



**BF-5326**

Seat No. \_\_\_\_\_

**Third Year B. Sc. Examination**

**May / June – 2014**

**Chemistry : Paper - X**

*(Structural Chemistry) (Old Course)*

Time : 3 Hours]

[Total Marks : 70

સૂચના : (૧) દરેક પ્રશ્નના ૧૪ ગુણ છે.

(૨) દરેક પ્રશ્ન ફરજિયાત છે.

૧ (અ) ગમે તે બે પ્રશ્નોના જવાબ આપો : ૧૦

(૧) એક અણુ  $420^\circ$  અને  $540^\circ$ ના ભ્રમણથી સમતુલ્ય રચના આપે છે. તો તેની ભ્રમણ અક્ષ નક્કી કરો અને ભ્રમણ સંજ્ઞા આપો.

(૨) સ્ટેગર્ડ ઈથેન ( $C_2H_6$  staggerd)માં બતાવો કે

$$i \times C_3^1 \equiv S_6^5$$

(૩) અયોગ્ય ભ્રમણ અક્ષ એટલે શું ? ઉદાહરણ આપી સમજાવો.

(બ) નિયમિત ચોરસ આકારના  $MA_4$  માંથી સામસામેના ૪ બે MA બંધોને ખેંચાણ આપતાં સેમિતિમાં શું ફેરફાર થશે ?

**અથવા**

(બ)  $S_4$  અક્ષ દ્વારા ઉત્પન્ન થતી બધી જ રચનાઓ ઉદાહરણ ૪ દ્વારા સમજાવો.

- ૨ (અ) ગમે તે બે પ્રશ્નોના જવાબ આપો : ૧૦
- (૧)  $nS^2$  વિન્યાસમાંથી ઉદ્ભવતી ટર્મ સંજ્ઞાઓ તારવો અને શક્તિના ચઢતા ક્રમમાં ગોઠવો.
- (૨) સ્પિન પસંદગી અને કક્ષકીય પસંદગી નિયમો લખો અને કયા કારણોથી  $d \leftrightarrow d$  સક્રાંતિ શક્ય બને છે ? સમજાવો.
- (૩)  $jj$  યુગ્મીકરણ પર નોંધ લખો.
- (બ)  $d^2$  અને  $d^8$ નો ઓર્ગલ ડાયાગ્રામ દોરો. ૪

### અથવા

- (બ)  $P^2$  વિન્યાસમાંથી ઉદ્ભવતી બધી જ સંજ્ઞાઓ તારવો અને ભૂમિ અવસ્થાની ટર્મ કારણ આપી અલગ તારવો. ૪
- ૩ (અ) ગમે તે બે પ્રશ્નોના જવાબ આપો : ૧૦
- (૧) ધાતુ કાર્બોનીલોમાં બેક બોન્ડિંગ ઘટના ચર્ચો.
- (૨) નીચેના ધાતુ કાર્બોનીલોનાં બંધારણો દોરો અને સમજાવો :
- (૧)  $Mn_2(CO)_6$  (૨)  $Fe_2(CO)_9$
- (૩)  $Fe_3(CO)_{12}$
- (૩)  $CO_2(CO)_8$  નું બંધારણ સમજવામાં  $IR$  વર્ણપટનો ઉપયોગ સમજાવો.
- (૪) અસરકારક પરમાણુ ક્રમાંક (EAN) યોગ્ય ઉદાહરણ આપી સમજાવો.

(બ) સંકીર્ણક્ષારોની રચના નક્કી કરવામાં ચુંબકીય ચાકમાત્રાનો ઉપયોગ ચર્ચો. ૪

**અથવા**

(બ) ચુંબકીય ચાકમાત્રા નક્કી કરવાની ગોચની રીત ચર્ચો. ૪

૪ (અ) નીચેના પૈકી કોઈ પણ બે પ્રશ્નોના જવાબ આપો : ૧૦

(૧) નીચેના અણુઓમાં થતા મૂળભૂત આંદોલનોની સંખ્યા ગણો. તે કેટલા ખેંચાણ આંદોલનો આપશે :

(૧) ઈથીલીન (૨) એસિટિલિન

(૩)  $PCl_5$

(૨) IR વર્ણપટ અને H-બંધન પર નોંધ લખો.

