Nuclear Magnetic Resonance

Introduction:

Nuclear magnetic resonance (NMR) spectrometry is basically another form of absorption spectrometry. Under appropriate conditions in a magnetic field, a sample can absorb electromagnetic radiation in the radio frequency (rf) region at frequencies governed by the characteristics of the sample. Absorption is a function of certain nuclei in the molecule. A plot of the frequencies of the absorption peaks versus peak intensities constitutes an NMR spectrum. This chapter covers proton magnetic resonance (^{1}H NMR) spectrometry.

With some mastery of basic theory, interpretation of NMR spectra merely by inspection is usually feasible in greater detail than is the case for IR or mass spectra. The present account will suffice for the immediate limited objective, identification of organic compounds in conjunction with other spectrometric information. References are given at the end of this chapter.

We begin by describing some magnetic properties of nuclei. All nuclei carry a charge. In some nuclei this charge "spins" on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis (Fig-1). The angular momentum of the spinning charge can be described in terms of quantum spin numbers I; these numbers have values of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, and so on (I = 0 denotes no spin). The intrinsic magnitude of the generated dipole is expressed in terms of nuclear magnetic moment, μ.

The spin number I can be determined from the atomic mass and the atomic number as shown in the next column.

Spectra of several nuclei can be readily obtained (e.g., $_1^1$H, $_1^3$H, $_6^{13}$C, $_7^{15}$N, $_9^{19}$F, $_{15}^{31}$P) since they have spin numbers I of ½ and a uniform spherical charge distribution (Fig. 1).

I	Atomic Mass	Atomic Number	Example (I)
Half-integer	Odd	Odd or even	$_1^1\text{H}\left(\frac{1}{2}\right)$, $_8^{17}\text{O}\left(\frac{5}{2}\right)$, $_7^{15}\text{N}\left(\frac{1}{2}\right)$
Integer	Even	Odd	$_1^2\text{H}(1)$, $_7^{14}\text{N}(1)$, $_5^{10}\text{B}(3)$
Zero	Even	Even	$_6^{12}\text{C}(0)$, $_8^{16}\text{O}(0)$, $_{16}^{36}\text{S}(0)$

Nuclei with a spin number I of 1 or higher have a non-spherical charge distribution. This asymmetry is described by an electrical quadrupole moment which, as we shall see later, affects the relaxation time and, consequently, the line width of the signal and the coupling with neighbouring nuclei. In quantum mechanical terms, the spin number I determines the number of orientations of a nucleus may assume in an external uniform magnetic field in accordance with the formulas $2I + 1$. We are concerned with the proton whose spin number I is $\dfrac{1}{2}$.

Thus in Fig.2, these are two energy levels and a slight excess of proton population in the lower energy state $(N_\alpha > N_\beta)$ in accordance with the Boltzmann distribution. The states are labelled α and β or $\dfrac{1}{2}$ and $-\dfrac{1}{2}$; ΔE is given by

$$\Delta E = \frac{h\gamma}{2\pi} B_0$$

where h is Planck's constant, which simply states that ΔE is proportional to B_0 (as shown in Fig. 2) since h, γ and π are constants. B_0 represents the magnetic field strength.
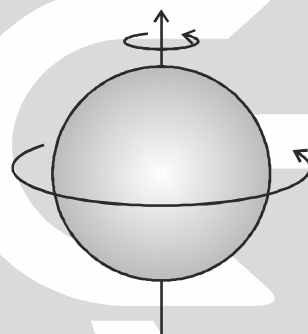

Fig. 1. Spinning charge on proton generates magnetic dipole

Once two energy levels for the proton have been established, it is possible to introduce energy in the form of radio frequency radiation (ν_1) to effect a transition between these energy levels in a stationary magnetic field of given strength B_0. The fundamental NMR equation correlating the applied radio frequency ν_1 with the magnetic field strength is

$$\nu_1 = \frac{\gamma}{2\pi} B_0$$

since $\qquad \Delta E = h\nu$

The introduced radio frequency ν_1 is given in megahertz (MHz). A frequency of 100 MHz is needed at a magnetic field strength B_0 of 2.35 tesla (T) for the proton (or any other desired combination of ν_1 and B_0 at the same ratio). At this ratio, the system is in resonance; energy is absorbed by the proton, raising it to the higher energy state, and a spectrum results. hence the name nuclear magnetic resonance spectrometry. The constant γ is called the magnetogyric ratio, a fundamental nuclear constant; it is the proportionality constant between the magnetic moment μ and the spin number I.

$$\gamma = \frac{2\pi\mu}{hI}$$

4. Find out the number of lines in the ^{31}P NMR signal for

(a) 3   (b) 6   (c) 18   (d) 90

Soln.
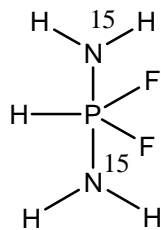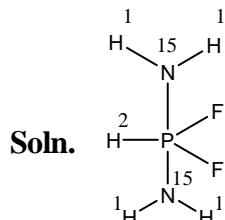
$$^{1}H \quad I = \frac{1}{2}; \quad ^{15}N \quad I = \frac{1}{2}; \quad ^{19}F \quad I = \frac{1}{2}$$

Four H^{1} are equivalent. Two nitrogen are equivalent.

