19002223

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Reg. No.....

Name.....

M.Sc. DEGREE (C.S.S.) EXAMINATION, NOVEMBER 2019

Third Semester

Faculty of Science

Branch III—Chemistry

AN3C12/AP3C12/PH3C12/PO3C12/CH3C12—SPECTROSCOPIC METHODS IN CHEMISTRY

(Common to all branches of Chemistry)

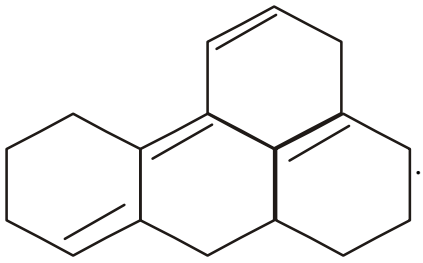
[2012—2018 Admission onwards]

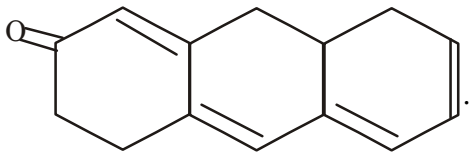
Time : Three Hours Maximum Weight : 30

Section A

Answer any **ten** *questions.*
Each question carries a weight of 1.

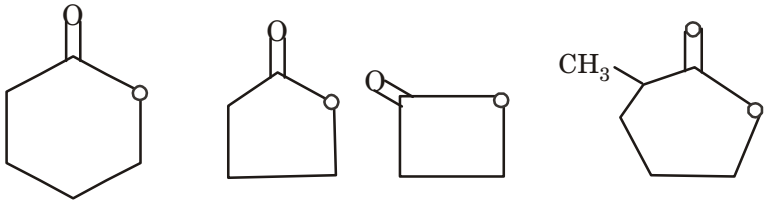
1. Explain the effect of solvent polarity on $\pi - \pi^t$ and $n - \pi^t$ transitions in UV spectra
2. Explain the phenomenon 'Circular dichroism'.
3. How is intramolecular and intermolecular hydrogen bonding distinguished using IR spectra.
4. What is Fermi Resonance ? How the corresponding peaks are identified in IR spectra.
5. Explain the term magnetic anisotropy as used in NMR spectroscopy.
6. What is decoupling and double resonance ? How they are useful in interpreting complex NMR spectra ?
7. Explain the application of McLafferty rearrangement in Mass spectra.
8. What is nitrogen rule ? Explain its use in determining the molecular mass.
9. How the presence of Chlorine and Bromine is indicated in mass spectra.
10. Calculate the λ_{max} values for the following compounds.

(a)  .

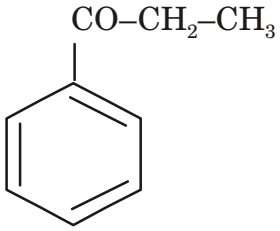
(b)  .

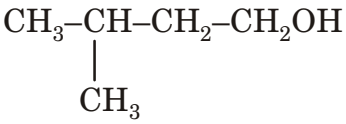
Turn over

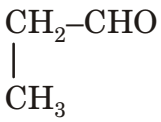
11. Arrange the following carbonyl compounds in the increasing order of stretching frequencies in IR spectra



12. Predict the base peak in the mass spectra of the following compounds :

(a) 

(b) 

(c) 

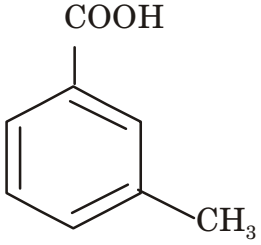
13. How is a π to π^t and n to π^t transitions distinguished in UV spectra. Explain using suitable examples.

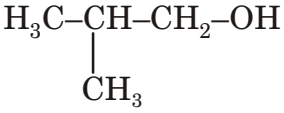
(10 × 1 = 10)

Section B

Answer **five** *questions by attempting not more than three questions from each bunch. Each question carries a weight of* 2.

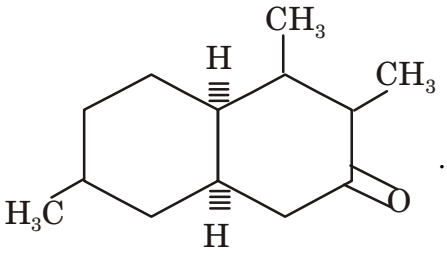
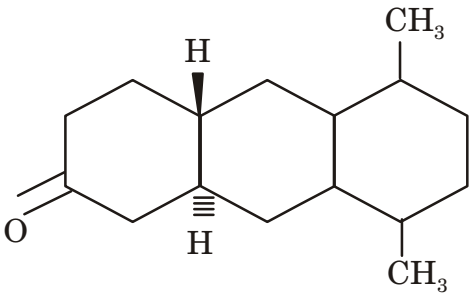
14. Sketch the approximate ^1H NMR and ^{13}C NMR spectrum of the following molecules :

(a) 

(b) 

15. What are Cotton curves ? What are its uses ? Explain stating specific examples.

16. Explain octant rule ? Predict the sign of optical rotation in the following molecules :

(a)  . (b) 

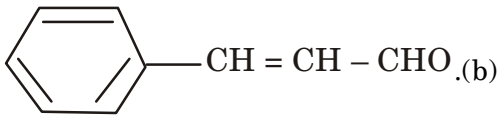
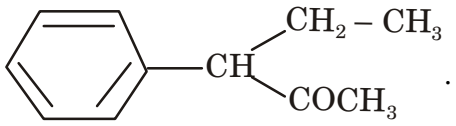
17. Sketch the H-H HOMOCOSY of : (a) 2-Bromopropane ; and (b) Isopropanol.

18. What is NOE ? What is the use of an NOE spectrum in structure elucidation ?

19. Give Karplus equations. Draw the Karplus curves and explain its important features.

20. Describe briefly the important methods used in the ionisation process in mass spectral Studies. Compare the advantages of the different methods.

21. Predict the signal patterns in DEPT-90 and DEPT-135 spectra of the following :

(a)  .(b)  .

(5 × 2 = 10)

Section C

Answer any **two** *questions.*
Each question carries a weight of 5.

22. Write briefly on the following :

(a) 2DNMR. (b) HOMOCOSY.

(c) MRI.

23. Give the spin-spin splitting patters of the following types in NMR spectra.

(a) AX_2. (b) AX_3.

(c) A_2X_3.

Turn over

24. An organic compound with molecular mass 58 is transparent above 200 nm, in its ultra violet spectrum. In infra red, the absorption bands formed are (a) 2941-2857 cm^{-1} (m) ; (b) 1458 cm^{-1} (m) and in NMR spectrum, two signals are formed (i) Triplet δ = 4.75 (J = 7.1 cps, 29.4 squares ; and (ii) quintet δ = 2.75 (J = 7.1 cps, 14.6 squares). Deduce the structure of the compound A.

25. An organic base with molecular formula $Cl_4H_{19}N$ shows the following spectral data IR : 3022 cm^{-1} (m) ; 1600 cm^{-1} ((m) ; 1510 cm^{-1} (m) ; 1680 cm^{-1} (w) ; 750 and 695 cm^{-1} (m)

UV : λ_{max} at 222 nm, €$_{max}$ 20,400 ; 210 nm, € $_{max}$ 20,000.

^{1}HNMR : δ 2.85 (3H, singlet) ; 1.5 (3H, singlet); 2.0 (4H, multiplet) ; 1.65 (4H multiplet) 6.55 (3H, multiplet) and 7.05 (2H, multiplet) Deduce the structure of the compound A.

(2 × 5 = 10)