(૩) રાસાયણિક સ્થાનાંતરને અસરકરતાં પરિબળો ચર્ચો.

(૪) PMR વર્ણપટમાં TMSનો સંદર્ભ તરીકે ઉપયોગ ચર્ચો.

(બ) સંકરણની CMR ઉપર શું અસર થાય છે ? ૪

**અથવા**

(બ)  $NH_3$  માં થતા મૂળભૂત કંપનોની સમજ અને સંખ્યા જણાવો. ૪

૫ નીચે આપેલ સ્પેક્ટ્રલ માહિતી પરથી ગમે તે બે સંયોજનોના બંધારણો નક્કી કરો : ૧૪

(૧) MW : 135

UV :  $220 \lambda_{max} 242 nm$  ( $\log \epsilon = 4.1$ )

IR : 3290(s), 3065(m), 2980-2800(m), 1664(s), 1598(m), 750(s), 688(s) $cm^{-1}$

NMR : (a) સિંગલેટ  $\delta = 2.09(3H)$

(b) સિંગલેટ  $\delta = 3.09(1H)$

(c) સંકીર્ણ સિગ્નલ  $\delta = 7.27 - 7.75 (5H)$

(૨) MW : 108

UV :  $\lambda_{\max}$  273 nm ( $\log \epsilon = 3.3$ )

IR : 3435(s), 3075-3045(m), 2955-2865(m),  
1596(s), 1496(s), 1468(s), 1240(s)  
748(s)  $\text{cm}^{-1}$

NMR : (a) સિંગલેટ  $\delta = 2.2(3H)$

(b) સિંગલેટ  $\delta = 4.9(1H)$

(c) સંકીર્ણ  $\delta = 6.85(4H)$

(૩) MF :  $C_8H_{11}N$

UV :  $\lambda_{\max}$  252 nm અને 298 nm  
( $\log \epsilon = 4.1$  અને 3.3)

IR : 3105-3035 (m), 2999-2805(m), 1604(s),  
1509(s), 1348(s), 1230-1165(s), 747(s),  
688(s)  $\text{cm}^{-1}$

NMR : (a) સિંગલેટ  $\delta = 2.83(6H)$

(b) સિંગલેટ  $\delta = 6.65 - 7.15(5H)$

(૪) અણુસૂત્ર :  $C_2H_3N$

UV : 220 nm થી ઉપર શોષણ નથી.

IR : 2950(s), 2255(s) અને 1370(m)  $\text{cm}^{-1}$

NMR : સિંગલેટ  $\delta = 1.8 \text{ ppm}$

## ENGLISH VERSION

- Instructions :** (i) All question of **14** marks.  
(ii) Each question is **compulsory**.

**1** (a) Answer any two of the following questions : **10**

- (1) A molecule gives similar structure by the rotation of  $420^\circ$  and  $540^\circ$  then identify its proper rotation axis with symbole.
- (2) Prove the equation in staggered  $C_2H_6$  :

$$i \times C_3^1 \equiv S_6^5$$

- (3) What is improper rotation axis ? Explain with proper examples.
- (b) Which changes may be occur in the molecular **4** symmetry by straching the trans bonds in regular square planar  $MA_4$  type compounds ?

**OR**

- (b) Giving suitable example explain all **4** possible configurations produced by  $S_4$  symmetry operation.

**2** (a) Answer any two of the following questions : **10**

- (1) Derive the possible terms from  $nS^2$  configuration and arrange them in the increasing order of their energy.

- (2) Write down the rules for spin choice and orbital choice. Give the reason of the possibility for  $d \leftrightarrow d$  transition ?
- (3) Write a short note on jj coupling.
- (b) Draw the Orgel diagram for  $d^2$  and  $d^8$ . 4

**OR**

- (b) Derive all the terms produced from  $P^2$  and 4  
 Devide the ground terms with proper reasons.
- 3** (a) Answer any two of the following questions : 10
- (1) Explain Back-bonding in metal carbonyls.
- (2) Explain and draw the structure of the following metal carbonyls.
- (1)  $Mn_2(CO)_6$  (2)  $Fe_2(CO)_9$
- (3)  $Fe_3(CO)_{12}$
- (3) Explain IR application to prove the structure of  $CO_2(CO)_8$ .
- (4) Giving suitable examples explain the term EAN. (Effective Atomic Number).
- (b) Discuss the use of magnetic susceptibility for 4  
 confirmation of complexes.