Two fluorine are equivalent. One ^{2}H is separate.

$$\text{Multiply} = \left(2 \times 4 \times \frac{1}{2} + 1\right)\left(2 \times 2 \times \frac{1}{2} + 1\right)\left(2 \times \frac{1}{2} \times 2 + 1\right)\left(2 \times 1 \times \frac{1}{2} + 1\right) = 5 \times 3 \times 3 \times 2 = 90$$

                $4H^{1}$ $2N^{15}$ $2F$ $1H$

Correct answer is (d)

5. The compound showing the following spectral characteristic is ^{1}H NMR $(\delta \text{ in ppm})$: 4.65 (2H, singlet), 3.65(4H, quartet), 1.25 (6H, triplet); ^{13}C NMR $(\delta \text{ in ppm}) = 15, 63, 95$; DEPT-135 $(\delta \text{ in ppm})$: 15(positive), 63 (negative), 95(negative); DEPT-90 $(\delta \text{ in ppm})$: 15(no peak), 63(no peak), 95 (no peak).

(a)

(b)

(c)

(d)
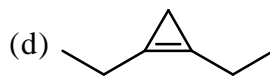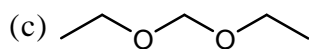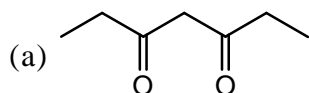
Soln. ^{1}H NMR– 4.65 (2H, singlet): Two hydrogens are attached with electronegative neighbour atom.

             3.65 (4H, quartet)

             1.25 (5H, triplet)

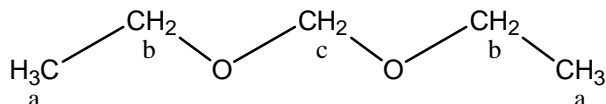^{13}C NMR   – 15, 63, 95 : (Three different type of carbon atoms are present).

DEPT-135   – yields CH and CH_3 positive while CH_2 is negative;

             15 positive $\rightarrow$ CH or CH_3

             63 positive $\rightarrow$ CH_2
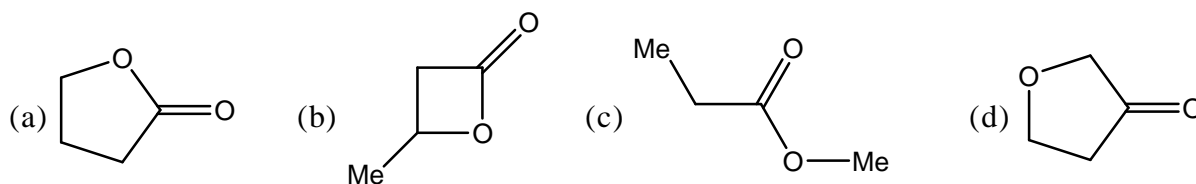
             95 negative $\rightarrow$ CH_2

DEPT-90   – yields only CH signals. All signals are negative. So, no CH unit is present.
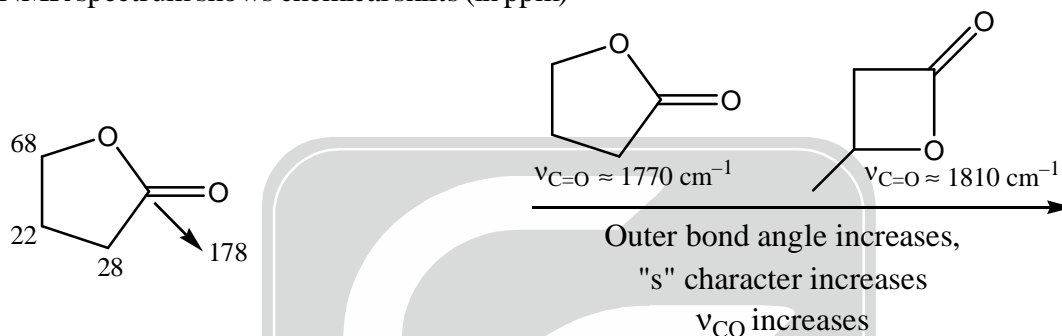
$6H_a$ show 1.25 ppm, triplet
$4H_b$ show 3.65 ppm, quartet
$2H_c$ show 4.65 ppm, singlet
Correct option is (c)

6. A compound with molecular formula $C_4H_6O_2$ shows band at 1770 cm^{-1} in IR spectra and peaks at 178, 68, 28, 22 ppm in ^{13}C NMR spectrums. The correct structure of the compound is

(a) (b) (c) Me (d)

Soln. Molecular formula of the compound $= C_4H_6O_2$.

IR spectra band at 1770 cm^{-1} that represents cyclic ester.
^{13}C NMR spectrum shows chemical shifts (in ppm)

$\nu_{C=O} \approx 1770$ cm^{-1} $\nu_{C=O} \approx 1810$ cm^{-1}

Outer bond angle increases,
"s" character increases
ν_{CO} increases

Correct option is (a)

7. A 400 MHz ^{1}H-NMR spectrum of organic compound exhibits a doublet. The two lines of the doublet are at δ 2.35 and 2.38 ppm. The coupling constant (J) value is
(a) 3 Hz   (b) 6 Hz   (c) 9 Hz   (d) 12 Hz

Soln.

2.38 ppm   2.35 ppm
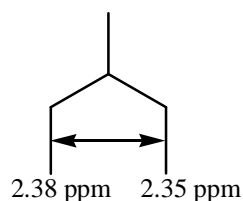
The gap between the two lines of the doublet $= (2.38 - 2.35)$ ppm $= 0.03$ ppm.
For a 400 MHz ^{1}H-NMR spectrometer,

     1 ppm $= 400$ Hz

   0.03 ppm $= (0.03 \times 400)$ Hz

          $= 12$ Hz

Therefore, the coupling constant (J) value is $= 12$ Hz.
Correct option is (d)