

**SARDAR PATEL UNIVERSITY**

M.Sc. Organic Chemistry,

Semester IV, External Examination

Saturday, Date: 16-11-2019

Time: 02:00 pm to 05:00 pm

Subject: Spectroscopy-II Paper: PS04CORC01

- N.B. (1) Figures to the right indicate marks.  
 (2) Attempt all questions.

[Total marks: 70]

**Q.1 Choose the correct option from the following.**

08

- In IR spectroscopy,  $-C\equiv N$  stretching is appeared at  
 (a)  $\sim 1600\text{ cm}^{-1}$  (b)  $\sim 2100\text{ cm}^{-1}$   
 (c)  $\sim 1800\text{ cm}^{-1}$  (d)  $\sim 2400\text{ cm}^{-1}$
- Which transition in UV spectroscopy requires high amount of energy?  
 (a)  $\sigma \rightarrow \sigma^*$  (b)  $\pi \rightarrow \pi^*$   
 (c)  $n \rightarrow \sigma^*$  (d)  $n \rightarrow \pi^*$
- Which of the following is NMR inactive?  
 (a)  ${}^6\text{C}^{13}$  (b)  ${}^6\text{C}^{12}$   
 (c)  ${}^1\text{D}^2$  (d)  ${}^7\text{N}^{15}$
- In  ${}^1\text{H}$  NMR, benzene gives \_\_\_\_\_ signal/s.  
 (a) 1 (b) 6  
 (c) 3 (d) 0
- ${}^{13}\text{C}$  has very poor relative abundance \_\_\_\_\_ that of  ${}^{12}\text{C}$ .  
 (a) 0.11% (b) 11.11%  
 (c) 11% (d) 1.1%
- Multiple-Bond correlation is studied by...  
 (a) HMBC (b) HSQC  
 (c) HMQC (d) DQF-COSY
- In mass spectra meta stable ion peak is appeared as  
 (a) sharp and at integral m/z value (b) diffused and at integral m/z value  
 (c) sharp and at non integral m/z value (d) diffused and at non integral m/z value
- Organic compound having one bromine shows MS signal for molecular ion peak as, M : M+2 and intensity  
 (a) 1:1 (b) 1:2  
 (c) 2:1 (d) 9:1

**Q.2 Answer the following questions. (Any seven)**

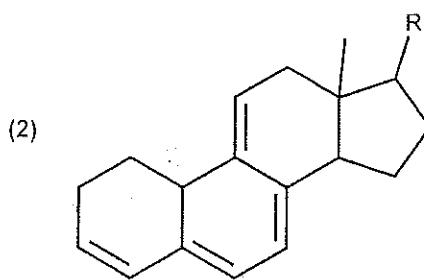
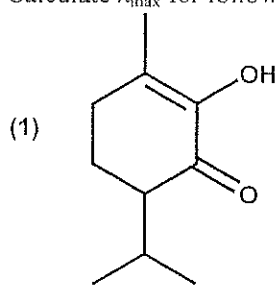
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- Calculate fundamental vibrations for  $\text{CO}_2$  molecule.
- State the Lambert's law.
- Define the term Auxochrome with example.
- Write a note on tetra methyl silane (TMS).
- Explain: Deshielding.
- Why  ${}^{13}\text{C}$  NMR spectra are generally recorded as proton decoupled spectra? Explain.
- What are the cross peaks?
- Discuss the various kinds of ions formed during mass spectrometry (MS) analysis.
- Write a note on chemical ionization method.

①

(P.T.O.)

- Q.3 A Discuss the various kinds of molecular vibrations in IR spectroscopy. 06  
 B Calculate  $\lambda_{\max}$  for following compounds. 06



OR

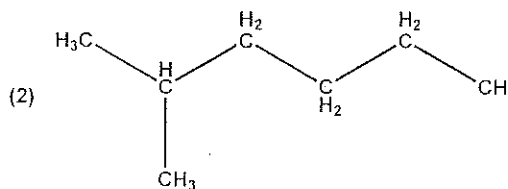
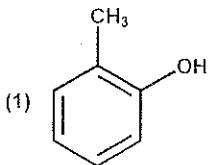
- B Calculate  $\lambda_{\max}$  for Lycopene and  $\beta$  Carotene using Fieser-Kuhn rule. 06

- Q.4 A Explain the various methods for simplification of complex NMR spectra. 06  
 B Discuss in brief: Geminal and Vicinal coupling. 06

OR

- B Explain the effect of relaxation process in NMR spectra. 06

- Q.5 A Draw the HETCOR spectrum of 2-methyl-3-pentanone. 06  
 B Calculate  $^{13}\text{C}$  NMR shift for following compounds. 06



OR

- B A compound with molecular formula  $\text{C}_5\text{H}_{10}\text{O}_2$  shows following signals in its proton  $^{13}\text{C}$  NMR. Interpret the data and assign the structure of the compound 06

- (a) 20.4  $\delta$ (quartet)  
 (b) 21.4  $\delta$ (quartet)  
 (c) 66.8  $\delta$ (doublet)  
 (d) 170  $\delta$ (singlet)

- Q.6 A Discuss the various kinds of Ionization processes in mass spectrometry. 06  
 B Discuss the following: (i) Nitrogen rule (ii) Mc Lafferty rearrangement 06

OR

- B Give the molecular formula for the compound giving following molecular ion group peaks in its mass spectrum. 06

m/z	94	95	96	97
Relative intensity	100	6.1	96	1.1

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Charts

Woodward-fieser rules for calculation U.V absorption maxima of substituted dienes.