**OR**

(b) Explain the 'Goy-method' for the calculation of magnetic susceptibility. 4

4 (a) Answer any two of the following : 10

(1) Calculate the fundamental vibrations in the following molecules :

(1) Ethylene (2) Acetyline

(3)  $\text{PCl}_5$

(2) Write a short note on "IR spectra and H-bond".

(3) Explain the factors affecting on chemical shift.

(4) Explain the uses of TMS in PMR..

(b) How hybridization affects CMR ? 4

OR

(b) Explain fundamental vibration : 4

Number of vibration and interpretation.

5 Confirm the structures of any two compounds 14

by using these spectral data giving below :

(1) MW : 135

UV :  $\lambda_{\max}$  242 nm ( $\log \epsilon = 4.1$ )

IR : 3290(s), 3065(m), 2980-2800(m), 1664(s),  
1598(m), 750(s), 688(s) $\text{cm}^{-1}$

NMR : (a) Singlet  $\delta = 2.09(3H)$

(b) Singlet  $\delta = 3.09(1H)$

(c) Complex signal  $\delta = 7.27 - 7.75(5H)$

(2) MW : 108

UV :  $\lambda_{\max}$  273 nm ( $\log \epsilon = 3.3$ )

IR : 3435(s), 3075-3045(m), 2955-2865(m),  
1596(s), 1496(s), 1468(s), 1240(s)  
748(s)  $\text{cm}^{-1}$

NMR : (a) Singlet  $\delta = 2.2(3H)$

(b) Singlet  $\delta = 4.9(1H)$

(c) Complex  $\delta = 6.85(4H)$

(3) MF :  $C_8H_{11}N$

UV :  $\lambda_{\max}$  252 nm and 298 nm

( $\log \epsilon = 4.1$  and  $3.3$ )

IR : 3105-3035 (m), 2999-2805(m), 1604(s),  
1509(s), 1348(s), 1230-1165(s), 747(s),  
688(s)  $\text{cm}^{-1}$

NMR : (a) Singlet  $\delta = 2.83(6H)$

(b) Singlet  $\delta = 6.65 - 7.15(5H)$



(4) M.F. :  $C_2H_3N$

UV : 220 nm (not a absorption above the 220 nm).

IR : 2950(s), 2255(s), 1370(m)  $cm^{-1}$

NMR : Singlet  $\delta = 1.8$  ppm

## SPECTROSCOPICAL DATA

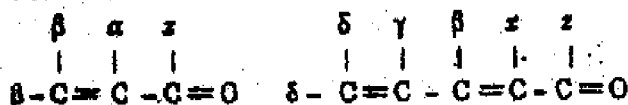
### Empirical Rules for Dienes :

Parent	Homoannular (cisoid)	Heteroannular (transoid)
	$\lambda = 253 \text{ nm}$	$\lambda = 214 \text{ nm}$
Increment for double bond extending conjugation	30	30
Alkyl subst. or ring residue	5	5
Exocyclic double bond	5	5
Polar grouping : -OCOCH <sub>3</sub>	0	0
-OR	6	6
-Cl, -Br	5	5
-NR <sub>2</sub>	60	60

Homocyclic Diene component  $\rightarrow 39 \text{ nm}$

### Empirical Rules for Enones :

#### Base values :



- (a)  $\gamma = \text{R}$  (ketones)
- 6 - membered ring or acyclic parent enone = 215 nm
  - 5 - membered ring parent enone = 202 nm
- (b)  $\gamma = \text{H}$  (aldehydes) = 207 nm
- (c)  $\gamma = \text{OH}$  (acids) or OR (esters) = 197 nm

