



**DBB-003-001506**

**B. Sc. (Sem. V) (CBCS) Examination**

**May/June - 2015**

**C-502 : Organic Chemistry & Spectroscopy**

**Faculty Code : 003**

**Subject Code : 001506**

Time : 2½ Hours]

[Total Marks : 70

- Instructions : (1) Question No. 1 carries 20 marks (M.C.Q).  
(2) Question no. 2 and 3 carry 25 marks each.  
(3) All questions are compulsory.

- 1 Give correct answers : (M.C.Q.) 20
- (1)  $\beta$ -phenyl ethyl amine acetylated with acetic anhydride followed by reaction with phosphorous oxychloride to obtain
- (A) 1-methyl isoquinoline  
(B) 1-methyl-3,4-dihydroisoquinoline  
(C) 1-methyl-3,4-dihydroquinoline  
(D)  $\beta$ -phenyl ethyl acetamide
- (2) 2-propanone reacts with sodamide followed by reaction with iodomethane to obtain
- (A) Diethyl ketone  
(B) Diethyl ether  
(C) 2-propanone  
(D) Ethyl methyl ketone

- (3) Which molecular formula is correct of conyryne ?
- (A)  $C_7H_{12}N_2$
  - (B)  $C_8H_{11}N$
  - (C)  $C_8H_{17}N$
  - (D)  $C_9H_{11}N_2$
- (4) Nicotine reacts with bromine and ethanoic acid to obtain
- (A) Dibromoticonine
  - (B) Dibromonicotine
  - (C) Dibromocotinine
  - (D) Dibromonicotinoate
- (5) Which method is utilized for determination of ring size of glucose ?
- (A) Methylation method
  - (B) Periodic acid method
  - (C) Zeisel's method
  - (D) Killani method
- (6) D(-) talose is a / an
- (A) Aldo tetrose
  - (B) Aldo pentose
  - (C) Aldo hexose
  - (D) Keto hexose

- (7) Sulphanilic acid is diazotized with  $\text{NaNO}_2 + \text{HCl}$  at  $0-5^\circ\text{C}$  temp. followed by coupled with  $\beta$ -naphthol to obtain
- (A) Chrysodine-G
  - (B) Orange-II
  - (C) Methyl orange
  - (D) Auramine-O
- (8) Which compound is utilized in cheap cold drink ?
- (A) Auramine-O
  - (B) Starch
  - (C) Atenolol
  - (D) Saccharin
- (9) Which molecular formula is correct of Thiazole ?
- (A)  $\text{C}_3\text{H}_3\text{NS}$
  - (B)  $\text{C}_3\text{H}_6\text{NS}$
  - (C)  $\text{C}_4\text{H}_3\text{NS}$
  - (D)  $\text{C}_3\text{H}_5\text{NS}$
- (10) 1,2-diamino ethane reacts ethanoic acid to yield
- (A) 2-methyl-4,5-dihydro imidazole
  - (B) 2-amino imidazole
  - (C) 2-amino pyrazole
  - (D) 2-amino thiazole
- (11) Which point group is present in  $\text{PtCl}_4^{2-}$  ?
- (A)  $\text{D}_{3h}$
  - (B)  $\text{C}_{4h}$
  - (C)  $\text{C}_{4v}$
  - (D)  $\text{D}_{4h}$

- (12) Which point group is present in Hydrogen peroxide (cis Non planar) molecule ?
- (A)  $C_2$
  - (B)  $C_{2h}$
  - (C)  $C_{2v}$
  - (D)  $C_{3h}$
- (13) Which molecule shows  $C_{\infty v}$  point group ?
- (A) Ammonia
  - (B) Carbon dioxide
  - (C) Hydrocyanic acid
  - (D) Boron trifluoride
- (14) Bathochromic shift is also known as
- (A) red shift
  - (B) blue shift
  - (C) violet shift
  - (D) None of these
- (15) According to Franck-Condon principle, during an electronic transition the interatomic distance remains
- (A) Changed
  - (B) Unaltered
  - (C) Altered
  - (D) None of these

- (16)  $1 \text{ m}\mu = \text{_____ cm}$
- (A) 1
  - (B)  $10^{-2}$
  - (C)  $10^{-4}$
  - (D)  $10^{-1}$
- (17) Finger print region of IR is
- (A)  $2.5 \mu$  to  $25 \mu$
  - (B)  $0.8 \mu$  to  $2.5 \mu$
  - (C)  $11 \mu$  to  $15 \mu$
  - (D)  $7 \mu$  to  $11 \mu$
- (18) In IR spectra for pressed pallet technique solid compound is used with substance of
- (A)  $\text{CaF}_2$
  - (B)  $\text{CaCl}_2$
  - (C) KBr
  - (D)  $\text{ZnBr}_2$
- (19) Which of the following is not observed in bending vibrations ?
- (A) Wagging
  - (B) Twisting
  - (C) Rocking
  - (D) All are involved

(20) Which molecule gives permanent dipole moment ?