Base value for heteroannular diene	214 nm
Base value for homoannular diene	253 nm
Double bond extending conjugation	+ 30 nm
Alkyl substituent or ring residue	+ 5 nm
Exocyclic double bond	+ 5 nm
Homo diene component	+ 39 nm
Ethanol solvent	+ 0 nm

<u>Base values:</u>			
• Acyclic $\alpha,\beta$ - unsaturated ketones		215 nm	
• Six membered cyclic $\alpha,\beta$ - unsaturated ketones		215 nm	
• Five membered cyclic $\alpha,\beta$ - unsaturated ketones		202 nm	
• $\alpha,\beta$ - unsaturated aldehyde		210 nm	
• $\alpha,\beta$ - unsaturated carboxylic acid/ester		195 nm	
<u>Increment for:</u>			
• Double bond extending conjugation		+30 nm	
• Alkyl substituent or ring residue	$\alpha$	+10 nm	
	$\beta$	+12 nm	
	$\gamma$ & higher	+18 nm	
• Polar groups	- OH	$\alpha$	+35 nm
		$\beta$	+30 nm
		$\gamma$	+30 nm
		$\delta$	+50 nm

CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton	Chemical shift, ppm
	$\delta$
Cyclopropane	0.2
Primary	$RCH_3$ 0.9
Secondary	$R_2CH_2$ 1.3
Tertiary	$R_3CH$ 1.5
Vinylic	$C=C-H$ 4.6-5.9
Acetylenic	$C\equiv C-H$ 2-3
Aromatic	$Ar-H$ 6-8.5
Benzylic	$Ar-C-H$ 2.2-3
Allylic	$C=C-CH_2$ 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	
Hydroxylic	$R-CHO$ 9-10
Phenolic	$R-OH$ 1-5.5
Enolic	$C=C-OH$ 4-12
Carboxylic	$RCOOH$ 15-17
Amino	$RNH_2$ 10.5-12 1-5

(3)

(P.T.O)

TABLE 5.1

<sup>13</sup> C Atoms	Shift (ppm) (A)
α	+9.1
β	-2.3
γ	+0.3
δ	+0.1
1° (3°)	-1.1
1° (4°)	-3.4
2° (3°)	-2.3
2° (4°)	-7.2
3° (2°)	-3.7
3° (3°)	-9.3
4° (1°)	-1.5
4° (2°)	-6.4

\*The notations 1° (3°) and 1° (4°) denote a CH<sub>3</sub> group bound to a R<sub>2</sub>CH group and to a R<sub>3</sub>C group, respectively. The notation 2° (3°) denotes a RCH<sub>2</sub> group bound to a R<sub>2</sub>CH group, and so on.

TABLE 5.2

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	
1-Methylpentane	11.5	29.5	36.9	(18.8)	
2,3-Dimethylbutane	19.5	34.3		3-CH <sub>3</sub> )	
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 <sub>3</sub> )	

TABLE 5.3

Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal\* (+ downfield, - upfield)

Y	Terminal		Internal		
	α	β	Terminal	Internal	
CH <sub>3</sub>	+9	+6	+10	+8	-2
CH=CH <sub>2</sub>	+20	+6	+6	+8	-0.5
C≡CH	+4.5	+5.5	+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 <sub>2</sub>	+22	+24	+2.3		-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 <sub>2</sub>	+29	+24	+11	+10	-5
NHR	+26	+24	+8	+6	-5
NRR	+37	+31	+8	+6	-4
NR <sub>2</sub>	+42		+6		-3
NR <sub>3</sub>	+31		+5		-7
NC <sub>2</sub>	+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

\*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.

Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm, + to the left, - to the right). Carbon Atom of Substituents in parts per million from TMS<sup>a</sup>

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 <sub>3</sub>	+9.3	+0.7	-0.1	-2.9	21.3
CH <sub>2</sub> CH <sub>3</sub>	+15.6	-0.5	0.0	-2.5	29.2 (CH <sub>2</sub> ), 15.8 (CH <sub>3</sub> )
CH(CH <sub>3</sub> ) <sub>2</sub>	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH <sub>3</sub> )
C(CH <sub>3</sub> ) <sub>3</sub>	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH <sub>3</sub> )
CH=CH <sub>2</sub>	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH <sub>2</sub> )
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C <sub>6</sub> H <sub>5</sub>	+12.1	-1.8	-0.1	-1.6	
CH <sub>2</sub> OH	+13.3	-0.8	-0.6	-0.4	64.5
CH <sub>2</sub> OCCH <sub>3</sub>	+7.7	~0.0	~0.0	~0.0	20.7 (CH <sub>3</sub> ), 66.1 (CH <sub>2</sub> ), 170.5 (C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH <sub>3</sub>	+31.4	-14.4	+1.0	-7.7	54.1
OC <sub>2</sub> H <sub>5</sub>	+29.0	-9.4	+1.6	-5.3	
OCCH <sub>3</sub>	+22.4	-7.1	-0.4	-3.2	23.9 (CH <sub>3</sub> ), 169.7 (C=O)
CH	+8.2	+1.2	+0.6	+5.8	192.0
CCH <sub>3</sub>	+7.8	-0.4	-0.4	+2.8	24.6 (CH <sub>3</sub> ), 195.7 (C=O)
CC <sub>2</sub> H <sub>5</sub>	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
CCF <sub>3</sub>	-5.6	+1.8	+0.7	+6.7	
COH	+2.9	+1.3	+0.4	+4.3	168.0
COCH <sub>3</sub>	+2.0	+1.2	-0.1	+4.8	51.0 (CH <sub>3</sub> ), 166.8 (C=O), 168.5