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BBA-003-010401 Seat No. _____

M. Sc. (Sem. IV) (CBCS) Examination

July – 2021

C - 401 : Spectroscopy

(Multidisciplinary)

(Old Course)

Faculty Code : 003

Subject Code : 010401

Time : $2\frac{1}{2}$ Hours] [Total Marks : **70**

Instruction : All questions are compulsory and carry EQUAL marks

1 Answer the following : (Any **Seven**) **14**

(a) Distinguish between germinal and vicinal coupling with suitable example.

(b) Discuss the advantage of ^{13}CMR spectroscopy.

(c) What is an IR Spectrum? When does a molecule absorb IR light?

(d) What is Nitrogen rule? Validate this rule using nitrobenzene and 2,4-dinitrobenzene.

(e) Draw the 1HNMR spectrum of p-Nitro toluene with splitting of the signals.

(f) Distinguish methyl propionate and ethyl acetate with the help of ^{1}HNMR spectroscopy.

(g) Write the principle of Mass-spectroscopy.

(h) Discuss types of UV absorption shift.

(i) Write the characteristic IR frequency of m-Chloro benzaldehyde.

(j) Give the full-form of HMQC, HMBC, NOESY and TOCSY.

2 Answer the followings : (Any **Two**) **14**

(a) Calculate ^{13}CNMR chemical shifts for the followings :

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

(ii) $CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

(iii) 2-Ethylhexanol

(b) Describe HSQC 2D NMR technique with suitable example.

(c) Discuss the (n+1) rule, its failure and solution with suitable example.

3 Answer the following : **14**

(a) What are the empirical rules for calculation of absorption maxima in case of polynes?

(b) Determine the molecular formula of a compound which gives the data in its mass spectrum.

m/z	120	130	131	132	133	134	135	136	137
Re*l. abundance*	30	100	31	98	12	32	1.7	3.5	0.07

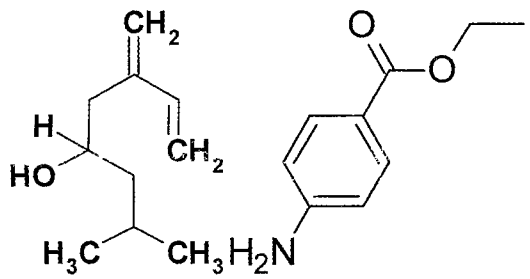
OR

(a) Draw the schematic diagram of Mass spectrophotometer and discuss it in details.

(b) Discuss McLafferty rearrangement with at least three different compounds

4 Answer the following : **14**

(a) Predict the ^{13}C NMR signal for the followings:



(b) Explain the Mass fragmentation of Methyl butyrate, Methyl benzoate and Acetophenone.

5 Answer the following : (Any **Two**) **14**

(a) Sketch the NMR spectrum of AMX and A_2B_2 system with suitable example.

(b) Write the applications of IR-spectroscopy.

(c) Write a note on Sample handling technique in IR spectroscopy.

(d) Draw the single beam UV-spectrophotometer and functioning it.

Data-table for the calculation of ^{13}C Chemical shift

TABLE 5.1

^{13}C Atoms	Shift (ppm) (Δ)
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

ª The notations 1° (3°) and 1° (4°) denote a CH_3 group bound to a R_3CH group and to a R_3C group, respectively. The notation 2° (3°) denotes a RCH_2 group bound to a R_2CH group, and so on.

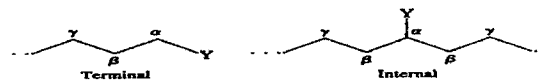
TABLE 5.2

^{13}C Shifts (δ) 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[a] (+ downfield, − upfield)

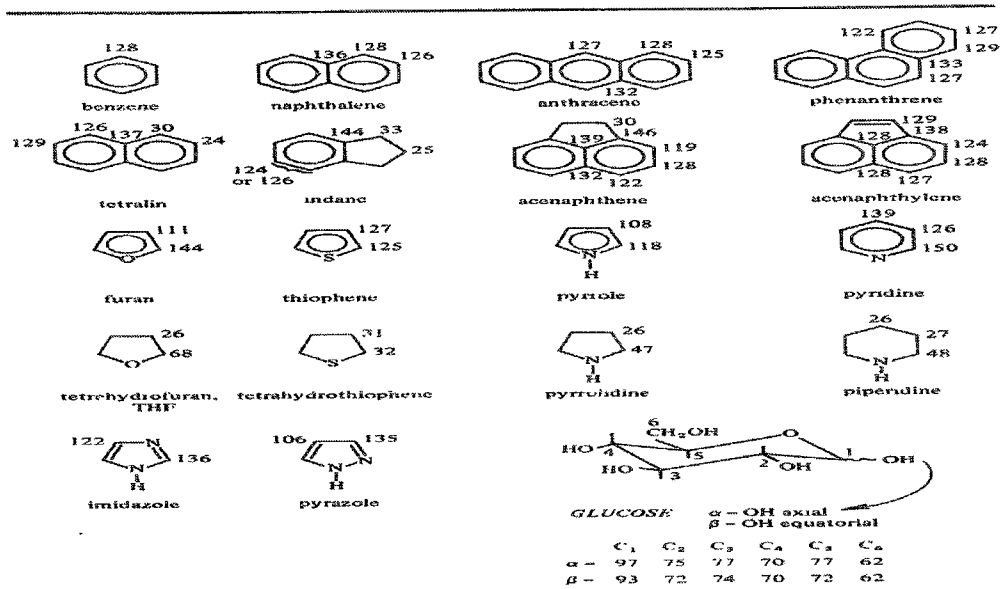


	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	+ 9	+ 6	+10	+ 8	−2
$CH{=}CH_2$	+20		+ 6		−0.5
C≡CH	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+ 3	+ 2	−2
COO^-	+25	+20	+ 5	+ 3	−2
COOR	+20	+17	+ 3	+ 2	−2
COCl	+33	+28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−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

ª 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.