- (A)  $\text{BF}_3$
- (B)  $\text{CO}$
- (C)  $\text{H}_2\text{O}_2$  (trans)
- (D)  $\text{NH}_3$

2 (a) Give answers in short : (any three) 6

- (i) Write reaction of furfuraldehyde with ammonium formate.
- (ii) Write reaction of 2-n-propyl pyridine with  $\text{KMnO}_4$  and Methyl iodide.
- (iii) Write reaction of nicotine with  $\text{Br}_2/\text{CH}_3\text{COOH}$  followed by reaction with sulphuric-sulphurous acid at  $140^\circ\text{C}$  temp.
- (iv) Write reaction of D(+) glucose with Benedict's solution.
- (v) Write reaction when D(-) fructose is oxidised with periodic acid.
- (vi) Give conversion of : Dulcin from Phenacetin

(b) Give answers of following questions : (any three) 9

- (i) Synthesis of
  - (a) Oxazine from ethylene oxide
  - (b) Phenothiazine from diphenylamine

- (ii) Synthesis of chrysothine - G from benzene
  - (iii) D(+) Mannose from D(+) Glucose
  - (iv) D(-) Fructose from D(-) Arabinose
  - (v) Synthesis of Papaverine
  - (vi) Explain Hoffmann rearrangement with mechanism using the example of Nicotinamide.
- (c) Give answers in brief : (any two) 10
- (i) Give reactions only
    - (a) Step up reaction
    - (b) D(-) fructose from D(+) glucose
  - (ii) Explain Arndt-Eistert reaction with mechanism using the example of 2-Furoic acid
  - (iii) Give synthesis of
    - (a) Pyrazole
    - (b) Imidazole
  - (iv) Give synthesis of
    - (a) Nicotine from 2-carboxy pyridine
    - (b) L(-) hygrinic acid from Nicotine
  - (v) Give synthesis of
    - (a) Adrenaline
    - (b) Auramine-O

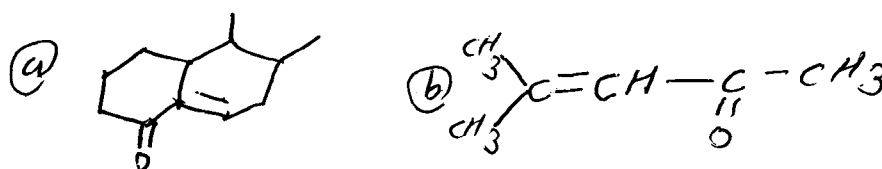
- 3 (a) Give answers in short : (any three) 6
- (i) Define law of closure
  - (ii) Explain  $S_n$  point group with example.
  - (iii) Define vibration energy
  - (iv) Define stretching vibrations
  - (v) Explain vertical plane of symmetry of  $H_2O$  molecule.
  - (vi) Explain Boric acid (planar) molecule and derive point group
- (b) Give answers of following questions : (any three) 9
- (i) Explain  $D_{\infty h}$  and  $C_{2h}$  point group with example.
  - (ii) Write application of UV spectra
  - (iii) Explain Fermi resonance.
  - (iv) Explain centre of symmetry with example.
  - (v) Write a note on hypsochromic shift and hyperchromic shift.
  - (vi) Write a note on finger print region.
- (c) Give answers in brief : (any two) 10
- (i) Give applications of IR and discuss the modes of fundamental vibrations.



(ii) The compound having molecular formula  $C_8H_{11}N$  shows the following results in IR spectra. Derive the structural formula of the compound :

IR = 3105-3035  $cm^{-1}$ ; 1604-1509  $cm^{-1}$ ; 1230-1135  $cm^{-1}$ ;  
2990-2805  $cm^{-1}$ , 1348  $cm^{-1}$

(iii) Calculate the  $\lambda_{max}$  value of following example :



(iv) Discuss the factors affecting the bonds of carbonyl ( $>C=O$ ) group in IR spectrum.

(v) Explain multiplication table for  $C_{3v}$  point group.

