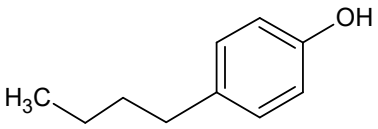
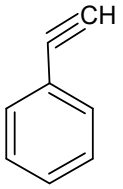
BIRLA INSTITUTE OF TECHNOLOGY, MESRA, RANCHI
(END SEMESTER EXAMINATION)

CLASS: IMSc/MSc **SEMESTER : IMSc IX/MSc III**
BRANCH: CHEMISTRY **SESSION : MO/2024**

SUBJECT: CH501 SPECTROSCOPIC ELUCIDATION OF MOLECULAR STRUCTURE
TIME: 3 Hours **FULL MARKS: 50**

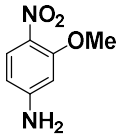
INSTRUCTIONS:
1. The question paper contains 5 questions each of 10 marks and total 50 marks.
2. Attempt all questions.
3. The missing data, if any, may be assumed suitably.
***4*. Before attempting the question paper, be sure that you have got the correct question paper.**
5. Tables/Data hand book/Graph paper etc. to be supplied to the candidates in the examination hall.

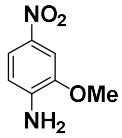
			CO	BL
Q.1(a)	(i) Among 1,3-cyclohexadiene and 1,4-hexadiene, which molecule will absorb at a long wavelength and why? (ii) Monochromatic radiation is incident on a solution of 0.5 molar concentration of an absorbing substance. The radiation intensity is reduced to one-fourth of the initial value after passing through the 10 cm length of the solution. Calculate the molar extinction coefficient of the substance.	[2+3]	2	3
Q.1(b)	(i) Calculate the normal mode of vibration for- i) CO_2, ii) Benzene, iii) H_2O and iv) CH_4 (ii) Discuss the Jablonski diagram for electronic transition and explain why peaks in UV-visible spectra are broad.	[2+3]	2	2
Q.2(a)	(i) Compound C_4H_{10} gave ^1H NMR spectrum consisting of two groups of lines (multiplets) with relative intensities in the ratio 3:2. Other compound of the same formula exhibited two lines with relative area of 9:1. What are these compounds. (ii) (a) Draw a clean diagram for the ^1H-NMR spectrum of Aspirin (2-acetoxybenzoic acid) mention the multiplicities of different signals. (b) Explain the multiplicities based on spin-spin coupling. (c) Draw a TCOSY NMR spectrum for the above-mentioned compound. (d)And correlate with ^1H NMR spectra.	[2+3]	1	3
Q.2(b)	(i) Explain why the aldehyde proton is highly de-shielded. (ii) An organic compound ($C_6H_{10}O_2$), which does not change the colour of ferric chloride solution, exhibited the following ^1H NMR spectral data: δ 7.3 (1H, t, J= 8 Hz), 7.0 (1H, d, J= 8 Hz), 6.95 (1H, s), 6.9 (1H, d, J= 8 Hz), 5.3 (1H, broad s, D_2O exchangeable), 4.6 (2H, s), 3.9 (3H, s). Find out the structure and assign all the peaks and explain the observations.	[2+3]	1	3
Q.3(a)	(i) Predict the 'base peak' in MS of 2-*methyl pentane*. Give reasons. (ii) Outline with appropriate reasons the MS molecular fragmentation patterns of all the four types of alkyl halides.	[2+3]	3	3
Q.3(b)	Discuss the fragmentation pattern in MS of the following compounds. Predict the 'base peak' in each case.   	[2.5+2.5]	3	3
Q.4(a)	Explain the hyperfine splitting and intensity ratio of the signals in EPR spectra of (i) 1,4 Benzosemiquinone radical anion and (ii) naphthalene anion radical. Nuclear Spin for N (I = 1) and H (I = 1/2). {EPR: Electron Paramagnetic Resonance}	[5]	2	3
Q.4(b)	Outline how Mossbauer spectroscopy can be used to determine oxidation state of a metal in a complex, taking the example of 'Sn'.	[5]	2	3

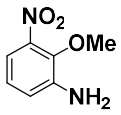
PTO

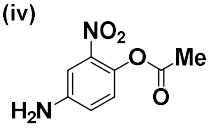
Q.5(a) (i) An organic compound ($C_7H_{12}O_2$) exhibited the following data in the ^1H NMR spectrum δ 7.10 (1H, dt, J= 16 Hz and 7.2 Hz), 5.90 (1H, dt, J= 16 Hz and 2 Hz), 4.1 (2H, q, J= 7.2 Hz), 2.10 (2H, m), 1.25 (3H, t, J= 7.2 Hz), 0.90 (3H, t, J= 7.2 Hz) ppm. The compound shows IR band at 1700 cm^{-1}. Find out the structure and assign all the peaks and explain the observations. [3+3] 3 3

(ii) The structure of the compounds that matches the ^1H NMR data given below is: ^1H NMR (DMSO-d6): δ 7.75 (1H, dd, J= 8.8 Hz), 7.58 (1H, d, J= 2.4 Hz), 6.70 (1H, d, J= 8.8 Hz), 6.50 (2H, broad s), 3.80 (3H, s). The compound shows m/z peak at 168. Identify the structure and assign all the peaks and explain the observations.

(i) 

(ii) 

(iii) 

(iv) 

Q.5(b) The ^1H NMR and ^{13}C NMR spectra of compound X ($C_5H_{10}O_2$) are shown below. Propose a structure for X. [2+2] 3 3