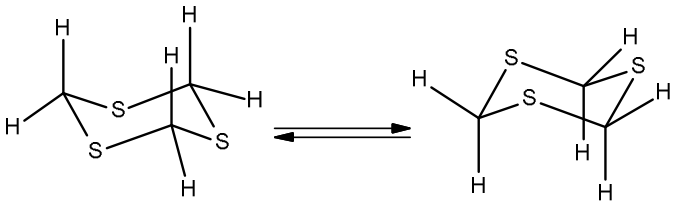
Application of spectroscopic methods in molecular structure determination

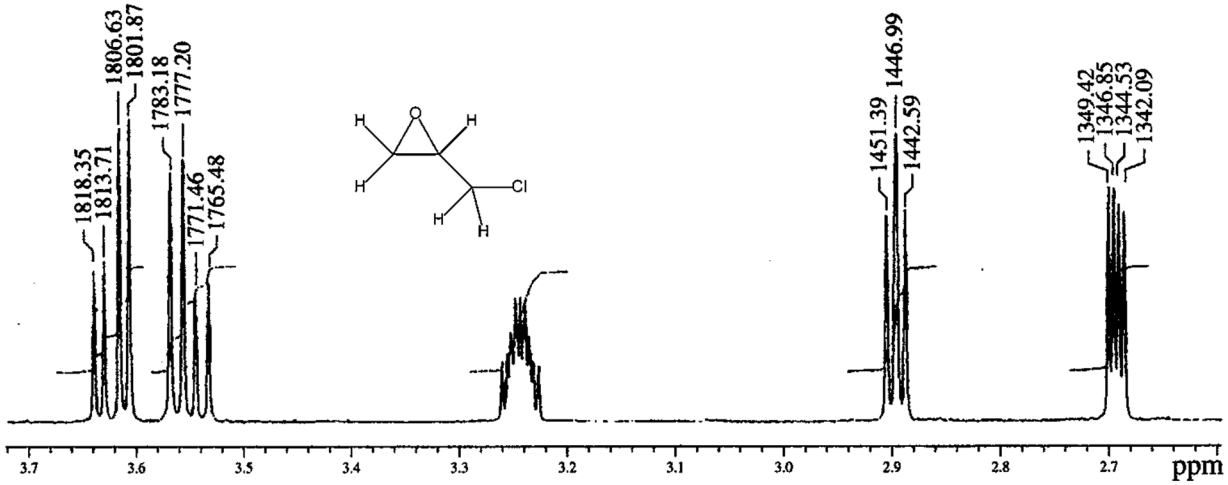
Assignment 3

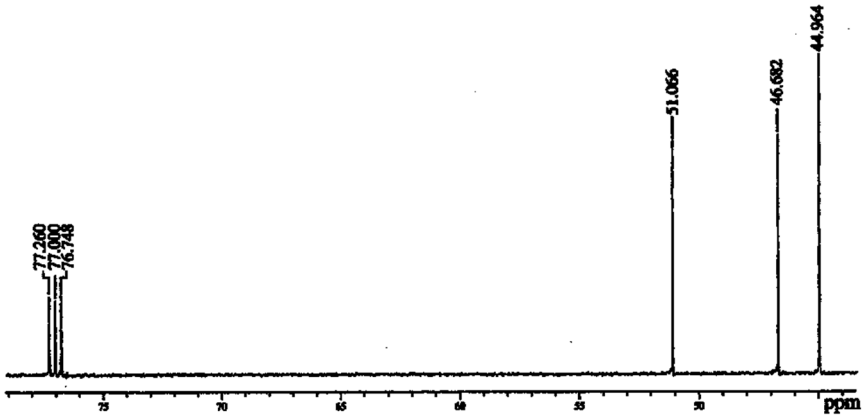
1. Sketch the ^{1}H NMR spectrum of 1,3,5-trithiane at room temperature and at -80 ^{o}C (slow exchange of the equilibrium shown below). (5 marks)



2. The ^{1}H and ^{13}C NMR spectra (in $CDCl_3$) of epichlorohydrin are shown below. Analyse the spectra and assign the signals to various protons and carbons, respectively, in the structure. ***Calculate the δ and J values from the ^{1}H NMR spectrum and explain the observed multiplicity of signals.***

(Treat the peak at δ 3.25 as a multiplet as the resolution is not good enough to find the correct multiplicity).