### Spectral Data

U.V. :

Empirical rules for Dienes :

(A) Homoannular    (b) Heteroannular  
 $\lambda = 253 \text{ nm.}$          $\lambda = 215 \text{ nm.}$

Increments for double bond extending conjugation	30 nm.	30 nm.
Exocyclic double bond	5	5
Alkyl substitution or ring residue	5	5
Homocyclic Diene components	39	39
Polar groups :		
- OCOCH <sub>3</sub>	0	0
- OR	6	6
- Cl, -Br	5	5
- NR <sub>2</sub>	60	60

(C) Simple Diene :

Parent  $\lambda = 217 \text{ nm.}$

Polar groups :

Alkyl subst for ring residue	5 nm
-Cl, -Br	17
-OH	5
-OR	5
-NR <sub>2</sub>	60
-SR	30

(D) Empirical Rules for Enones and Dienones :

(a) Z = C	$\lambda$
(1) 6 membered ring or acyclic	215
(2) 5 membered ring	202
(b) Z = H	207
(c) Z = OH or OR	193
(d) Acyclic dienone	245
Increment for :	
Double bond extending conjugation	30
Alkyl group of ring residue	$\alpha$ 10
	$\beta$ 12
	$\gamma$ or higher 18
Exocyclic double bond position	5
Homocyclic diene component	39

Polar groups	$\alpha$	$\beta$	$\gamma$	$\delta'$ other
-Cl	15	12	.	.
-OH	35	30	50	50
-OR	35	30	17	31
-NR <sub>2</sub>	.	93	.	.
-O	.	75	.	.
-NHCOR	.	95	.	.
-OCOCH <sub>2</sub>	6	6	.	6
-SR	.	85	.	.
-Br	25	30	.	.
-NO <sub>2</sub>	.	95	.	.

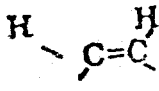
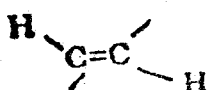
(e) Empirical Rules for Benzoyl Derivative :

Parent Chromophor :	mm
Z = alkyl or ring residue	246
Z = H	250
Z = -OH or -OR	230

Increment for each substituent :	Q	M	R
Alkyl or ring residue	3	3	10
-OH; -OCH <sub>3</sub> -OR	7	7	25
-O	11	20	78
-Cl	0	0	10
-Br	2	2	15
-NH <sub>2</sub>	13	13	58
-NHCOCH <sub>2</sub>	20	20	45
-NHCH <sub>3</sub>	.	.	73
-N(CH <sub>2</sub> ) <sub>3</sub>	20	20	55

Infra - Red Data

Alkene (stretching)	-C-H	2850-2960(v)
Alkene	=C-H	3100-3200(m)
Alkyene	=C-H	3200-3300(s)
Aromatic	ArC-H	3010-3100(m)
Aromatic ring	C=C	1500-1600(v) (two to three)
Alkene	>C=C<	1610-1680(v)
Alkyene	-C=C <sup>2</sup> .	2100-2260(s)
Alkene (Bending)	-C-H	1340(w)
	-C(C <sub>2</sub> H <sub>3</sub> ) <sub>3</sub>	1430-1470(m) & 1380-1385(s)
	-C(CH <sub>2</sub> ) <sub>3</sub>	1365 (8)
Aldehyde	-C-H	2820-2000(w)&2650 2760(a)
Aldehyde	C=O	1740-1720(s)
Ketone	C=O	1725-1710(s)
Carboxylic acid	C=O	1725-1705(s)
Ester	C=O	1750-1730(s)
Amide	C=O	1670-1640(s)
Anhydride	C=O	1810-1860(s)&1740-1790
Alcohols, Ethers, esters		
Carboxylic acids, Anhydride	C-O	1300-1000(s)

Alcohols, phenols :		
Free	O-H	3650-3600(sh)
bonded	O-H	3500-3200(b)
Carboxylic acids free		
Free	O-H	3500-3650(m)
H-bonded	O-H	2500-3200(b)
amines (stretch)	N-H	3330-3500(m)
Bnding	-N-H	1640-1550(m)
Nitrile	-C=N	2210-2280(s)
Ether	-O-	1070-1150(s)
Alkene bending		
disubstituted Cis.		-690(s)
disubstituted Trans.		960-970(s)
Aromatic substitution :		
Type C-H out of plane bending		
No. of adjacent H atom.		range cm
5		750(s) & 700(s)
4		750
3		780
2		830
1		850