

Reg. No. :

Name :

III Semester M.Sc. Degree (CBSS – Reg./Sup./Imp.) Examination, October 2022
(2019 Admission Onwards)

CHEMISTRY

CHE 3C.09 : Organic Chemistry – III

Time : 3 Hours

Max. Marks : 60

SECTION – A

Answer all questions in one word or one sentence. Each question carries 1 mark.

- Aniline absorption shifts from 230 nm in neutral medium to 203 nm in acidic medium. Why?
- What is the significance of the fingerprint region in the IR spectra?
- How many different types of protons are there in allyl chloride?
- Predict the number of peaks in the ^{13}C -NMR spectrum of p-dimethoxy benzene and m-dimethoxy benzene.
- What are the major fragments and their m/z values in the mass spectrum of nitrobenzene?
- What is a metastable ion? What is its significance?
- Draw the structure of coumarin. What is its use in medicine?
- Sketch the structures of the pyrimidine bases present in DNA.

(8×1=8)

SECTION – B

Answer any 8 questions. Answer may be two or three sentences. Each question carries 2 marks.

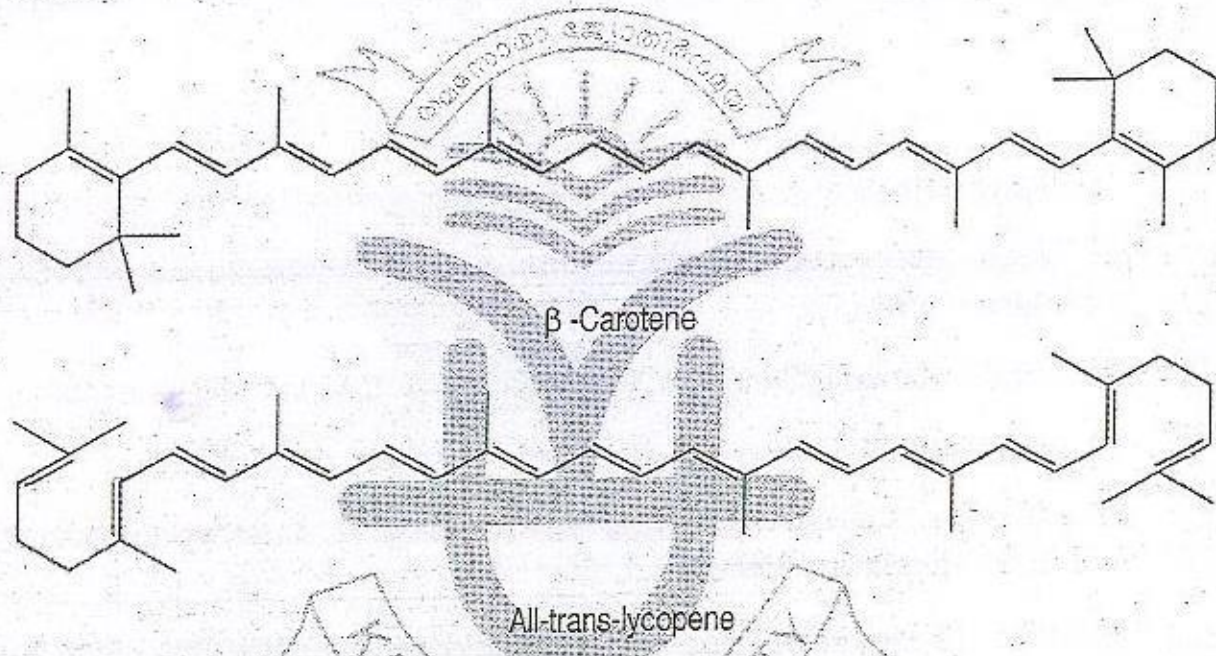
- Propene and propyne show C-C multiple bond stretching in IR spectrum, while ethylene and ethyne do not show such bands. Why?

