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SEAT No._____ **No. of printed pages : 04**

[98, 99, 100, 102]

SARDAR PATEL UNIVERSITY

M. Sc. (Semester – IV) (CBCS) Examination

Tuesday, 10th April 2018

2:00 p.m. to 5:00 p.m.

PS04CANC01/PS04CPHC01/PS04CINC01/PS04CIPC01 : Spectroscopy - II

Total Marks : 70

Note : Figures to the right indicate full marks.

Q . 1 Select the correct answer from the alternatives given below to the each questions; **(08)**

[i] Peaks resulting from $n \rightarrow \pi^*$ transitions undergo _____ shifts with increasing solvent polarity.

(a) Blue shift (b) Red shift

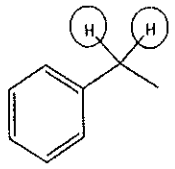
(c) Hypochromic shift (d) Hyperchromic shift

[ii] Which of the following bonds would be expected to have the highest frequency stretch ?

(a) carbon – carbon single bond (b) carbon – carbons double bond

(c) carbon – carbon triple bond (d) carbon – chlorine bond

[iii] The circled protons are _____ type of protons.



(a) Homotopic (b) Enantiotopic

(c) Diastereotopic (d) Both A and B

[iv] Increasing order of proton chemical shift in ^1H NMR spectra for following compounds is _____

$CHCl_3$	CH_3Cl	CH_4	CH_2Cl_2
I	II	III	IV

(a) I < II < III < IV (b) IV < III < II < I

(c) IV < I < III < II (d) III < II < IV < I

[v] In DEPT-90 spectrum, only _____ carbon atoms are observed.

(a) Quaternary (b) $-CH_3$

(c) $-CH_2$ (d) –CH

[vi] The ^{13}C satellite peaks are observed in _____ spectra.

(a) HETCOR (b) HMQC

(c) HMBC (d) In all of these

[vii] Mclafferty rearrangement occurs in _____.

(a) C_3 aldehyde (b) C_3 and lower aldehydes

(c) C_4 and higher aldehydes (d) all aldehydes

[viii] The maximum number of carbon atoms in a compound having M : M+1 : M+2 ratio of 100 : 1.1 : 0.01 in mass spectrum will be _____.

(a) 1 (b) 2 (c) 3 (d) 4

C.P.T.O.

Q . 2 Answer the following in short; **(ANY SEVEN)** **(14)**

[a] Explain allowed and forbidden transitions in UV spectroscopy ?

[b] How H-bonding affect IR absorption bands of organic compounds?

[c] How spin decoupling (i.e. double resonance) can be used in simplification ^{1}H NMR spectrum of 1-nitro propane?

[d] What are pople notations? Assign pople notations for isopropyl benzene and *o*-dichloro benzene .

[e] Write a short note on proton decoupled ^{13}C NMR techniques.

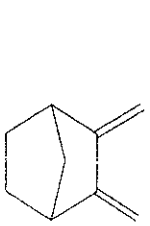
[f] What is Double Quantum Filtered COSY (DQF-COSY) NMR?

[g] Define relaxation delay time.

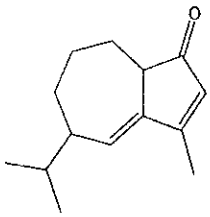
[h] How is molecular formula of a compound calculated from Isotope abundance method?

[i] The force constant for carbon monoxide molecule is 1840 $N.m^{-1}$. Calculate vibrational frequency (in cm^{-1}). Given atomic masses are ; $^{12}C = 19.9 \times 10^{-27}$ kg, $^{16}O = 26.6 \times 10^{-27}$ kg. Speed of light, $C = 3 \times 10^{8}$ $m.s^{-1}$.

