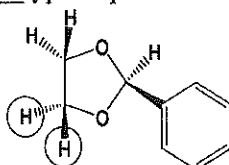


SARDAR PATEL UNIVERSITY**M. Sc. SEMESTER – IV (Analytical Chemistry) Examination****Monday, 18th March 2019****Time: 02.00 p.m. to 05.00 p.m.****PS04CANC21: Spectroscopy-II****Total Marks: 70****Q. 1 Select the correct answer from the alternatives given below to the each question [08]**

- [1] Among following, _____ have highest " $>C=O$ " stretching frequency.
 [a] Acetone [b] Formaldehyde
 [c] Acetaldehyde [d] Acetamide
- [2] Electronic transition(s) expected from n-hexane is(are) _____.
 [a] $\sigma \rightarrow \sigma^*$ [b] $\pi \rightarrow \pi^*$
 [c] $n \rightarrow \sigma^*$ [d] Both a & c
- [3] Anthracene will show _____ CMR signals in its ^{13}C NMR spectrum.
 [a] 5 [b] 3
 [c] 7 [d] 4
- [4] Two protons present in 1,1-difluoro ethene are _____.
 [a] Both chemically and magnetically equivalent [b] Chemically non-equivalent but magnetically equivalent
 [c] Chemically equivalent but magnetically non-equivalent [d] Both chemically and magnetically non-equivalent
- [5] The circled protons are _____ type of protons.

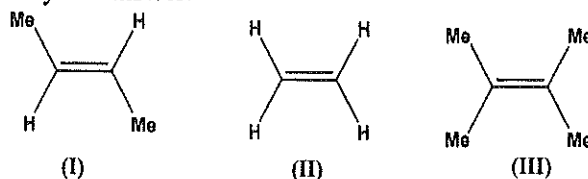


- [a] Diastereotopic [b] Enantiotopic
 [c] Homotopic [d] Both b and c
- [6] _____ is known as inverse detected HETCOR.
 [a] HMQC [b] HMBC
 [c] INADEQUATE [d] DQF-COSY
- [7] Which of the following is CORRECT for molecular ion peak?
 [a] It is peak with highest intensity. [b] It is peak with highest m/z value.
 [c] It has non-integral m/z values. [d] It is denoted by m^* .
- [8] If an organic compound contains one Br and two Cl atom in its molecular formula then relative abundance of $M:M+2:M+4:M+6$ will be
 [a] 1 : 3 : 3 : 1 [b] 3 : 7 : 5 : 1
 [c] 9 : 15 : 7 : 1 [d] 2 : 2 : 3 : 1

Q. 2 Answer the following questions (ANY SEVEN)

[14]

- [1] Calculate total numbers of fundamental modes of vibrations for Benzene.
 [2] Arrange following compounds in increasing order of λ_{\max} for $\pi \rightarrow \pi^*$ transition and justify the answer.

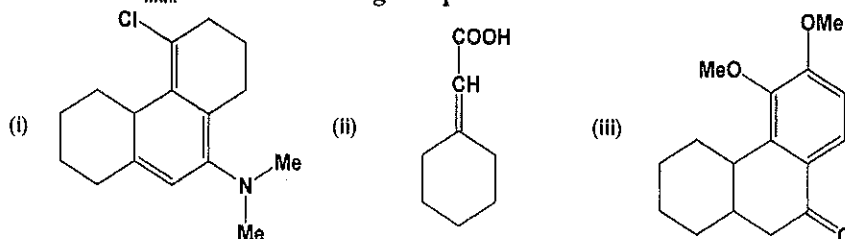


- [3] Define : (i) Bathochromic shift (ii) Hypochromic effect
 [4] Sketch the ^1H NMR spectrum of **ethylacetate** by taking approximate δ value for each signal and showing appropriate multiplicity.
 [5] What are pople notations? Assign pople notations to **ethanol** and **1,1-dibromo ethane**.
 [6] How will you differentiate following pairs of isomers by ^{13}C NMR?
 (i) 2-Pentanone and 3-Pentanone
 (ii) 1-Butyne and 2-Butyne
 [7] Give full form of: (i) HMBC (ii) DQF-COSY
 [8] What are metastable ion peaks? Enlist their important characteristics.
 [9] What is nitrogen rule? Explain with suitable examples.

