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

M.Sc.(Chem.) Semester - 4 (*CBCS*) Examination
April/May-2023 (NEW COURSE)
Modern Spectroscopy (Elective)

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

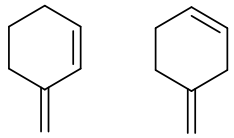
Instructions:

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

Q.1(A) Answer the following questions. **(04)**

1. Give four structures of each **(I)** Auxochrome **(II)** Chromophore

2. How will you distinguish following pair of isomers using UV spectroscopy?

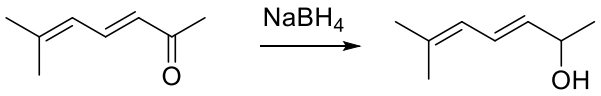


(I) (II)

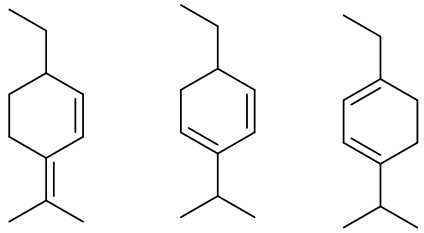
Q.1(B) Answer the following question. (Any Two) **(10)**

1. Discuss the effect of following factors on the shifting of λmax with one example: **(I)** Exocyclic double bond **(II)** Ring residue

2. How can UV spectroscopy be used to determine the completion of the following reaction?



3. Arrange the following compounds based on their increasing value of λmax:



(I) (II) (III)

Q.2(A) Answer the following questions. **(04)**

1. Draw a schematic diagram of FTIR-spectrophotometer.

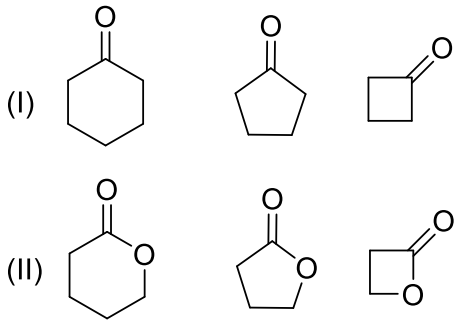
2. Why diatomic molecules Cl_2 and H_2 are IR inactive but HCl and H_2O are IR active?

Q.2(B) Answer the following question. (Any Two) **(10)**

1. Discuss various solid sample handling techniques in FT-IR and write its advantages.

2. Write a note on normal modes of molecular vibrations in the IR spectroscopy.

3. Arrange the following set of compounds (I & II) according to their increasing IR frequency. Give reasons for it.

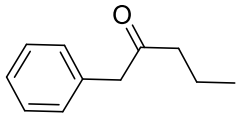


Q.3(A) Answer the following questions. **(04)**

1. How will you distinguish compounds having Cl and Br functional group using Mass Spectrum?
2. Explain base peak and molecular ion peak for the benzyl alcohol.

Q.3(B) Answer the following question. (Any Two) **(10)**

1. Discuss FAB ionization method.
2. Write a note on Time of Flight Mass analyzer including its advantages and disadvantages.
3. The following compound shows peak at m/e 162, 134, 120 and 91 in the mass spectrum. Discuss its fragmentation for these peaks.



Q.4(A) Answer the following questions. **(04)**

1. Give difference between ^{1}H NMR and ^{13}C NMR.
2. What is chemical shift? How it is represented? Give chemical shifts of most common solvents utilized in NMR.

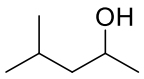
Q.4(B) Answer the following question. (Any Two) **(10)**

1. Describe shielding-deshielding effect of hybridization with suitable examples.
2. A compound with 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 d 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). Analyze the given spectroscopic data, explain the signaling pattern and deduce the structure of unknown compound.

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 d 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. Analyze the given spectroscopic data, explain the signaling pattern and deduce the structure of unknown compound.

