SARDAR PATEL UNIVERSITY
M.Sc. (Organic Chemistry), Semester – III Examination
March 19, 2019: Tuesday
Time: 02:00 p.m. – 05:00 p.m.
## Organic Spectroscopy [PS03CORC21]

Total marks: 70

Q-1 Select the correct answer and mention only the code of correct answer against their   [08]
question numbers.

a. Pople notation for the protons present in isopropyl bromide is _____ .
   (i) A_3X (iii) A_2X_2
   (ii) A_6X (iv) A_2X

b. In PMR spectrum of *p*-xylene ___ signals are obtained.
   (i) 1   (iii) 3
   (ii) 2   (iv) 4

c. Which of the following NMR experiment does not show signal for quaternary carbon?
   (i) DEPT 45° & 90°   (iii) DEPT 90° & 135°
   (ii) DEPT 90°   (iv) DEPT 45° & 135°

d. In HMQC spectra, the connectivity between ^1H & ^{13}C observed is _____ .
   (i) ^1J (ii) ^2J (iii) ^3J (iv) both (ii) and (iii)

e. When fundamental vibrations couple with _____ region, it is called fermi resonance.
   (i) Fingerprint   (iii) Overtone
   (ii) Far IR   (iv) Signature

f. In UV, methanol will show absorption for the electronic transition _____ .
   (i) $n{\rightarrow}\sigma^*$ (ii) $\pi{\rightarrow}\pi^*$ (iii) $n{\rightarrow}\pi^*$ (iv) $\sigma{\rightarrow}\sigma^*$

g. The ratio of M : M+2 : M+4 : M+6 for three Br atoms in mass spectra is _____ .
   (i) 1:2:1   (ii) 1:3:3:1   (iii) 1:4:4:1   (iv) 1:4:6:4:1

h. In recording mass spectrum using CI method, the carrier gas used is _____ .
   (i) Nitrogen   (ii) Butane   (iii) Argon   (iv) Methane

Q-2 Answer ANY SEVEN of the following in questions.   [14]

a. Explain the spin relaxation processes in case of PMR spectroscopy.
b. Sketch the PMR spectrum for 1-nitro propane by taking approximate δ value for each
   signal & showing appropriate multiplicity.
c. How can you differentiate following geometrical isomers by PMR spectra?

(A)   (B)
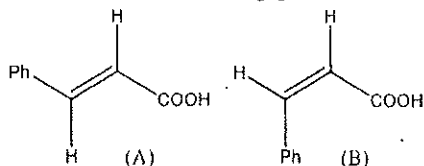
d. Write the full form of: (i) HMQC (ii) NOESY

P. T. O.

e. What are difficulties observed in production of ^{13}C spectra?

f. In IR, s-*trans* benzal acetone absorbs at 1674 cm⁻ while s-*cis* benzal acetone absorbs at 1699 cm⁻. Explain.

g. Write a note on Chromophores and Auxochromes.

h. What is Nitrogen rule? Which of the following compounds will follow it?
   (i) C_5H_5N (ii) $C_{15}H_{10}NCl$ (iii) C_8H_9OS

i. An organic compound gave the following molecular ion group peaks in the mass spectrum

	M	M+1
m/z	142	143
Abundance	100	1.14

What is the molecular formula for the compound?

Q-3 [A] Calculate λ_{max} for the following compounds.   **[06]**
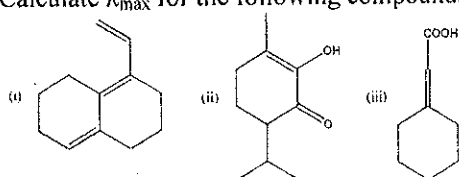
Q-3 [B] (i) Explain how 1°, 2° & 3° amines can be differentiated on the basis of IR **[03]** spectroscopy.

(ii) How o-hydroxy acetophenone & p-hydroxy acetophenone can be differentiated on **[03]** the basis of their IR spectra?

OR

Q-3 [B] (i) With suitable examples explain the effect of conjugation, H-bonding & ring size on **[03]** C=O stretching frequency in ketones.

