Reg. No…….. Name…… **25P344**

M.Sc. DEGREE END SEMESTER EXAMINATION - OCTOBER 2025

SEMESTER – 3: CHEMISTRY/PHARMACEUTICAL CHEMISTRY

COURSE: 24P3CHET12/24P3CPHT12: SPECTROSCOPIC METHODS IN CHEMISTRY

(Regular 2024 Admission)

Time: Three Hours Max. Weights: 30

PART A

Answer any 8 questions. Weight: 1

1. A conjugated diene absorbs at 240 nm in hexane but shifts to 255 nm in ethanol. Analyze the reason for this bathochromic shift based on solvent polarity and transition type. (U, CO3)
2. Predict the λ_{max} for the following compound using Woodward–Fieser rules: CH_2=CH–CH=CH–$COCH_3$. Include all increments and assumptions. (A, CO2)
3. Explain Nuclear Overhauser Effect. How is it useful in ^{13}C NMR spectroscopy? (U, CO1)
4. Write briefly on long range coupling in NMR spectroscopy. (U, CO1)
5. How would you differentiate between *cis*- and *trans*-stilbene using IR spectroscopy? (U, CO3)
6. What are the differences expected in the NMR and IR spectra of *ortho-hydroxybenzaldehyd*e and *para-hydroxybenzaldehyde*? (A, CO2)
7. Arrange the following compounds in the increasing order of their carbonyl IR absorption frequencies: acetophenone, benzaldehyde, benzoic acid and benzamide. Justify your order. (A, CO2)
8. Analyze the ^1H NMR splitting patterns of the following compound: CH_2F–CH_2–OCH_3. Assign the proton environments and coupling constants. (A, CO2)
9. What information can be obtained from a COSY spectrum? Illustrate briefly. (U, CO1)
10. Explain how the Cotton effect can be used to determine absolute configuration in chiral ketones. (U, CO1)

(1 x 8 = 8)

PART B

Answer any 6 questions. Weights: 2

11. Briefly explain the methods used to simplify a non-first order NMR spectrum into a first order spectrum. (U, CO1)
12. Explain the fragmentation patterns of phenol and 2-pentanone using mass spectral data. (U, CO3)

13. Compare the suitability of EI and ESI for analysing (a) aliphatic ketones and (b) peptides. Justify your choice. (U, CO1)
14. Describe the octant rule and apply it to predict the sign of the Cotton effect for a given cyclic ketone. (U, CO1)
15. Design an IR-based experiment to monitor the Beckmann rearrangement. Identify which peaks would disappear and appear during the reaction. (A, CO2)
16. Discuss the impact of vibrational coupling on IR absorption bands. Illustrate with examples. (U, CO1)
17. Explain how you would use DEPT-90 and DEPT-135 spectra to identify CH_2, CH_3 and quaternary carbons in ethyl propionate. (U, CO3)
18. Write briefly on chiroptical techniques and their applications. (U, CO1)

(2 x 6 = 12)

PART C

Answer any 2 questions **Weights: 5**

19. An organic compound with molecular formula $C_{11}H_{14}O_3$ showed the following data: IR (cm^{-1}): 3065, 2950, 1732, 1605, 1250; ^1H NMR (δ, ppm): 7.8 (d, 2H), 6.9 (d, 2H), 5.1 (s, 2H), 3.8 (s, 3H), 2.6 (q, J = 7.4 Hz, 2H), 1.2 (t, J = 7.4 Hz, 3H); ^{13}C NMR (δ, ppm): 195, 151, 130, 129, 114, 66, 52, 28, 14; DEPT-135: Positive signals at δ 130, 129, 28, 14; negative at δ 66, 52; DEPT-90: Positive at δ 129, 130; EI-MS (m/z): 208 (M^+), 165, 135 (base peak). Identify the structure and assign all data. (U, CO3)
20. (a) Explain cross-polarisation. How does it help the NMR analysis of less sensitive nuclei. (b) Write briefly on HETEROCOSY technique. (U, CO1)
21. Discuss the theory and applications of the following Mass spectroscopic techniques: (i) HR MS, (ii) LC MS (iii) GC MS and (iv) MALDI-TOF. (U,CO1)
22. (a) How you would confirm the success of the benzoin condensation reaction using a combination of IR and NMR data. (b) For the Fries rearrangement product of phenyl acetate, predict and justify the spectral changes observed in IR and ^1H NMR compared to the starting ester. (A, CO2)

(5 x 2 = 10)