647510 **MSC4AnE1404A** **Seat No :_____**

M.Sc.(Chem.) Semester - 4 (*CBCS*) Examination
April/May-2022 (NEW COURSE)
Modern Spectroscopy (Elective)

Time: 2:30 Hours **Marks: 70**

Instructions:

1. All questions are compulsory.
2. Figures to the right indicate marks.

Q.1 (a) **Answer the following** **4 Marks**

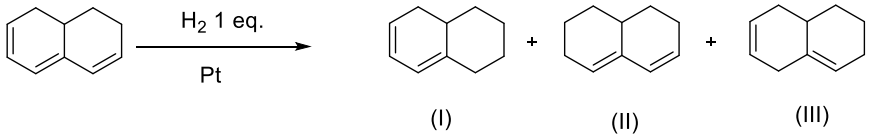
(1) Discuss Auxochrome and Chromophore with example. 2

(2) Describe various applications of UV-Visible spectroscopy. 2

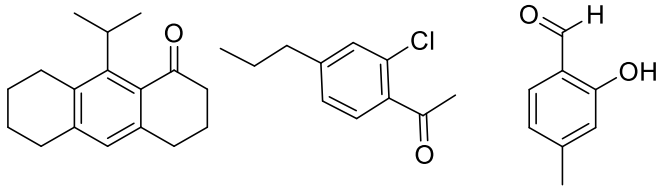
Q.1 (b) **Answer any two questions out of three.** **10 Marks**

(1) Explain Red shift and Blue shift with one example each. 5

(2) The following triene on partial hydrogenation gives three products, which are separated by chromatography, how can you identify the product by application of Woodward-Fischer rules? 5



(3) Arrange the following compounds in decreasing order in their wavelength (λmax): 5



Q.2 (a) **Answer the following** **Marks**

(1) Which of the following molecule is IR active? Justify your answer: 2
(i) H_2 (ii) CO (iii) O_2 (iv) CO_2

(2) How will you determine types of hydrogen bonding from IR spectroscopy? 2

Q.2 (b) **Answer any two questions out of three.** **Marks**

(1) Discuss ATR technique for IR spectroscopy with its advantages. 5

(2) Explain various factors affecting carbonyl frequency with suitable example 5

(3) (a)What is degree of freedom? Deduce equation of vibrational degree of freedom for non-linear and linear molecules. 5
(b) Discuss Fermi Resonance with example

Q.3 (a) **Answer the following** **4 Marks**

(1) Draw a schemetic diagram of Mass spectrometer including various components **4**

Q.3 (b) Answer any two questions out of three. **10 Marks**

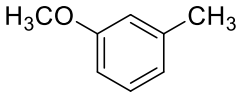
(1) When cyclohexanone was subjected to Mass spectroscopy with ESI-MS, peak appeared at 98, 83, 70, 55, 42. Carry out the fragmentation of molecule and deduce the structure of each fragment ion corresponding to the above peak appeared in the spectrum 5

(2) Discuss electrospray ionization method briefly. 5

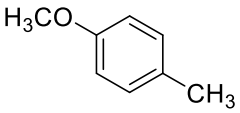
(3) Explain Mclafferty rearrangement in Mass spectroscopy with example. 5

Q.4 (a) **Answer the following** **4 Marks**

(1) How will you distinguish following isomers (A & B) by PMR? 4



A



B

Q.4 (b) **Answer any two questions out of three.** **10 Marks**

(1) What is Spin-spin coupling? Discuss AMX spectra with suitable example. 5

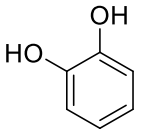
(2) An unknown compound having Molecular Formula $C_7H_4N_2O_2$ showed Molecular Ion peak (M+) at 148.12 m/z and base peak at 103.12 m/z. The FT-IR analysis showed characteristic bands at 1350 cm^{-1}, 1550 cm^{-1}, 2250 cm^{-1}. The PMR spectrum was obtained in the 400 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed peak at δ ppm; 7.77 (t, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 8.51(d, *J* = 8.8 Hz, 1H), 8.57(s, 1H). Interpret the given spectroscopic data and deduce the structure of unknown compound. 5

(3) An unknown compound having Molecular Formula $C_{10}H_{12}O_3$ showed Molecular Ion peak (M+) at 180.20 m/z. The FT-IR analysis showed characteristic bands at 1750 cm^{-1}. The PMR spectrum was obtained in the 500 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed peak at δ ppm; 1.40 (t, 3H), 3.80 (s, 3H), 4.15 (q, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 15.20, 32.34, 64.23, 114.16, 122.94, 136.55, 162.63, 169.80. Interpret the given spectroscopic data and deduce the structure of unknown compound. 5

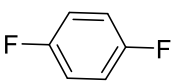
Q.5 (a) **2 Questions of 2 Marks Each.** **4 Marks**

(1) Why ^{13}C NMR is less sensitive compare to ^{1}H NMR ?