Explain the three signals seen around 77ppm in the carbon-13 spectrum (15 marks)

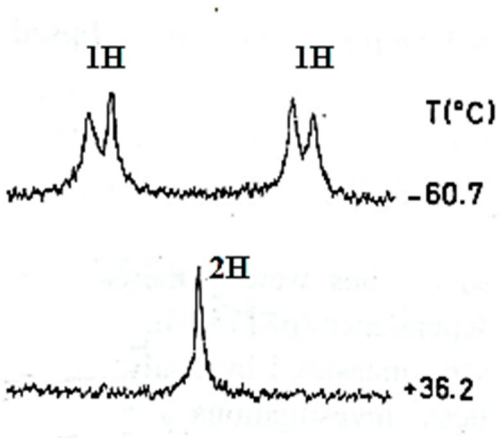
3. Deduce the structure of the organic compound from the given data. Calculate all the chemical shifts and coupling constants from the spectrum. Assign the spectral data to the structure.

(10 marks each)

(a) C_5H_6O: 6.4 (dd, 1H, J = 6.0 and 0.5), 4.60 (dd, 1H, J = 6.0 and 3.0), 3.8 (s, 3H), 3.10 (dd, 1H, J = 3.0 and 0.5). (Clue: ^{13}C NMR shows 5 signals of which four of them appear in the range of 50 to 90 ppm and the 5th one around 155 ppm.)

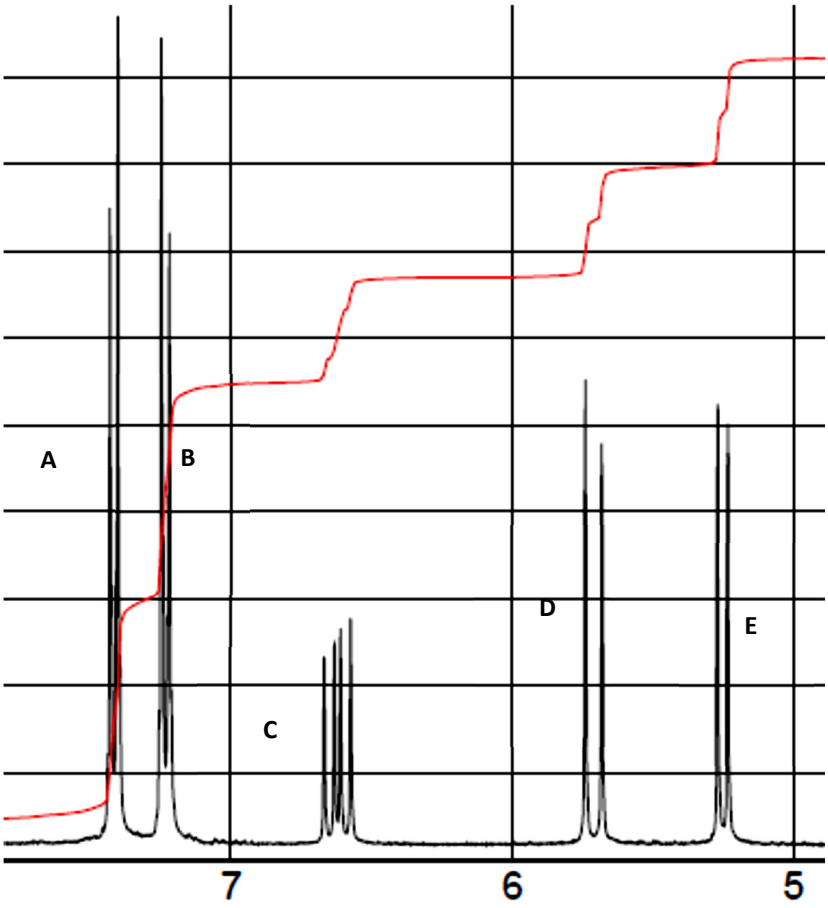
(b) $C_6H_{12}O$: 2.3 (sextet, 1H, J = 7.0), 2.05 (s, 3H), 1.56 and 1.29 (multiplet, each 1H), 0.95 (d, 3H, J = 7.0), 0.78 (t, 3H, J = 7.0). (Clue: multiplets at 1.56 and 1.29 showed mirror symmetry and appeared to be overlapping quintet of an AB quartet with apparent J values of 14 and 7.3)

4. The aromatic region (only) of the ^1H NMR spectrum of N-methyl-2,4,6-trinitroaniline is shown below at two different temperatures. Explain the spectral pattern at these temperatures based on the dynamic process involved. (5 marks)



5. There 6 isomers possible for bromostyrene (C_8H_7Br). Identify the isomer to which the following ^1H NMR (300 MHz) spectrum belongs to. Assign the signals (**A** to **E**) to various protons in the structure.

(5 marks)



END OF ASSIGNMENT