M.Sc. 4th Semester Examination, 2024

CHEMISTRY

(*Spectroscopy*)

PAPER—CEM-401

Full Marks : 50

Time : 2 hours

Answer **all** questions

The figures in the right hand margin indicate marks

Candidates are required to give their answers in their own words as far as practicable

GROUP – A

Answer any **four** questions : 2 × 4

1. What is Karplus equation ? Show the plot and explain.

2. What are the full forms of DEPT, HMBC ?

3. Which reference compound is used for NMR in D_2O as a solvent ? Write its structure.

4. Discuss on "nuclear decay scheme for ^{57}Fe Mössbauer resonance".

5. Write down the expression for specific and molar ellipticity.

6. What is NMR shift reagent ? Give an example and explain the mechanism of its activity.

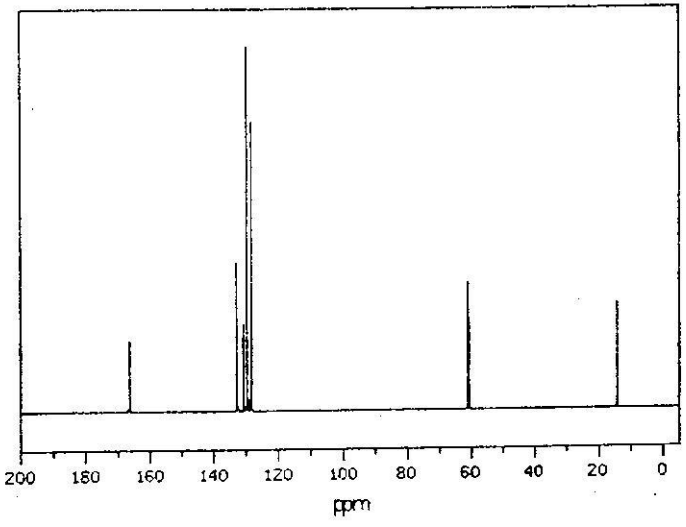
GROUP – B

Answer any **four** questions : 4×4

7. A compound $C_9H_{10}O_2$ has the following spectral characteristics :
FTIR : 1723 cm^{-1}(s),

(*Continued*)

^{1}H NMR (90 MHz , $CDCl_3$) δ(ppm) : 8.05 (2H), 7.52 (1H), 7.41 (2H), 4.35 (q, 2H), 1.38 (t, 3H) ^{13}C NMR is given below :



Suggest a structure of this compound. 4

8. Write short note on "quadrupole splitting" in Mössbauer spectroscopy. 4

9. Derive the expression for "recoil energy". Explain why recoilless emission and absorption of γ-ray is essential for Mössbauer spectroscopic study. 3 + 1

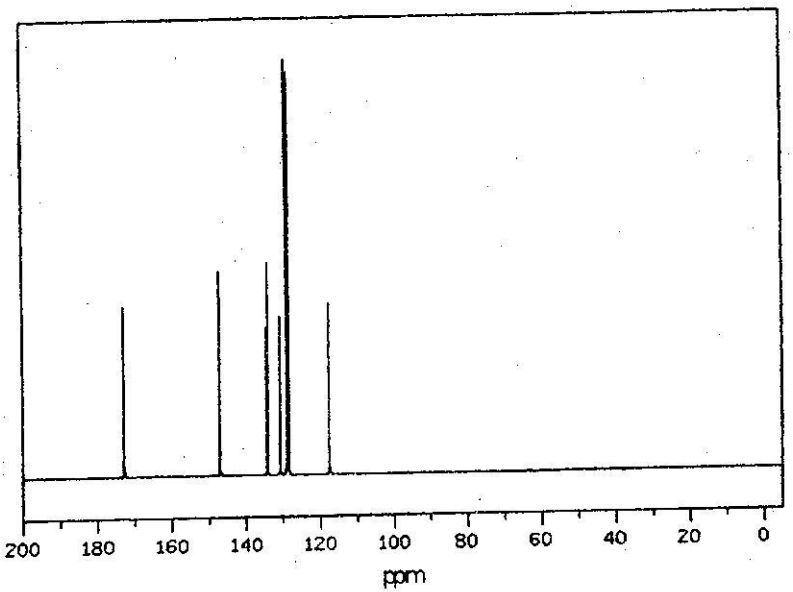
10. A compound having molecular formula $C_9H_8O_2$ has the following spectral characteristics :

FTIR (cm^{-1}) : 1686(s), 1631(s), 1678(m), 1496(m), 1450(s)

^1H NMR (90 MHz, $CDCl_3$) δ(ppm) : 11.2 (1H), 7.8 (d, 1H, 16.1 Hz), 7.56 (2H), 7.42 (1H), 7.40 (2H), 6.47 (1H).

^{13}C NMR is given below. Suggest the structure of the compound.