#### Increments for :

Double bond extending conjugation	30 nm
Homocyclic Diene component	39 nm
Exocyclic double bond	5 nm

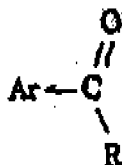
Addition for each substituent :

	$\alpha$	$\beta$	$\gamma$	$\delta$
- R (alkyl) group or ring residue	10 nm	12 nm	18 nm	18 nm
- OH (hydroxy)	35	30	30	50
- OR (alkoxy)	35	30	17	31
- Cl (chloro)	15	10	12	12
- Br (Bromo)	25	31	25	25
- NH <sub>2</sub> , - NHR, - NR <sub>2</sub> (amino)	-	38	-	37
- NO <sub>2</sub> (Nitro)	-	35	-	37
- COOCH <sub>3</sub>	6	6	-	6
Solvent correction	Variable			

$\lambda_{OH}$   
 $\lambda_{max} (calc.) = Total$

### Empirical Rules for Benzoyl Derivatives:

Parent chromophore



R = alkyl or ring residue

R = H

R = OH or OR (alkoxy)

246 nm

250 nm

230 nm

Increment for each substituent :

- alkyl or ring residue

- OH, - OCH<sub>3</sub>, - OAlkyl

- O<sup>-</sup>

- Cl

- Br

- NH<sub>2</sub>

- NHCOCH<sub>3</sub>

- NHCH<sub>3</sub>

- N(CH<sub>3</sub>)<sub>2</sub>

o, m, 3; p 10 nm

o, m, 7; p 25 nm

o, 11; m 20; p 78 nm

o, m 0 (zero); p 10 nm

o, m 2; p 16 nm

o, m 13; p 58 nm

o, m, 20; p 45 nm

p 73 nm

o, m 20; p 85 nm

### NMR (PMR) Chemical Shift :

Type of proton	Chemical Shift ppm (δ)	Type of protons	Chemical shift ppm (δ)
Primary $R-CH_3$	0.9	Alcohols $HO-CH$	3.4 - 4
Secondary $R_2-CH_2$	1.3	Ethers $HO-OR$	3.3 - 4
Tertiary $R_3-CH$	1.5	Esters $R-COO-CH$	3.7 - 4.1
Vinyllic $C=C-H$	4.6 - 5.9	Acids $HO-COOH$	2 - 2.5
Acetylenic $C\equiv C-H$	2 - 3	Carbonyl $HO-C=O$	2 - 2.7
Aromatic $Ar-H$	6 - 8.5	Aldehydic $R-CHO$	9 - 10
Benzylic $Ar-CH_2$	2.2 - 3	Hydroxylic $R-OH$	1 - 5.5
Allylic $C=C-CH_2$	1.7	Phenolic $Ar-OH$	4 - 12
Chloride $HC-Cl$	3 - 4	Enolic $C=C-OH$	15 - 17
Bromide $HC-Br$	2.5 - 4	Carboxylic $R-COOH$	10.5 - 12
Iodide $HC-I$	2 - 4	Esters $HC-COOR$	2 - 2.2
Amine $R-NH_2$	1 - 5	Cyclopropane	0.22

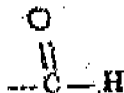
#### Aromatic substitution type C-H out of plane bending

Number of adjacent Hydrogen atom	
6	750(s) & 900(s)
4	750
3	780
2	830
1	880

### SELECTED IR - GROUP FREQUENCIES

Group	Compounds	Frequency $\bar{\nu}$ ( $cm^{-1}$ )
 -C-H 	Alkane, stretching	2850 - 2960 (s)
	Alkane, bending	1430 - 1480
 =C-H	Alkene, stretching	3010 - 3095 (m)
	Alkene, bending (cis)	700 - 780 (s)
	Alkene, bending (trans)	900 - 980 (s)
$\equiv C-H$	Alkyne, stretching	3200 - 3300 (s)
Ar-H	Aromatic, stretching	3000 - 3100 (m)
	Aromatic, bending (out of plane)	

	mono substituted	770 - 730 (s)
	and	710 - 690 (s)
	ortho substituted	735 - 770 (s)
	meta substituted	690 - 710 (s)
	and	750 - 810 (s)
	para substituted	800 - 860 (s)