Table 3.14 δ values for the carbons in aromatic and heterocyclic molecules (sp^2 and sp^3 carbons listed)



	C_1	C_2	C_3	C_4	C_5	C_6
α –	97	75	77	70	77	62
β –	93	72	74	70	72	62

TABLE 5.9

Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm, if downfield, = upfield) Carbon Atom of Substituents in parts per million 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	
CH_3	9.3	+0.7	−0.1	−2.9	21.3
CH_2CH_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)
$C{\equiv}CH$	−5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C_6H_5	+12.1	−1.8	−0.1	−1.6	
CH_2OH	+13.3	−0.8	−0.6	−0.4	64.5
$CH_2OC(=O)CH_3$	+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_6H_5	+29.0	−9.4	+1.6	−5.3	
$OC(=O)CH_3$	+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	192.0
$C(=O)CH_3$	+7.8	−0.4	−0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
$C(=O)C_6H_5$	+9.1	+1.5	−0.2	+3.8	196.4 (C=O)
$C(=O)CF_3$	−5.6	+1.8	+0.7	+6.7	
$C(=O)OH$	+2.9	+1.3	+0.4	+4.3	168.0
$C(=O)OCH_3$	+2.0	+1.2	−0.1	+4.8	51.0 (CH_3), 166.8 (C=O) 168.5
$C(=O)Cl$	+4.6	+2.9	+0.6	+7.0	
$C{\equiv}N$	−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
$NHC(=O)CH_3$	+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_2NH_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.

Table 3.17 δ values for the carbons in carbonyl groups and some other multiple-bonded environments (solvent shifts, ± 2 ppm, are commonly observed for C=O)

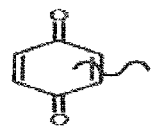
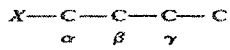
R—CHO	aliphatic aldehydes	200–205
Ar—CHO C=C—CHO	aryl and conjugated aldehydes*	190–194
R—CO—R'	dialkyl ketones	205–218
Ar—CO—R Ar—CO—Ar C=C—CO—	aryl and conjugated ketones	196–199
	cyclohexanone derivatives	209–213
	cyclopentanone derivatives	214–220
	bicyclic ketones	215–219
	simple quinones	180–187
R—COOH R—COO⊖	carboxylic acids and salts	166–181
R—COO—R'	aliphatic esters	169–176
Ar—COOAr C=C—COO—	esters with conjugation in the acid *or* alcohol moiety	164–169
	lactones	170–178
—CO—O—CO—	anhydrides, all classes	163–175
—CON<	amides, all classes including lactams	162–179

Table 3.17 (*continued*)

—CO—NH—CO—	imides	168–184
—COCl	acyl chlorides, all classes	167–172
—NH—CO—NH—	ureas	153–163
—O—CO—O—	carbonates	152–156
R—C≡N	nitriles	114–124
R—N≡C	isonitriles	156–158
R—N=C=O	isocyanates	120–130
>C=NOH	oximes	148–158
>C=NNHCONH$_2$	semicarbazones	158–160
>C=N—NH—	hydrazones	145–149
>C=N—R	imines	157–175

*Note: δ 177

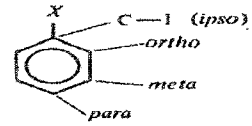
Table 3.15 Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chains



X	α-shift			β-shift	γ-shift
	$X-CH_2-$	$X-\underset{R}{\overset{}{CH}}-$	$X-\underset{R}{\overset{R}{C}}-$		
	1° or	2° or	3°		
$-CH_3$	9	6	3	9	−3
—R: see table 3.11					
axial $-CH_3$	1	–	–	5	−6
equatorial $-CH_3$ (in cyclohexanes)	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 3.16 Influence of functional group X on the chemical shift positions (δ) of nearby carbons in alkene groups and benzene rings

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



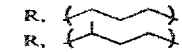
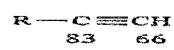
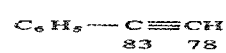
	Alkenes		Benzenes			
	C—1	C—2	C—1 (*ipso*)	*ortho*	*meta*	*para*
—CH_3	10	−8	9	0	0	−2
R, 	16	−8	15	0	0	−2
R,	23	−8	21	0	0	−2
—$CH=CH_2$	15	−6	9	0	0	−2
—CH≡CH	–	–	−6	4	0	0
—C_6H_5, —Ar	13	−11	13	−1	1	−1
—F	25	−34	35	−14	1	−5
—Cl	3	−6	6	0	1	−2
—Br	−8	−1	−5	3	2	−2
—I	−38	7	−32	10	3	−1
—NH_2	–	–	18	−13	1	−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_3H, —SO_2N<	–	–	16	0	0	4
—PMe_2	–	–	14	1.6	0	−1
—PAr_2	–	–	9	5	0	0

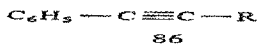
Table 3.13 δ values for the carbons in alkynes (sp)

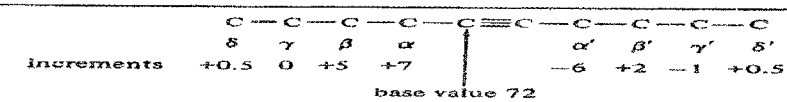
REPRESENTATIVE ALKYNES

acetylene (ethyne) CH≡CH δ 72







EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

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