(ii) Discuss the important absorptions shown by saturated aliphatic carboxylic acid. **[03]**

Q-4 [A] (i) List the various methods for simplification of complex ^{1}H NMR spectrum. Discuss **[03]** the use of shift reagents in detail.

(ii) An aldehyde upon hydrolysis results a compound with molecular formula $C_5H_8O_4$ **[03]** which shows the following signals in PMR spectrum. Assign the structure of the compound by interpreting PMR data.
   (a) 0.95 (t, 3H)
   (b) 1.85 (q, 2H)
   (c) 3.10 (t, 1H)
   (d) 12.35 (Broad (D₂O exchangeable), 2H)

Q-4 [B] (i) Draw the structures of all three isomers of difluoroethylene and show that in each **[03]** isomer the protons are chemically equivalent but magnetically non-equivalent.

(ii) Discuss the use of symmetry operations for checking the chemical shift equivalence **[03]** between protons in PMR spectroscopy.

OR

Q-4 [B] (i) With suitable examples explain long range coupling in PMR spectroscopy. **[03]**

(ii) Sketch the expected PMR spectrum for styrene by taking approximate δ value for **[03]** each signal & show that styryl group is an AMX system with three coupling constants.

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**Q-5 [A]** Calculate ^{13}C NMR chemical shift for the following compounds. **[06]**

(i)   (ii)   (iii)
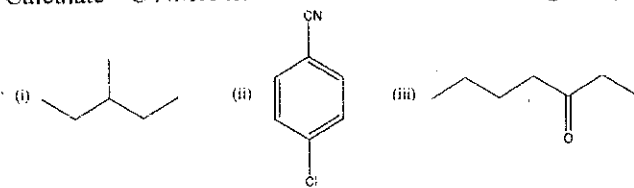
Q-5 [B] (i) Predict number of signals and multiplicity for following deutarated solvents in ^{13}C **[03]** NMR at 25 °C.

(a) $CDCl_3$
(b) Dichloromethane-d_2
(c) Benzene-d_6

(ii) Sketch the expected ^1H-^1H COSY and ^1H-^{13}C HETCOR spectrum of 4-heptanone. **[03]**

OR

Q-5 [B] (i) Using the given ^{13}C NMR values sketch ^{13}C NMR, DEPT 90° and DEPT 135° **[03]** spectra for Limonene,
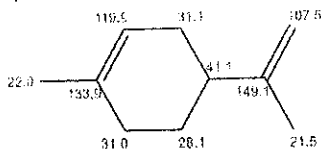
(ii) Indicate what kinds of structural information are provided by HMBC & **[03]** INADEQUATE spectra.

Q-6 [A] Write fragmentation pattern for following compounds **[06]**

(i) Benzyl alcohol   (ii) 2-Hexene   (iii) n-Butanol

Q-6 [B] Discuss the field desorption, electron impact and electron spray ionization techniques **[06]** used in mass spectroscopy.

OR

Q-6 [B] A compound has molecular formula $C_{11}H_{12}O_2$. It gives the following spectral data. **[06]** Interpret the spectral data and determine the structure of the compound.

IR (cm⁻): 3030 (-CH stretching alkene), 2940 (-CH alkane), 1712 (-C=O stret.), 1639 (-C=C alkene), 1585 (Aromatic ring), 1200 (-C-O ester), 770 and 710 (-C=C out of plane bending)

Mass (m/z): 176, 131 (base peak), 103, 77, 51

^1H NMR

Signal (δ)	Multiplicity	Protons
a. 1.31	t (J = 7.1 Hz)	3H
b. 4.2	q (J = 7.1 Hz)	2H
c. 6.43	d (J = 15.8 Hz)	1H
d. 7.24-7.57	m	5H
e. 7.67	d (J = 15.8 Hz)	1H·

^{13}C NMR

^{13}C (δ)	DEPT-135°
C_1 14.3	+Ve
C_2 60.4	-Ve
C_3 118.4	+Ve
C_4 128.1	+Ve
C_5 128.9	+Ve
C_6 130.2	+Ve
C_7 134.5	-
C_8 144.5	+Ve
C_9 166.8	-

---X---X---

③

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)
-NO₂	Nitro compounds	1515-1560
		1345-1385

TABLE 5.1
Alkane α, β, γ Carbon Chemical Shift Parameters in Acyclic and Alicyclic Hydrocarbons

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

ᵃThe notations 1° (3°) and 1° (4°) denote a CH₃ group bound to a R₂CH group and to a R₃C group, respectively. The notation 2° (3°) denotes a RCH₂ group bound to a R₃CH group, and so on.