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- Explain how *cis*-stilbene is distinguished from *trans*-stilbene using UV spectra.
- Comment on the aromatic nature of cyclooctatetraene on the basis of its NMR spectrum.
- An organic compound having the molecular formula $\text{C}_3\text{H}_7\text{Cl}$ exhibits the following signals in the ^1H NMR spectrum : (i) δ 0.9 (3H, t); δ 1.6 (2H, m); δ 3.3 (2H, t). Suggest the probable structure.
- Calculate the λ_{max} and ϵ_{max} for the following molecules using Woodward-Fieser rules.



- Explain the term off-resonance decoupling.
- What is nitrogen rule? Explain the rule taking the example of nitrobenzene.
- Explain the principle of TOF analyser.
- Phenetole in its mass spectrum exhibits an ion peak at $\frac{m}{z}$ 94. Explain its formation.
- Name the following compounds based on Hantzsch-Widman system of nomenclature.



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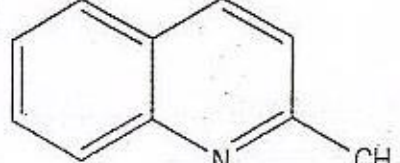
- Pyrrole is more reactive at 2-position than 3-position in electrophilic substitution reactions. Explain.
- Give any method of synthesis of oxirane.

(8×2=16)

SECTION – C

Short paragraph questions. Answer any 4 questions. Each question carries 3 marks.

- An organic molecule having molecular formula $\text{C}_2\text{H}_5\text{NO}$ shows in its IR spectrum an absorption band at 1680 cm^{-1} . When reduced with LiAlH_4 it forms $\text{C}_2\text{H}_7\text{N}$ whose IR spectrum lacks the peak at 1680 cm^{-1} , instead it exhibits a band at 3300 cm^{-1} . Suggest the probable structure.
- a) An organic compound in hexane exhibits λ_{max} at 305 nm and in ethanol at 307 nm. What should be the nature of the transition and why?
b) Sketch the first order NMR spectrum of ethanol.
- Explain Nuclear Overhauser Effect.
- What is FAB? What are its advantages and disadvantages?
- a) Explain McLafferty rearrangement with an example.
b) Give a synthesis of the following:



- How is pyrimidine ring constructed? Give one method of synthesis of thymine.

(4×3=12)

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SECTION – D

Essay type questions. Answer 4 questions. Each question carries 6 marks.

- a) The principal flavour constituent of cinnamon is a compound whose mass spectrum shows the molecular ion at m/z 132 ($\text{C}_9\text{H}_8\text{O}$), with the base peak at m/z 131, and a significant peak at m/z 103. IR spectrum : 1690 cm^{-1} (s); UV spectrum : 284 (intense), 308 (weak) nm. ^1H NMR spectrum: δ 9.75 (1H, d, J = 8 Hz); 7.45 (1H, d, J = 16 Hz), 7.4 (5H, m) and 6.7 (1H, dd, J = 16, 8 Hz). Deduce the structure of the molecule and comment on its stereochemistry with respect to the NMR spectrum.
OR
b) Discuss the various factors affecting the positions frequencies of absorption in the IR spectrum.
- a) An organic compound having the molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$, gave the following spectral data :
UV : λ_{max} 274 nm ($\epsilon = 2050$)
IR : ν 3031, 2941, 1724, 1608, 1504, 1060 and 830 cm^{-1}
 ^1H NMR δ : 2.35 (3H, s); 3.82 (3H, s) and 7.20–7.85 (4H, m)
MS (m/z) : 150, 145, 119.
What is the probable structure of the compound?
OR
b) Discuss the terms :
i) Lanthanide shift reagents and
ii) CIDNP.
- a) Write short notes on :
i) MALDI and ii) EI.
OR
b) What are the common methods for the simplification of complex spectra in NMR spectroscopy? Explain with suitable examples.
- a) Explain the synthesis strategies for the synthesis of indole and benzofurans citing examples.
OR
b) Describe the methods of synthesis of selenophanes, tellurophanes and naphthyridines.

(4×6=24)