(2) Calculate the ^{13}C chemical shift of each aromatic carbon for following (A & B):



A



B

Q.5 (b) Answer any two questions out of three. **10 Marks**

(1) Distinguish the following 2D experiments with suitable example: 5

(i) COSY vs TOCSY

(ii) HMBC vs HSQC

(2) An unknown compound having Molecular Formula $C_{12}H_{13}NO_3$ showed Molecular Ion peak (M+) at 219.24 m/z. The FT-IR analysis showed characteristic bands at 1040 cm^{-1}, 1250 cm^{-1} 1725 cm^{-1} and 2235 cm^{-1}. The PMR spectrum was obtained in the 400 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed peak at δ ppm; 1.36 (t, 3H), 1.48 (t, 3H), 4.20 (q, 2H), 4.33 (q, 2H), 6.95-6.98 (d, J = 9.2 Hz, 1H), 8.14-8.17 (dd, J = 9.2 & 2.0 Hz, 1H), 8.19-8.20 (d, J = 2.0 Hz, 1H). Interpret the given spectroscopic data and deduce the structure of unknown compound 5

(3) An unknown compound having Molecular Formula $C_7H_{14}O_3$ showed Molecular Ion peak (M+) at 146.19 m/z . The PMR spectrum and 2D spectrum were obtained in the 600 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The spectrum showed following signals and cross peaks in the 2D spectrum. Interpret the given spectroscopic data and deduce the structure of unknown compound. 5

δ ppm	Signal multiplicity	No.of protons	^1H-^1H COSY
1.16	t	3H	Cross peak with q (3.50)
1.25	t	3H	Cross peak with q (4.15)
2.57	t	2H	Cross peak with t (3.71)
3.50	q	2H	-
3.71	t	2H	-
4.15	q	2H	-

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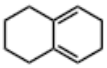
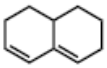
UV Spectroscopy

Woodward Fieser Rules for Dienes

	 *s-trans*	 homoannular (cisoid)	 heteroannular (transoid)
base values:	**217 nm**	**253 nm**	**214 nm**

Increments:

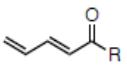
For each additional conjugated double bond		+ 30 nm
For each exocyclic double bond		+ 5 nm
For each alkyl group or Ring Residue		+ 5 nm
For each of the following groups:		
	- OR	+ 6 nm
	- O(C=O)R	+ 0 nm
	- Cl	+ 6 nm
	- Br	+ 6 nm
not affected by solvent	- SR	+ 30 nm
	- NR_2	+ 60 nm
	- Ph	+ 60 nm

Where both types of cyclic dienes are present, the base with the longer λmax is used.

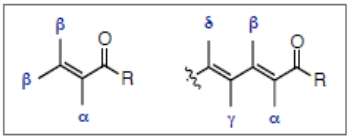
Solvent Correction	nm
H_2O	- 8
EtOH	0
$CHCl_3$	+ 1
Dioxane	+ 5
Et_2O	+ 7
Hydrocarbon	- 11

UV Spectroscopy

Woodward Fieser Rules for Enones

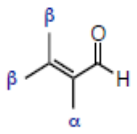
	 acyclic enone	 6-membered ring enone	 5-membered ring enone	 acyclic dienone
base values:	**215 nm**	**215 nm**	**202 nm**	**245 nm**

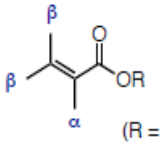
Increments:		α	β	γ	δ and higher
For each additional conjugated double bond		+ 30 nm			
For each exocyclic double bond		+ 5 nm			
For each homodiene component		+ 39 nm			
For each alkyl group		+ 10 nm	+ 12 nm	+ 18 nm	+ 18 nm
For each of the following groups:	- OH	+ 35 nm	+ 30 nm		+ 50 nm
	- OR	+ 35 nm	+ 30 nm	+ 17 nm	+ 31 nm
	- O(C=O)R	+ 6 nm	+ 6 nm		+ 6 nm
	- Cl	+ 15 nm	+ 12 nm		
	- Br	+ 25 nm	+ 30 nm		
	- SR	+ 30 nm	+ 85 nm		
	- NR_2	+ 60 nm	+ 95 nm		