Q. 3

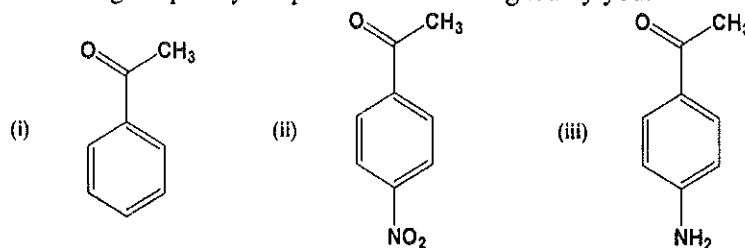
- [a] Calculate λ_{\max} for the following compounds:

[06]



- [b] Answer the following questions.

- [1] Arrange following compounds in increasing order of $>\text{C}=\text{O}$ stretching frequency. Explain the order assigned by you.



- [2] How will you distinguish following pairs of compounds by IR?
 (i) Acetone and Propanal
 (ii) Ethylamine and Triethylamine
 (iii) *o*-Hydroxy acetophenone and *p*-Hydroxy acetophenone

OR

- [b] Answer the following questions.

- [1] Discuss various stretching and bending vibrations.
 [2] Discuss characteristic absorptions observed in IR spectra of
 (i) Alkynes (ii) Amides

Q. 4

[a] Answer the following questions.

- [1] List the various methods for simplification of complex $^1\text{H-NMR}$ spectrum. Discuss "proton exchange and deuterium exchange" with example. [03]
- [2] Draw the structures of all the possible isomers for the compound with molecular formula $\text{C}_4\text{H}_9\text{Br}$. How many ^1H NMR signal(s) will be produced by each isomer? [03]

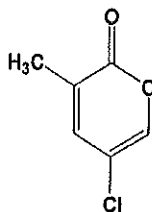
[b] Answer the following questions.

- [1] Define coupling constant. Discuss long range and geminal coupling constants in detail. [03]
- [2] Discuss "effect of neighboring π -electrons on chemical shift in $^1\text{H-NMR}$ " with examples. [03]

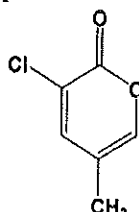
OR

[b] Answer the following questions.

- [1] Discuss various relaxation processes involved in NMR. [03]
- [2] What is Nuclear Overhauser Effect (NOE)? How one can distinguish following isomers using NOE- ^1H NMR spectra. [03]



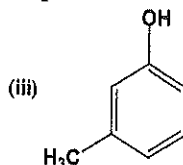
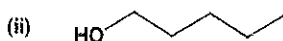
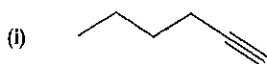
(I)



(II)

Q. 5

[a] Calculate ^{13}C NMR chemical shift for the following compounds. [06]



[b] Answer the following questions.

- [1] Sketch 'broad band decoupled' and 'off-resonance' $^{13}\text{C-NMR}$ spectra for 1-chloropropane by taking approximate δ -value for each signal. [03]
- [2] Discuss important characteristics of DEPT- 45° , DEPT- 90° and DEPT- 135° spectra. [03]

OR

[b] Answer the following questions.

- [1] " $^{13}\text{C-NMR}$ spectra are sometimes useful to distinguish stereoisomers also". Explain with example. [03]
- [2] Draw DQF-COSY and HMBC spectra for propanal by taking approximate chemical shift value for each signal. [03]

Q.6

[a] Answer the following questions.

- [1] Discuss general rules for predicting prominent peaks in EI-Mass spectra. [03]
- [2] Write fragmentation pattern for following compounds. [03]
(i) 2-Pentanone (ii) Propionamide (iii) 2-Hexene

[b] Answer the following questions.

- [1] Discuss mass spectra of aromatic and alkyl aryl hydrocarbons with suitable examples. [03]
- [2] Discuss following ionization techniques in mass spectrometry. [03]
(i) CI (ii) ESI

OR

[b] Spectral data for the compound with molecular formula $C_{10}H_{12}O_2$ is given below. Interpret the data and assign the structure for the compound. [06]

IR: 3005, 2960, 1712, 1600, 1500, 820 cm^{-1} .