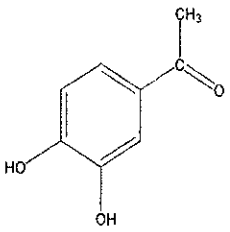
Q . 3 [a] Calculate the absorption maximum of following compounds in the UV-spectrum. **(06)**



(i)

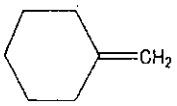


(ii)

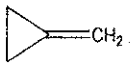


(iii)

[b] [i] Arrange the following compounds in order of their increasing frequency (in cm^{-1}) of absorption due to C = C stretching. **(03)**



(i)



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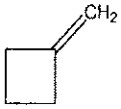
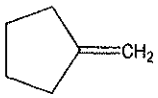


(iii)



(iv)

Assign reason for your answer.

[ii] Considering an example of ethylacetoacetate and acetonylacetone, explain how UV is useful to know about keto-enol toutomerism? **(03)**

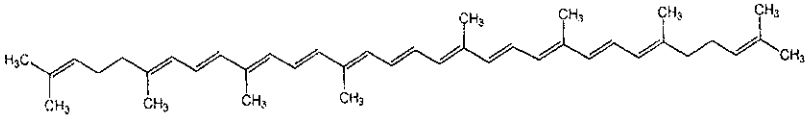
OR

[b] [i] Discuss application of IR-spectroscopy (any six points). **(03)**

[ii] Calculate λ_{max} and ε_{max} for following structure as per Fieser-Kuhn rules for a conjugated polyene. **(03)**

[$\lambda_{max} = 114 \times 5\ M + n\ (48.0 - 1.7\ n) - 16.5\ R_{endo} - 10\ R_{exo}$,

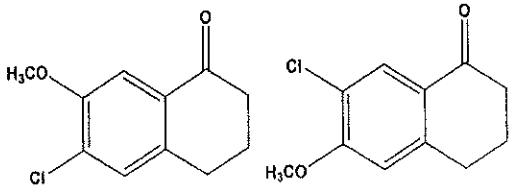
$\varepsilon_{max} = (1.74 \times 10^{4})n$]



Q.4 [a] [i] Write the structures of all the possible isomers for molecular formula $C_3H_6Br_2$. Predict the number of ^1H NMR signals for each of them. (03)

[ii] List various methods for simplification of complex ^1H NMR Spectra. Discuss "use of shift reagents" in detail. (03)

[b] [i] Explain Nuclear Overhauser Effect (NOE) in ^1H NMR. How one can distinguish following isomers using NOE-^1H NMR spectra. (03)



(I) (II)

[ii] Discuss **"Geminal and Vicinal"** coupling constants in detail. (03)

OR

[b] [i] Predict the structure for the compound with molecular formula C_4H_7OCl which shows **four signals in ^1H NMR** as given below: (03)

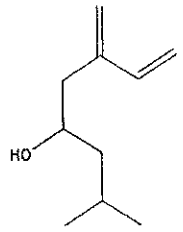
(a) 3H, doublet, 1.2 ppm,
(b) 1H, multiplet, 2.8 ppm,
(c) 2H, doubtet, 3.6 ppm
(d) 1H, doublet, 9.8 ppm

[ii] List the various aspects of ^1H NMR. What type of information is provided from those aspects? (03)

Q.5 [a] Calculate the ^{13}C chemical shift (in ppm) for the following compounds. (06)
(1) 3-methylpentane, (2) 3-pentanol, (3) Z - 3-methyl-2-pentene

[b] [i] Write a short note on 2D NMR spectroscopy. (03)

[ii] Describe the DEPT spectra of the following compound: (03)



OR

[b] Discuss the ^{13}C-^1H COSY NMR giving a suitable example. (06)

Q.6 [a] Discuss the different ionization methods used in mass spectroscopy. (06)

[b] [i] Write the differences in mass spectrum of normal and branched alkanes. (03)

[ii] Describe the mass spectra of alcohols giving suitable examples. (03)

OR

[b] Discuss the various fragmentations and rearrangements of organic compounds in mass spectroscopy. (06)

(P.T.O.)