(*Continued*)



11. Compound **A** having molecular formula $C_6H_{10}O_2$ show the following spectral data :

FTIR (cm^{-1}) : 1695

^{1}H-NMR (δ) : 6.95 (1H, dq, J_1 = 16 Hz and J_2 = 6.8 Hz), 5.81 (1H, dq, J_1 = 16 Hz, and J_2 = 1.7 Hz), 1.88 (3H, dd, J_1 = 6.8 Hz and J_2 = 1.7 Hz), 4.13 (2H, q, J = 7 Hz), and 1.24 (3H, t, J = 7 Hz).

Mass Spectra (important peaks, m/z) : 114 (M+), 69 (base peak) and 41 (w)
Suggest a probable structure. 4

12. An organic compound having molecular formula C_5H_8O shows following spectral data :

UV-VIS-λ_{max} (ETOH) = 277 nm, ε_{max} = 4600
IR (cm^{-1}) 3020, 1685,

^{1}H-NMR δ (ppm) : 6.2 (d, J = 17 Hz, 1H), 5.4(m, J = 17 Hz, 1H), 2.3 (s, 3H), 1.9 (d, 3H).

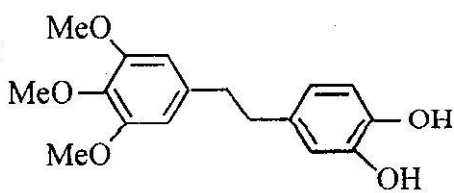
Draw the structure of the compound.

GROUP – C

Answer any **two** questions : 8×2

13. (*i*) How mass spectral analysis can be used to distinguish the structural isomers. Explain with the help of suitable examples. (*ii*) Prove that in the benzylic

system the mass spectral fragmentation is not straight forward rather it passes through stable tropylium cation intermediate. (*iii*) Differentiate the following compounds with the help of mass spectroscopy ? 8

(*a*) 

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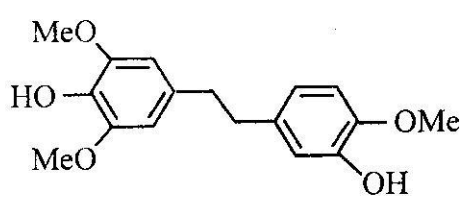
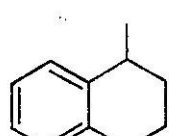
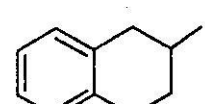


(*b*)  and 

14. (*a*) An organic compound having molecular formula $C_4H_6O_2$ shows a very strong IR band at 1720 cm^{-1} and only one singlet signal in its ^1H nmr spectra. Draw the structure of the compound.

(*b*) An organic compound having molecular formula $C_{10}H_{12}O_2$ shows following spectral data

^1H-NMR-δ (8.0, 2H, m); δ (7.2, 3H, m); δ (5.2, 1H, m); δ (1.3, 6H, d), IR-1730 cm^{-1}, 3050 cm^{-1} and 2950 cm^{-1}. Draw the structure of the compound. 4+ 4

15. (*a*) Write down the differences between plane polarized and circularly polarized light.

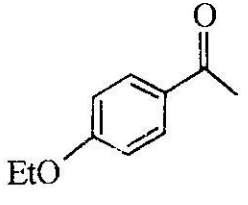
(*b*) Write down the ethanol effect on the structure of the CD band of B-DNA conformation. 4 + 4

16. (*a*) Compound **C** ($C_8H_{12}O_4$) shows the following ^1H NMR spectral data :

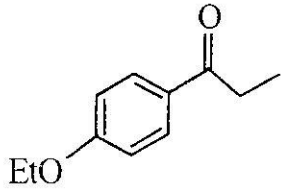
^1H-NMR (δ) : 6.80 (s, 2H), 4.25 (q, J = 7 Hz, 4H), 1.30 (t, J = 7 Hz, 6H). Suggest a possible structure.

(*b*) An organic compound exhibited the following ^1H NMR spectral data (δ) : 7.80 (2H, d, 8 Hz), 6.80 (2H, d, 8 Hz), 4.10 (2H, q, J = 7.2 Hz), 2.4 (3H, s), 1.25 (3H, t, J = 7.2 Hz). Write the structure of the compound among the choices given below : 4 + 4

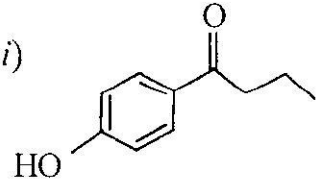
(*i*)



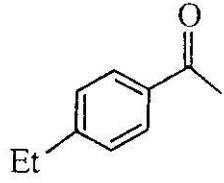
(*ii*)



(*iii*)



(*iv*)



[Internal Assessment – 10 Marks]