1H NMR			^{13}C NMR		
Signal (δ)	Multiplicity	Protons	^{13}C (δ)	DEPT 90°	DEPT 135°
2.1	singlet	3H	30	-	+Ve
3.6	singlet	2H	50	-	-Ve
3.8	singlet	3H	55	-	+Ve
6.9	doublet	2H	114	+Ve	+Ve
7.1	doublet	2H	127	-	-
			130	+Ve	+Ve
			159	-	-
			207	-	-

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

— X —

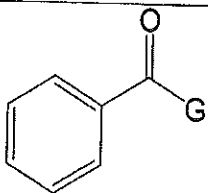
(4)

[101]

SEAT No. _____

P504CANC21

Base value for homo-annular diene	253 nm
Base value for hetero-annular diene	214 nm
Increment for:	
Double bond extending conjugation	+30 nm
Alkyl substituent or ring residue	+5 nm
Exocyclic double bond	+5 nm
Polar groups (auxochrome):	
-OAc	+0 nm
-OR	+6 nm
-SR	+30 nm
-Cl, -Br	+5 nm
-NR ₂	+60 nm

	G	Base value
	Alkyl or ring residue (Ketone)	246 nm
	H (Aldehyde)	250 nm
	-OR / -OH (Ester/ Acid)	230 nm

Alkyl / ring residue	o, m	+ 3 nm
	p	+ 10 nm
- OCH ₃ / - OH / -OR	o, m	+ 7 nm
	p	+ 25 nm
-O ⁻ (Oxy anion)	o	+11 nm
	m	+20 nm
	p	+78 nm
- Cl	o, m	+ 0 nm
	p	+ 10 nm
- Br	o, m	+ 2 nm
	p	+ 15 nm
- NH ₂	o, m	+13 nm
	p	+58 nm
- NHCOCH ₃	o, m	+ 20 nm
	p	+ 45 nm
- NHCH ₃	o, m	+ 73 nm
-N (CH ₃) ₂	o, m	+ 20 nm
	p	+ 85 nm

(P.T.O.)

①

Table 3. Characteristic absorption for α,β -unsaturated carbonyl compounds (enones)			
Base values:			
Acyclic α,β -unsaturated ketones	215 nm		
Six membered cyclic α,β -unsaturated ketones	215 nm		
Five membered cyclic α,β -unsaturated ketones	202 nm		
α,β -unsaturated aldehyde	210 nm		
α,β -unsaturated carboxylic acid/ester	195 nm		
Increment for:			
Double bond extending conjugation	+30 nm		
Homocyclic diene component	+39 nm		
Exocyclic double bond	+5 nm		
Alkyl substituent or ring residue			
	α	+10 nm	
	β	+12 nm	
	γ & higher	+18 nm	
Polar groups:			
	-OH	α	+35 nm
		β	+30 nm
		δ	+50 nm
	-OCOCH ₃	α, β, δ	+6 nm
	-OCH ₃	α	+35 nm
		β	+30 nm
		γ	+17 nm
		δ	+31 nm
	-SR	β	+85 nm
	-Cl	α	+15 nm
		β	+12 nm
	-Br	α	+25 nm
		β	+30 nm
	-NR ₂	β	+95 nm
Solvent correction:			
	Ethanol	+0 nm	
	Methanol	+0 nm	
	Chloroform	+1 nm	
	Ether	+7 nm	
	Water	-8 nm	
	Hexane	+11 nm	
	Cyclohexane	+11 nm	

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

CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton	Chemical shift, ppm	
	δ	
Cyclopropane	0.2	
Primary	RCH ₃	0.9
Secondary	R ₂ CH ₂	1.3
Tertiary	R ₃ CH	1.5
Vinylic	C=C-H	4.6-5.9
Acetylenic	C≡C-H	2-3
Aromatic	Ar-H	6-8.5
Benzylic	Ar-C-H	2.2-3
Allylic	C=C-CH ₃	1.7
Fluorides	HC-F	4-4.5
Chlorides	HC-Cl	3-4
Bromides	HC-Br	2.5-4
Iodides	HC-I	2-4
Alcohols	HC-OH	3.4-4
Ethers	HC-OR	3.3-4
Esters	RCOO-CH	3.7-4.1
Esters	HC-COOR	2-2.2
Acids	HC-COOH	2-2.6
Carbonyl compounds	HC-C=O	2-2.7
Aldehydic		9-10
Hydroxylic		1-5.5
Phenolic		4-12
Enolic	C=C-OH	15-17
Carboxylic	RCOOH	10.5-12
Amino	RNH ₂	1-5

(P.T.O.)