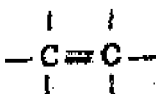


Aldehyde stretching (two bands)  $\left\{ \begin{array}{l} 2700 - 2740 \\ 2820 - 2900 \end{array} \right.$



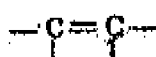
C---H (bending)

1380 - 1485, 1395 - 1370



Alkane

600 - 1500



Alkene  $\left\{ \begin{array}{l} \text{cis } 1650 - 1660 \\ \text{trans } 1670 - 1680 \end{array} \right.$

1620 - 1680 (v)



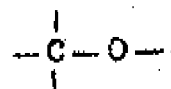
Alkyne

2100 - 2260 (v)



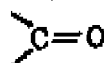
Aromatic ring

1500 - 1600 (v)  
(a group of bands)



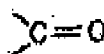
Alcohols, Phenols, Acids

1050 - 1300 (s)



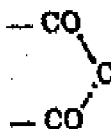
Aldehydes, Ketones, Acids,  
Esters

1690 - 1760 (s)



Amides (-CONH<sub>2</sub>)

1650 - 1680 (s)



Anhydride (Two bands)

$\left\{ \begin{array}{l} 1740 - 1790 (s) \\ 1800 - 1850 (s) \end{array} \right.$

$\text{--O--H}$	Monomeric Alcohols, Phenols	3590 - 3650 (v)
$\text{--O--H}$	H-bonded Alcohols, Phenols	3200 - 3500 (v)
$\text{--O--H}$	Monomeric Carboxylic acid	3500 - 3650 (m)
$\text{--O--H}$	H-bonded Carboxylic acid	2500 - 3000 (V, b)
$\begin{array}{c}   \\ \text{--C--N--} \\   \end{array}$	Amide, Amine $\text{--}\overset{ }{\text{C}}=\text{N--}$	1180 - 1360 (s)
$\text{--C}\equiv\text{N}$	Nitrile	2210 - 2280 (s)
$\begin{array}{c}   \\ \text{--N--H} \\   \end{array}$	Amide, Amine	3200 - 3500 (m)
$\text{--NO}_2$	Nitro (Two bands)	1300 - 1370 (s) 1500 - 1570 (s)
$\begin{array}{c}   \\ \text{--C--X} \\   \end{array}$	Halide	500 - 800

: CMR - Chemical Shifts :

<b>Alkanes</b>	$\delta$ ppm	<b>Ethers</b>	$\delta$ ppm
Cyclopropanes	0 - 8	$\text{CH}_3\text{--O}$	46 - 60
Cycloalkanes	5 - 25	$\text{RCH}_2\text{--O}$	42 - 70
$\text{R--CH}_3$	5 - 25	$\text{R}_2\text{CH--O}$	65 - 77
$\text{R--CH}_2\text{--R}$	22 - 45	$\text{R}_3\text{C--O}$	70 - 83
$\text{R}_2\text{CHR}$	30 - 53		
$\text{R}_3\text{C--R}$	28 - 50		
		<b>Unsaturated Compounds</b>	
<b>Halogens</b>		<b>Aromatics</b>	110 - 133
$\text{CH}_2\text{X}$	5 - 25	<b>Alkenes</b>	100 - 143
$\text{RCH}_2\text{X}$	5 - 38	<b>Alkynes</b>	75 - 95

$R_2CHX$	30 - 62
$R_2CX$	35 - 75
<i>Amines</i>	
$CH_3-N$	10 - 45
$R-CH_2-N$	45 - 55
$R_2CH-N$	50 - 70
$R_2C-N$	60 - 75

<i>Carbonyl Carbons</i>	
$R COOR$	160 - 177
$R COOH$	162 - 183
$R CHO$	185 - 205
$R COR$	190 - 220

*Hetero atoms*

$RCH_2-S$	22 - 42	$Ar-N$	130 - 138
$RCH_2-P$	10 - 25	$Ar-O$	130 - 150
$Ar-P'$	120 - 130	$R-CN$	118 - 123