UV Spectroscopy

Woodward Fieser Rules for Other Conjugated Carbonyls





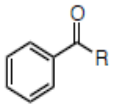
(R = H or R')

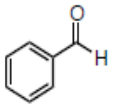
	aldehydes	carboxylic acid or ester
Base Values		
unsubstituted aldehyde or ester	208 nm	195 nm
with α or β alkyl groups	220 nm	208 nm
with α,β or β,β alkyl groups	230 nm	217 nm
with α,β,β alkyl groups	242 nm	225 nm
for an exocyclic α,β double bond		+ 5 nm
for an endocyclic α,β double bond in a 5- or 7-membered ring		+ 5 nm

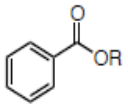
as for enones, solvent correction is also relevant

UV Spectroscopy

Woodward Fieser Rules for Benzoyl Derivatives







	aryl ketones (R = alkyl)	benzaldehydes	benzoic acids and esters
base values:	246 nm	250 nm	230 nm

Increments:	ortho	meta	para
For each alkyl group or RR	+ 3 nm	+ 3 nm	+ 10 nm for RR +7 nm
For each OH or OR (R = alkyl)	+ 7 nm	+ 7 nm	+ 25 nm
For each $O^{\ominus}$	+ 11 nm	+ 20 nm	+ 78 nm
For each of the following groups:			
- Cl	+ 0 nm	+ 0 nm	+ 10 nm
- Br	+ 2 nm	+ 2 nm	+ 15 nm
- NH_2	+ 13 nm	+ 13 nm	+ 58 nm
- $NH(C{=}O)CH_3$	+ 20 nm	+ 20 nm	+ 45 nm
- $NHCH_3$			+ 73 nm
- $N(CH_3)_2$	+ 20 nm	+ 20 nm	+ 85 nm

CHARACTERISTIC INFRARED ABSORPTION BANDS OF FUNCTIONAL GROUPS

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Alkanes and Alkyls	2850-3000	s	C-H stretch
	1450-1470	s	C-H bend
	1370-1390	m	CH_3 C-H bend
	1365 + 1395 (two bands)	m	$-CH(CH_3)_2$ or $-(CH_3)_3$ bend
	715-725	w	$-(CH_2)_n$ bend
Alkenes	3020-3140	w-m	=C-H stretch
	1640-1670	vw-m	C=C stretch
$RCH=CH_2$	910 + 990 (two bands)	m + s	=C-H bend
$RR'C=CH_2$	885-895	s	=C-H bend
cis-RCH=CHR'	665-730	m-s, broad	=C-H bend
trans-RCH=CHR'	960-980	s	=C-H bend
RCH=CR'R"	790-840	s	=C-H bend
Alkynes			
R-C≡C-H	3265-3335	s, sharp	≡C-H stretch
	2100-2140	m	C≡C stretch
	610-700	s, broad	≡C-H bend
R-C≡C-R'	2190-2260	vw-w	C≡C stretch
Alkyl halides			
R-F	1000-1350	vs	C-F stretch
R-Cl	750-850	s	C-Cl stretch
R-Br	500-680	s	C-Br stretch
R-I	200-500	s	C-I stretch
Alcohols	3300-3400	s, broad	O-H stretch
C=C-CH_2-OH	1035-1050	m-s	C-O stretch
R-CH_2-OH (1^o) or C=C-CH(R)-OH	1050-1085	m-s	C-O stretch
RR'CH-OH (2^o) or C=C-CRR'-OH	1085-1125	m-s	C-O stretch
RR'R"C-OH (3^o)	1125-1205	m-s	C-O stretch
Ar-O-H	1180-1260	m-s	C-O stretch
Ethers			
R-O-R'	1085-1150	s	C-O-C stretch
Ar-O-R	1020-1075 and 1200-1275 (two band)	m-s	=C-O-C sym. & asym. stretch
Aldehydes	2700-2725	m	H-C=O stretch
R-CH=O	1720-1740	s	C=O stretch
C=C-CH=O or Ar-CH=O	1685-1710	s	C=O stretch
Ketones			
RR'C=O	1710-1720	s	C=O stretch
C=C-C(O)-R	1665-1685	s	C=O stretch
Ar-C(O)-R	1675-1695	s	C=O stretch
four member cyclic	1770-1780	s	C=O stretch
five member cyclic	1740-1755	s	C=O stretch
six member cyclic	1710-1720	s	C=O stretch

