.4
2° (3°)*	-2.5
2° (4°)	-7.2
3° (2°)	-3.7
3° (3°)	-9.5
4° (1°)	-1.5
4° (2°)	-8.4

*The notations 1° (3°) and 1° (4°) denote a CH₃ group bound to a R₃CH group and to a R₂C group, respectively. The notation 2° (3°) denotes a RCH₂ group bound to a R₂CH group, and so on.

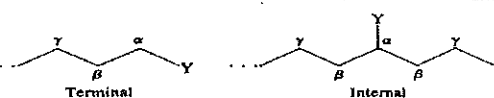
TABLE 5.2

Shifts of the ¹³C NMR Parameters in Some Linear and Branched Cyclic Alkanes (ppm from TMS)

Compound	C-1	C-2	C-3	C-4	C-5
Methane	-2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH ₃)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH ₃)	

TABLE 5.3

Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal* (+ downfield, - upfield)



Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+ 9	+ 6	+10	+ 8	-2
CH=CH ₂	+20		+ 6		-0.5
C≡CH	+ 4.5		+ 5.5		-3.5
COOH	+21	+16	+ 3	+ 2	-2
COO ⁻	+25	+20	+ 5	+ 3	-2
COOR	+20	+17	+ 3	+ 2	-2
COCl	+33	+28		+ 2	
CONH ₂	+22		+ 2.5		-0.5
COR	+30	+24	+ 1	+ 1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+ 9	+ 7	-2
OH	+48	+41	+10	+ 8	-5
OR	+58	+51	+ 8	+ 5	-4
OCOR	+51	+45	+ 6	+ 5	-3
NH ₂	+29	+24	+11	+10	-5
NH ₃ ⁺	+26	+24	+ 8	+ 6	-5
NHR	+37	+31	+ 8	+ 6	-4
NR ₂	+42		+ 6		-3
NR ₃ ⁺	+31		+ 5		-7
NO ₂	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	-3
SH	+11	+11	+12	+11	-4
SR	+20		+ 7		-3
F	+68	+63	+ 9	+ 6	-4
Cl	+31	+32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	- 6	+ 4	+11	+12	-1

*Add these increments to the shift values of the appropriate carbon atom in Table 5.2 or to the shift value calculated from Table 5.1.

Source: F.W. Wehrli, A.P. Marchand, and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*, 2nd ed., London: Heyden, 1983.

¹³C shifts for substituted benzenes
Base value for benzene is 128.5 ppm

TABLE 5.9

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH ₃	9.3	+0.7	-0.1	-2.9	21.3
CH ₂ CH ₃	+15.6	-0.5	0.0	-2.6	29.2 (CH ₂), 15.8 (CH ₃)
CH(CH ₃) ₂	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH ₃)
C(CH ₃) ₃	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH ₃)
CH=CH ₂	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH ₂)
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C ₆ H ₅	+12.1	-1.8	-0.1	-1.6	
CH ₂ OH	+13.3	-0.8	-0.6	-0.4	64.5
CH ₂ OCCH ₃	+7.7	-0.0	-0.0	-0.0	20.7 (CH ₂), 66.1 (CH ₂), 170.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH ₃	+31.4	-14.4	+1.0	-7.7	54.1
OC ₂ H ₅	+29.0	-9.4	+1.6	-5.3	
OCCH ₃	+22.4	-7.1	-0.4	-3.2	23.9 (CH ₂), 169.7 (C=O)
CH	+8.2	+1.2	+0.6	+5.8	192.0
CCH ₃	+7.8	-0.4	-0.4	+2.8	24.6 (CH ₂), 195.7 (C=O)
CC ₂ H ₅	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
CCF ₃	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	168.0
COCH ₃	+2.0	+1.2	-0.1	+4.8	51.0 (CH ₂), 166.8 (C=O) 168.5
CCl	+4.6	+2.9	+0.6	+7.0	
C≡N	-16.0	+3.6	+0.6	+4.3	119.5
NH ₂	+19.2	-12.4	+1.3	-9.5	
N(CH ₃) ₂	+22.4	-15.7	+0.8	-11.8	40.3
NHCCH ₃	+11.1	-9.9	+0.2	-5.6	
NO ₂	+19.6	-5.3	+0.9	+6.0	
N=C=O	+5.7	-3.6	+1.2	-2.8	129.5
F	+35.1	-14.3	+0.9	-4.5	
Cl	+6.4	+0.2	+1.0	-2.0	
Br	-5.4	+3.4	+2.2	-1.0	
I	-32.2	+9.9	+2.6	-7.3	
CF ₃	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH ₃	+10.2	-1.8	+0.4	-3.6	15.9
SO ₂ NH ₂	+15.3	-2.9	+0.4	+3.3	
Si(CH ₃) ₃	+13.4	+4.4	-1.1	-1.1	

*See D. E. Ewing, *Org. Magn. Reson.*, 12, 499 (1979) for chemical shifts of 709 monosubstituted benzenes.

(P.T.O.)