TABLE 5.2
The ¹³C Shifts for Some Linear and Branched-Chain 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-CH₃)	
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-CH₃)	

TABLE 5.3
Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal* (+ downfield, - upfield)
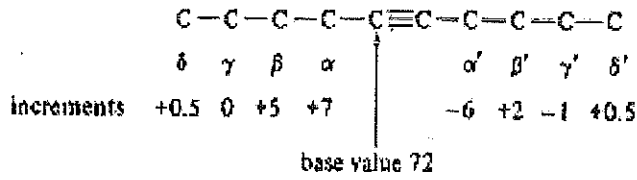

	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH₃	+ 9	+ 6	+10	+ 8	-2
CH=CH₂	+20		+ 6		-0.5
C≡CH	← 4.5		+ 5.5		-3.5
COOH	+21	+16	+ 3	+ 2	-2
COO⁻	+25	+20	+ 5	+ 3	-2
COOR	+20	+17	+ 3	+ 2	-2
COCl	+33	+28		+ 2	
CONH₂	+22		+ 2.5		-0.5
COR	+30	+24	+ 1	+ 1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+ 9	+ 7	-2
OH	+48	+41	+10	+ 8	-5
OR	+58	+51	+ 8	+ 5	-4
OCOR	+51	+45	+ 6	+ 5	-3
NH₂	+29	+24	+11	+10	-5
NH₃⁺	+26	+24	+ 8	+ 6	-5
NHR	+37	+31	+ 8	+ 6	-4
NR₂	+42		+ 6		-3
NR₃⁺	+31		+ 5		-7
NO₂	+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.

EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

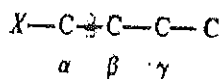Chemical shift (δ) = 72 + Σ(increments for carbon atoms)

$$C-C-C-C-C\equiv C-C=C-C-C$$

	δ	γ	β	α		α'	β'	γ'	δ'
increments	+0.5	0	+5	+7		−6	+2	−1	+0.5

base value 72

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

TABLE 5.9

Chemical Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5) and of the Carbon Atom of Substituent Groups (ppm from TMS)*

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	
CH₃	9.3	+0.7	−0.1	−2.9	21.3
CH₂CH₃	+15.6	−0.5	0.0	−2.6	29.2 (CH₂), 15.8 (CH₃)
CH(CH₃)₂	+20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH₃)
C(CH₃)₃	+22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH₃)
CH═CH₂	+9.1	−2.4	+0.2	−0.5	137.1 (CH), 113.3 (CH₂)
C≡CH	−5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C₆H₅	+12.1	−1.8	−0.1	−1.6	
CH₂OH	+13.3	−0.8	−0.6	−0.4	64.5
CH₂OCCH₃ (‖O)	+7.7	−0.0	−0.0	−0.0	20.7 (CH₃), 66.1 (CH₂), 170.5 (C═O)
OH	+26.6	−12.7	+1.6	−7.3	
OCH₃	+31.4	−14.4	+1.0	−7.7	54.1
OC₆H₅	+29.0	−9.4	+1.6	−5.3	
OCCH₃ (‖O)	+22.4	−7.1	−0.4	−3.2	23.9 (CH₃), 169.7 (C═O)
CH (‖O)	+8.2	+1.2	+0.6	+5.8	192.0
CCH₃ (‖O)	+7.8	−0.4	−0.4	+2.8	24.6 (CH₃), 195.7 (C═O)
CC₆H₅ (‖O)	+9.1	+1.5	−0.2	+3.8	196.4 (C═O)
CCF₃ (‖O)	−5.6	+1.8	+0.7	+6.7	
COH (‖O)	+2.9	+1.3	+0.4	+4.3	168.0
COCH₃ (‖O)	+2.0	+1.2	−0.1	+4.8	51.0 (CH₃), 166.8 (C═O) 168.5
CCl (‖O)	+4.6	+2.9	+0.6	+7.0	
C≡N	−16.0	+3.6	+0.6	+4.3	119.5
NH₂	+19.2	−12.4	+1.3	−9.5	
N(CH₃)₂	+22.4	−15.7	+0.8	−11.8	40.3
NHCCH₃ (‖O)	+11.1	−9.9	+0.2	−5.6	
NO₂	+19.6	−5.3	+0.9	+6.0	
N═C═O	+5.7	−3.6	+1.2	−2.8	179.5
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	
CF₃	+2.6	−3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	−3.3	
SCH₃	+10.2	−1.8	+0.4	−3.6	15.9
SO₂NH₂	+15.3	−2.9	+0.4	+3.3	
Si(CH₃)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.