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Carboxylic Acids	2500-3500	s, broad	O-H stretch
R-C(O)-OH	1710-1715	s, broad	C=O stretch
C=C-C(O)-OH or Ar-C(O)-OH	1680-1710	s	C=O stretch
Esters	aliphatic 1160-1210 acetates ~1240 aromatic 1250-1310	s-vs	O=C-O-C stretch
R-C(O)-O-R	1735-1750	s	C=O stretch
C=C-C(O)-O-R or Ar-C(O)-O-R	1715-1730	s	C=O stretch
R-C(O)-O-Ar	1760-1790	s	C=O stretch
Acyl Chlorides			
R-C(O)-Cl	1785-1815	s	C=O stretch
Ar-C(O)-Cl	1770-1800	s	C=O stretch
Anhydrides			
R-C(O)-O-C(O)-R	~1750 + ~1815	s,s	C=O symmetric
Ar-C(O)-O-C(O)-Ar	~1720 + ~1775 (both two bands)	s,s	& asym. stretch
Nitriles			
R-C≡N	2240-2260	m-s	C≡N stretch
C=C-C≡N or Ar-C≡N	2220-2240	s	C≡N stretch
Amines			
$R-NH_2$	~3400 + ~3500 (two bands)	w	N-H symmetric & asym. stretch
	1580-1650	w-m	N-H bend
RR'N-H	3310-33350	w	N-H stretch
Amides			
$R-C(O)-NH_2$	3200-3400 and 3400-3500 (two bands)	w-m	N-H symmetric & asym. stretch
	1650-1690	s, broad	C=O stretch
	1590-1655	m-s	N-H bend
R-C(O)-NH-R	3400-3500	w-m	N-H stretch
	1640-1690	s, broad	C=O stretch
	1510-1560	m-s	N-H bend
R-C(O)-NR'R"	1630-1680	m-s	C=O stretch
Nitro Compounds			
$R-NO_2$	~1550 and ~1370	s s	N-O symmetric & asym. stretch
C=C-NO_2 or Ar-NO_2	~1525 and ~1335 (both two bands)	s s	N-O symmetric & asym. stretch
Aromatic Compounds	3010-3100	m	Ar C-H stretch
	1450-1600 (two to four bands)	m-s sharp	ring C=C stretch
monosubstituted	730-770 and 690-710 (two bands)	s s	C-H bend
o-disubstituted	735-770	s	C-H bend
m-disubstituted	750-810 and 690-710	s s	C-H bend
p-disubstituted	810-840	s	C-H bend

Intensity abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Standard chemical shift value (ppm from TMS)

^{13}C chemical shifts for some linear and branched-chain alkanes

Alkane	C-1	C-2	C-3	C-4	C-5
Methane	-2.5				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2	13.4	
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
Isobutene	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Neopentane	31.7	28.1			
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	

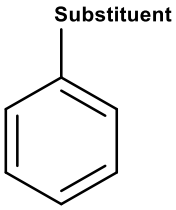
Olefinic carbons	
Substituent carbon C	**Correction**
α	+10.6
β	+7.2
γ	-1.5
α'	-7.9
B'	-1.8
γ'	-1.5
z *(cis)*	-1.1

Increments* (ppm) for substituents Y on alkanes

Substituent	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	+9	+6	+10	+8	−2
$HC{=}CH_2$	+20		+6		−0.5
$C{\equiv}CH$	+4.5		+5.5	+2	−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
NH_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

Data Sheet

Increments in the shifts of the aromatic carbon atoms of monosubstituted benzenes (ppm from benzene at 128.5 ppm)



Substituent	C-1	C-2 (*ortho*)	C-3 (*meta*)	C-4 (*para*)
H	0.0	0.0	0.0	0.0
CH_3	+9.3	+0.7	–0.1	–2.9
CH_3CH_2	+15.6	–0.5	0.0	–2.6
$CH(CH_3)_2$	+20.1	–2.0	0.0	–2.5
$HC{=}CH_2$	+9.1	–2.4	+0.2	–0.5
C_6H_5	+12.1	–1.8	–0.1	–1.6
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
OH	+26.6	–12.7	+1.6	–7.3
OCH_3	+31.4	–14.4	+1.0	–7.7
CHO	+8.2	+1.2	+0.6	+5.8
$COCH_3$	+7.8	–0.4	–0.4	+2.8
COOH	+2.9	+1.3	+0.4	+4.3
CN	–16.0	+3.6	+0.6	+4.3
NO_2	+19.6	–5.3	+0.9	+6.0
NH_2	+19.2	–12.4	+1.3	–9.5
$NHCOCH_3$	+11.1	–9.9	+0.2	–5.6
$COOCH_3$	+2.0	+1.2	–0.1	+4.8

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