Registration Number:

Date & Session

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU - 27
B.Sc. (CHEMISTRY)– IV SEMESTER
SEMESTER EXAMINATION: APRIL 2023
(Examination conducted in May 2023)
CH 422 – CHEMISTRY IV

(For current batch students only)

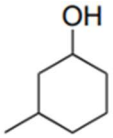
Time: 2 Hours **Max Marks: 60**

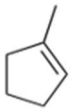
This paper contains FOUR printed pages and THREE parts.
(Spectral data is provided in the end of this question paper)

PART-A

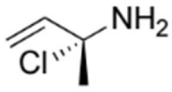
Answer any SEVEN of the following questions. **(7 x 2 = 14)**

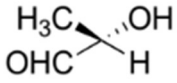
1. Differentiate between line and band spectrum.
2. The chemical shift of benzene proton is 2181 Hz. Calculate the chemical shift of this proton in ppm when the instrument is operated at a frequency of 300 MHz.
3. What is zero-point energy in vibrational spectroscopy. Give the expression.
4. Between RCOOR and $RCONH_2$, which molecule will show higher C=O frequency? Justify.
5. Give the IUPAC name of the following compounds.

(i) 

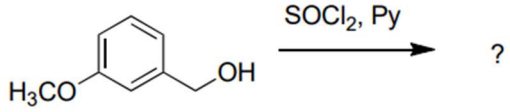
(ii) 

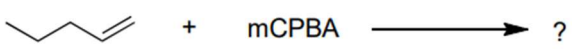
6. Neopentane has lower boiling point than n-pentane. Give reason.
7. What are meso compounds? Give an example.
8. Apply Cahn Ingold Prelog rule and assign the R or S nomenclature for the following compounds.

(i) 

(ii) 

9. Complete the following reactions.

(i) 

(ii) 

Part B

Answer any SIX of the following questions. **(6 x 6 = 36)**

10. a) Discuss the isotopic substitutional effect in the CO molecule and its influence on the spacings of spectral lines in a rotational spectrum.

    b) The rotational spectrum of HI consists of a series of equally spaced spectral lines with spacing equal to 12.8 cm^{-1}. Calculate the moment of inertia and the internuclear distance. (Atomic mass of H atom and I atom is 1.672 x 10^{-27} kg and 210.70 x 10^{-27} kg, respectively, h = 6.626 x 10^{-34} Js, c = 3 x 10^{8} m/s). (3 + 3)

11. a) What is Raman effect? Discuss the origin of Stokes and anti-Stokes lines using energy level diagram.

    b) Explain the effect of conjugation on UV absorption maxima by taking ethylene and 1,3-butadiene as an example. (3 + 3)

12. a) The ^{1}H NMR spectrum of pure ethanol is different from impure ethanol. Substantiate.

    b) How can you distinguish the IR spectra of primary, secondary and tertiary amines? (3 + 3)

13. Write a note on spin-spin splitting and coupling constant.

14. Discuss the conformational analysis of butane with potential energy diagram.

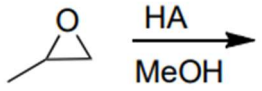
15. a) Write the possible enantiomers and diastereomers of 2,3-dibromopentane.

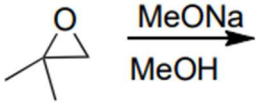
    b) Draw all the possible stereoisomers of 1,2-dimethylcyclopropane. (3 + 3)

16. a) The concentration of a cholesterol solution is 6.15 g/100 mL. This solution in a 5 cm polarimeter tube causes an observed rotation of +1.2 º. Calculate the specific rotation of the cholesterol.

    b) With suitable example explain the mechanism of Williamson ether synthesis. (3 + 3)

17. Explain the mechanism for the ring opening of unsymmetrical epoxides.

(i) 

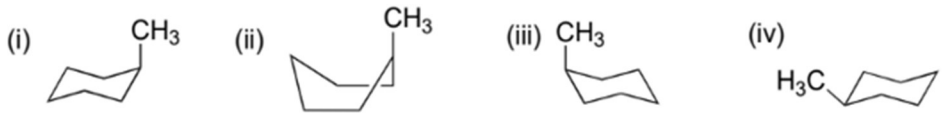
(ii) 

Part C

Answer any TWO of the following questions. **(2 x 5 = 10)**

18. a) The total number of bending vibrations of a linear molecule is 6. How many atoms are there in this molecule. Find the total number of vibrations if this molecule would be non-linear.

    b) Identify the most stable conformations among the following. Justify. (3 + 2)



19. Sketch the functional isomers of the following compounds.

    a) C_2H_6O

    b) $C_2H_4O_2$

    c) C_3H_6O

20. The ^1H NMR of a compound with molecular formula $C_6H_{12}O_2$ consists of four signals (Data is given in the table). IR spectrum of this compound shows two strong peaks at 1736 and 1199 cm^{-1}. Predict the structure of this compound with proper reasoning.

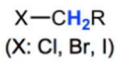
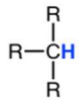
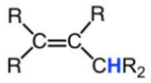
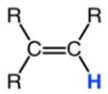
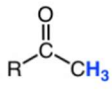
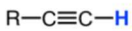
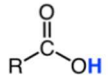
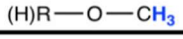
Splitting	δ	Integral ratio
triplet	1.1	3H
doublet	1.2	6H
septet	4.8	1H
quartet	2.3	2H

Important Spectral Data

Table 1: IR data

Important IR Stretching Frequencies		
Type of bond	**Wavenumber (cm^{-1})**	**Intensity**
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

Table 2: Approximate values of chemical shifts for ^1H NMR

Type of Proton	Chemical Shift (ppm)	Type of Proton	Chemical Shift (ppm)
	0.9 – 1.2		3.1 – 3.8
	1.2 – 1.5		variable, 1 – 5
	1.4 – 1.9		variable, 1 – 5
	1.5 – 2.5		4.5 – 6.0
	2.0 – 2.6		6.0 – 8.5
	2.2 – 2.5		9.5 – 10.5
	2.5 – 3.0		10 – 13
	3.3 – 4.0		