9

Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chains

$$X-C-C-C-C$$
$$\alpha\ \ \beta\ \ \gamma$$

X	α-shift			β-shift	γ-shift
	$X-CH_2-$	$X-CH-R$	$X-C(R)(R)-$		
	1° or	2° or	3°		
—CH₃	9	6	3	9	-3
—R: see table 3.11					
axial —CH₃	1	–	–	5	-6
equatorial —CH₃	6	–	–	9	0
(in cyclohexanes)					
—CH=CH₂	22	16	12	7	-2
—C≡CH	4	–	–	3	-3
—C₆H₅, —Ar	23	17	11	10	-3
—F	70	–	–	8	-7
—Cl	31	35	42	10	-5
—Br	19	28	37	11	-4
—I	-7 to 20	–	–	11	-2
—NH₂, —NHR, —NR₂	29	24	18	11	-4
—NO₂	62	–	–	3	-5
—NHCOR, —NRCOR	10	–	–	0	0
—NH₃⁺	25	–	–	7	-3
—CN	3	4	–	2	-3
—SH	2	–	–	2	-2
—OH	50	45	40	9	-3
—OR	50	24	17	10	-6
—OCOR	52	50	45	7	-6
—COOH,—COOR,—CON<	20	16	13	2	-3
—COR,—CHO	30	24	17	2	-3
—SO₃H,—SO₂N<	50	–	–	3	0

Data Chart For UV-Spectroscopy

Table 7.5 *Empirical Rules for Dienes*

	Homoannular (cisoid)	Heteroannular (transoid)
Parent — *Butadiene*	$\lambda = 217$ / $\lambda = 253$ nm	$\lambda = 214$ nm
Increments for:		
Double-bond-extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar groupings:		
—OCOCH$_3$	0	0
—OR	6	6
—Cl, —Br	5	5
—NR$_2$	60	60

Table 7.7 *empirical rules for enones*

$$\overset{\delta}{-}\text{C}=\overset{\gamma}{\text{C}}-\overset{\beta}{\text{C}}=\overset{\alpha}{\text{C}}-\text{C}=$$

$$\overset{\beta}{-}\overset{}{\text{C}}=\overset{\alpha}{\text{C}}-\text{C}=\text{O}$$

Base values:		
Six-membered ring or acyclic parent enone		= 215 nm
Five-membered ring parent enone		= 202 nm
Acyclic dienone		= 245 nm
Increments for:		
Double-bond-extending conjugation		30
Alkyl group or ring residue	α	10
	β	12
	γ and higher	18
Polar groupings:		
—OH	α	35
	β	30
	δ	50
—OCOCH$_3$	α,β,δ	6
—OCH$_3$	α	35
	β	30
	γ	17
	δ	31
—Cl	α	15
	β	12
—Br	α	25
	β	30
—NR$_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39

Table 7.12 *Empirical rules for benzoyl derivatives*

Parent chromophore:

R = alkyl or ring residue — 246
R = H — 250
R = OH or Oalkyl — 230

Increment for each substituent:

Substituent	position	
Alkyl or ring residue	o, m	3
	p	10
—OH, —OCH$_3$, or —Oalkyl	o, m	7
	p	25
	o	11
—O$^-$	m	20
	p	78
—Cl	o, m	0
	p	10
—Br	o, m	2
	p	15
—NH$_2$	o, m	13
	p	58
—NHCOCH$_3$	o, m	20
	p	45
—NHCH$_3$	p	73
—N(CH$_3$)$_2$	o, m	20
	p	85

(5)