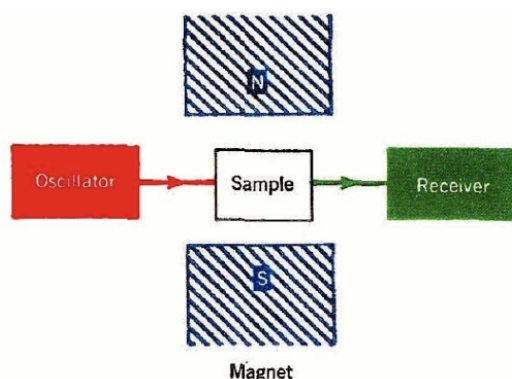


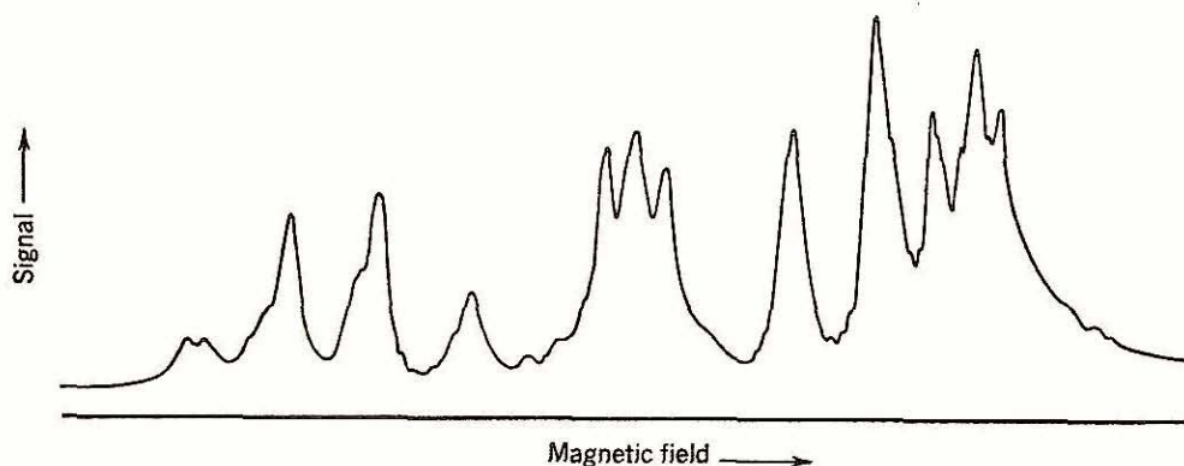
## 1.1: Introduction

The development of nuclear magnetic resonance spectroscopy subsequent to the initial discoveries by Purcell<sup>1</sup> and Bloch<sup>2</sup> in 1946 is now recognized as one of the most important events in the last fifty years for the advancement of organic chemistry. Nuclear magnetic resonance (NMR) techniques are throwing new light on many difficult organic problems. With the possible exception of gas-liquid chromatography, no new experimental method has been so rapidly accepted or proved so widely applicable. It is the purpose of this book to present the elements of NMR spectroscopy in a form suitable for practical use by organic chemists. Examples of applications will be mainly drawn from high resolution proton resonance spectroscopy, but the principles so illustrated will often be useful in dealing with other types of NMR spectroscopy.

An NMR spectrometer consists basically of a magnet, radio-frequency (rf) transmitter or oscillator, and a suitable rf detector. When a sample of a material comprised of atoms having nuclei with certain magnetic properties (to be described later) is placed in the magnet pole gap and subjected to the rf field of the oscillator, absorption of rf energy (resonance) occurs at particular combinations of the oscillator frequency and the magnetic field strength and an rf signal is picked up by the detector. Customarily, the detector output is measured at constant oscillator frequency as a function of the magnetic field strength, although there are advantages to the alternative procedure of maintaining the magnetic field constant and varying the oscillator frequency.<sup>3</sup>



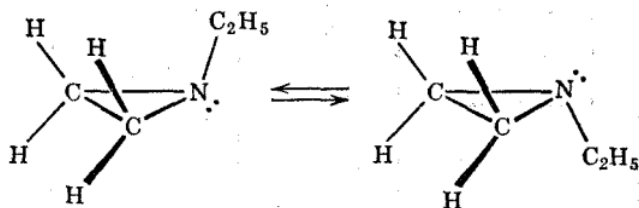
Information of chemical interest arises from the fact that nuclei of atoms in different chemical environments are also generally in quite different magnetic environments and come into resonance with a fixed frequency oscillator at different values of the applied magnetic field. Figure 1-1 shows a nuclear magnetic resonance spectrogram of a typical organic molecule, N-ethylethylenimine.



**Fig. 1-1.** Proton NMR spectrum of N-ethylethylenimine at an oscillator frequency of 40 Mc and a magnetic field of 9,400 gauss.

Besides the obvious utility of such a spectrogram to serve as a fingerprint of the compound in question, much more information may be gleaned from the spectrum than is provided by a qualitative examination of its major features. For example, it can be stated with a high degree of certainty that an ethyl group is present and also that the methyl of the ethyl group is rotating about the bond

connecting it to the methylene considerably more than 15 times per second. In addition, the spectrum shows the imine nitrogen to have a configuration such that the nitrogen atom and the three carbon atoms to which it is directly attached do not lie in a plane. Furthermore, we can say that the nitrogen atom is not undergoing configurational inversion of the kind shown in the following equation at a rate approaching or greater than 80 times per second.



Clearly, the NMR spectrum of the compound is a veritable treasure trove of useful information not easily obtainable in any other way.

We shall now consider the connection between the structure of an organic molecule and its NMR spectrum with the intention of ultimately getting at the principles which enable one to derive the kind of inferences made above. At the outset, we shall show how magnetic nuclei can absorb rf energy and produce an rf signal in the detector. Only the "crossed-coil" nuclear induction apparatus developed by Bloch, Hansen, and Packard will be considered, since it provides the basis for the commercially available high-resolution spectrometers.

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1 E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev., 69, 37 (1946).

2 F. Bloch, W. W. Hansen, and M. E. Packard, Phys. Rev., 69, 127 (1946).

3 B. Baker and L. W. Burd, Rev. Sci. Instr., 28, 313 (1957).

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