3

Table 5.1 The ¹³C Shift Parameters in Some Linear and Branched Hydrocarbons

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

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-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 (+ left, - right)

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

EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

$$\text{Chemical shift } (\delta) = 72 + \Sigma(\text{increments for carbon atoms})$$

	C	-	C	-	C	-	C	-	C	≡	C	-	C	-	C	-	C
		δ	γ	β	α						α'	β'	γ'	δ'			
increments		+0.5	0	+5	+7						-6	+2	-1	+0.5			

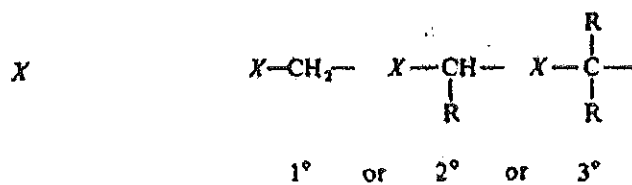
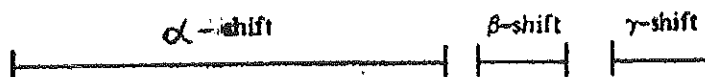
base value 72

Table 3.16 Influence of functional group X on the chemical shift positions (δ) nearby carbons in alkene groups and benzene rings

Base values: ethylene (δ 123) and benzene (δ 128)

	Alkenes		Benzenes			
	C-1	C-2	C-1 (ipso)	ortho	meta	para
-CH ₃	10	-8	9	0	0	-2
R,	16	-8	15	0	0	-2
R,	23	-8	21	0	0	-2
-CH=CH ₂	15	-6	9	0	0	-2
-CH≡CH	-	-	-6	4	0	0
-C ₆ H ₅ , -Ar	13	-11	13	-1	1	-1
-F	25	-34	35	-14	1	-5
-Cl	3	-6	6	0	1	-2
-Br	-8	-1	-5	3	2	-2
-I	-38	7	-32	10	3	-1
-NH ₂	-	-	18	-13	1	-10
-NHR	-	-	20	-14	1	-10
-NR ₂	-	-	22	-16	1	-10
-NO ₂	22	-1	20	-5	1	6
-NHCOR, -NRCOR	-	-	10	-7	1	-4
-CN	-15	15	-16	4	1	6
-SH	-	-	4	1	1	-3
-OH	-	-	27	-13	1	-7
-OR	29	-39	30	-15	1	-8
-OCOR	18	-27	23	-6	1	-2
-COOH, -COOR, -CON<	4	9	2	2	0	5
-COR, -CHO	14	13	9	1	1	6
-SO ₃ H, -SO ₂ N<	-	-	16	0	0	4
-PMe ₂	-	-	14	1.6	0	-1
-PAr ₂	-	-	9	5	0	0

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



	1°	or	2°	or	3°		
$-CH_3$	9		6		3	9	-3
$-R$: see table 3.11							
axial $-CH_3$ equatorial $-CH_3$ (in cyclohexanes)	1		-		-	5	-6
	6		-		-	9	0
$-CH=CH_2$	22		16		12	7	-2
$-C\equiv CH$	4		-		-	3	-3
$-C_6H_5, -Ar$	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
$-NH_2, -NHR, -NR_2$	29		24		18	11	-4
$-NO_2$	62		-		-	3	-5
$-NHCOR, -NRCOR$	10		-		-	0	0
$-NH_3^+$	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
$-SO_3H, -SO_2N<$	50		-		-	3	0

TABLE 4.12 Incremental Shifts for the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from benzene at 128.5 ppm). ¹³C Chemical Shifts of Substituents in ppm from TMS^a

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 O(C=O)CH ₃	7.7	~0.0	~0.0	~0.0	20.7 (CH ₃), 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 ₆ H ₅	29.0	-9.4	1.6	-5.3	
O(C=O)CH ₃	22.4	-7.1	-0.4	-3.2	23.9 (CH ₃), 169.7 (C=O)
(C=O)H	8.2	1.2	0.6	5.8	192
(C=O)CH ₃	7.8	-0.4	-0.4	2.8	24.6 (CH ₃), 195.7 (C=O)
(C=O)C ₆ H ₅	9.1	1.5	-0.2	3.8	196.4 (C=O)
(C=O)F ₃	-5.6	1.8	0.7	6.7	
(C=O)OH	2.9	1.3	0.4	4.3	168
(C=O)OCH ₃	2.0	1.2	-0.1	4.8	51.0 (CH ₃), 166.8 (C=O)
(C=O)Cl	4.6	2.9	0.6	7.0	168.5
(C=O)NH ₂	5.0	-1.2	0.0	3.4	
C≡N	-16	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
NH(C=O)CH 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	

^aSee Ewing, D.B. (1979): *Org. Magn. Reson.*, 12, 499, for 709 chemical shifts of monosubstituted benzenes.

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