Q.5(A) Answer the following questions. **(04)**

1. What is DEPT analysis? Discuss its application with one example.
2. Calculate the chemical shift of each carbon of following compound:



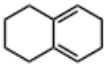
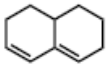
Q.5(B) Answer the following question. (Any Two) **(10)**

1. Write a note on 2D NMR spectrum and its applications.
2. An unknown compound having Molecular Formula C_9H_7N showed characteristic bands at 1450 cm-^{1}, 2235 cm^{-1} and 3100 cm^{-1} in the FT-IR spectrum. 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 d ppm; 5.46 (d, J = 10.8 Hz, 1H), 5.88 (d, J = 18.0 Hz, 1H), 6.73 (dd, J = 11.2 Hz, 17.5 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 111.1, 117.7, 118.8, 126.7, 132.3, 135.3, 141.8. Analyze the given spectroscopic data, explain the signaling pattern and deduce the structure of unknown compound.
3. An unknown compound having Molecular Formula $C_5H_{10}O$ showed strong absorption bands at 1715 cm^{-1} in FT-IR. The PMR spectrum was obtained in the 100 MHz instrument using $CDCl_3$ as solvent and TMS as internal standard. The peaks appeared at d ppm; 0.97 (d, 6H), 2.16-2.26(m, 1H), 2.3 (dd, 2H) and 9.85 (t,1H). The ^{13}C NMR analysis showed peak at d ppm: 24, 28, 54, 205. Analyze the given spectroscopic data, explain the signaling pattern and deduce the structure of unknown compound.

****

UV Spectroscopy

Woodward Fieser Rules for Dienes

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

Increments:

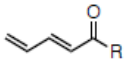
For each additional conjugated double bond		+ 30 nm
For each exocyclic double bond		+ 5 nm
For each alkyl group or Ring Residue		+ 5 nm
For each of the following groups:		
	- OR	+ 6 nm
	- O(C=O)R	+ 0 nm
	- Cl	+ 6 nm
	- Br	+ 6 nm
not affected by solvent	- SR	+ 30 nm
	- NR_2	+ 60 nm
	- Ph	+ 60 nm

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

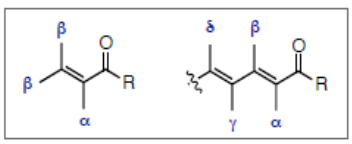
Solvent Correction	nm
H_2O	- 8
EtOH	0
$CHCl_3$	+ 1
Dioxane	+ 5
Et_2O	+ 7
Hydrocarbon	- 11

UV Spectroscopy

Woodward Fieser Rules for Enones

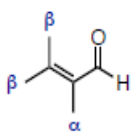
	 acyclic enone	 6-membered ring enone	 5-membered ring enone	 acyclic dienone
base values:	**215 nm**	**215 nm**	**202 nm**	**245 nm**

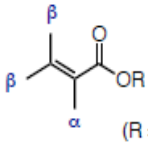
Increments:		α	β	γ	δ and higher
For each additional conjugated double bond		+ 30 nm			
For each exocyclic double bond		+ 5 nm			
For each homodiene component		+ 39 nm			
For each alkyl group		+ 10 nm	+ 12 nm	+ 18 nm	+ 18 nm
For each of the following groups:	- OH	+ 35 nm	+ 30 nm		+ 50 nm
	- OR	+ 35 nm	+ 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





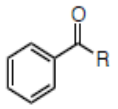
(R = H or R')

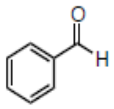
	aldehydes	carboxylic acid or ester
Base Values		
unsubstituted aldehyde or ester	208 nm	195 nm
with α or β alkyl groups	220 nm	208 nm
with α,β or β,β alkyl groups	230 nm	217 nm
with α,β,β alkyl groups	242 nm	225 nm
for an exocyclic α,β double bond		+ 5 nm
for an endocyclic α,β double bond in a 5- or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

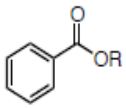
as for enones, solvent correction is also relevant

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 C-H bend
o-disubstituted	735-770	s	C-H bend
m-disubstituted	750-810 and 690-710	s s	C-H bend 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)	

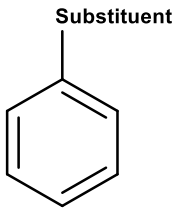
Olefinic carbons	
Substituent carbon C	**Correction**
α	+10.6
β	+7.2
γ	-1.5
α'	-7.9
B'	-1.8
γ'	-1.5
z *(cis)*	-1.1

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