CONJUGATED DIENE

i) Base value for homoannular diene = 253 nm
ii) Base value for heteroannular diene = 214 nm
iii) Alkyl substituent or Ring residue attached to the parent diene = 5 nm
iv) Double bond extending conjugation = 30 nm
v) Exocyclic double bonds = 5 nm
vi) Polar groups: a) -OAc = 0 nm, b) -OAlkyl = 6 nm, c) -Cl, -Br = 5 nm

α, β UNSATURATED CARBONYL COMPOUNDS OR KETONES:

1. Base value:
   a) Acyclic α, β unsaturated ketones = 214 nm
   b) 6 membered cyclic α, β unsaturated ketones = 215 nm
   c) 5 membered cyclic α, β unsaturated ketones = 202 nm
   d) α, β unsaturated aldehydes = 210 nm
   e) α, β unsaturated carboxylic acids & esters = 195 nm
2. Alkyl substituent or Ring residue in α position = 10 nm
3. Alkyl substituent or Ring residue in β position = 12 nm
4. Alkyl substituent or Ring residue in γ and higher positions = 18 nm
5. Double bond extending conjugation = 30 nm
6. Exocyclic double bonds = 5 nm
7. Homodiene compound = 39 nm
8. Polar groups: a) -OH in α position = 35 nm, -OH in β position = 30 nm
   -OH in δ position = 50 nm
   b) -OAc in α, β, γ, δ positions = 6 nm
   c) -OMe in α position = 35 nm, -OMe in β position = 30 nm, -OMe in γ position = 17 nm, -OMe in δ position = 31 nm,
   d) -Cl in α position = 15 nm, Cl in β position = 12 nm
   e) -Br in α position = 25 nm, -Br in β position = 30 nm
   f) $-NR_2$ in β position = 95 nm

Characteristic IR Absorption Frequencies

Bond		cm⁻¹
C-H	Alkanes	2850-2960
C-H	Alkenes	3020-3080
C-H	Arenes	3000-3100
C-O	Alcohols, ethers	1000-1300
C=O	Aldehydes, Ketones...	1690-1760
O-H	Alcohols	3200-3600
	Acids	2500-3000
N-H	Amines	3300-3500

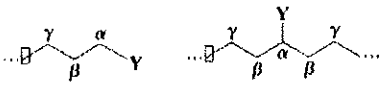
AROMATIC COMPOUNDS:

1) Base value: for a) ArCOR = 246 nm
b) ArCHO = 250 nm
c) $ArCO_2H$ = 230 nm
d) $ArCO_2R$ = 230 nm
2) Alkyl group or ring residue in ortho and meta position = 3 nm
3) Alkyl group or ring residue in para position =10 nm
4) Polar groups: a) -OH, $-OCH_3$, -OAlkyl in o, m position = 7 nm
b) -OH, $-OCH_3$, -OAlkyl p position = 25 nm
c) -O (oxonium) in o position = 11 nm
d) -O (oxonium) in m position = 20 nm
e) -O (oxonium) in p position = 78 nm
f) -Cl in o, m position = 0 nm
g) -Cl in p position = 10 nm
h) -Br in o, m position = 2 nm
i) -Br in p position = 15 nm
j) $-NH_2$ in o, m position = 13 nm
k) $-NH_2$ in p position = 58 nm
l) $-NHCOCH_3$ in o, m position = 20 nm
m) $-NHCOCH_3$ in p position = 45 nm
n) $-NHCH_3$ in p position = 73 nm
o) $-N(CH_3)_2$ in o, m position = 20 nm
p) $-N(CH_3)_2$ in p position = 85 nm

Table 1. ^{13}C shift parameters in hydrocarbons.

^{13}C 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

Table 2. ^{13}C shift parameters for different substituents.



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

Table 3. ^{13}C shift parameters for substituents at different positions in alkenes.

α	10.6
β	7.2
γ	−1.5
α′	−7.9
β′	−1.8
γ′	−1.5
Z(*cis*) correction	−1.1