

## Chapter 16

# Understanding How to Analyze Structures of Products (Part 3): Nuclear Magnetic Resonance (NMR)

### Key Concepts

NMR measures the extent to which a nucleus experiences a magnetic field. The electronic environment of a magnetic nucleus is determined by:

**Proximity to a Pi Bond:** Movement of electrons within a pi bond creates a magnetic field that adds to the force of an externally applied field.

**How well the nucleus is shielded by the atom's electron cloud:** If an electron-withdrawing atom is nearby, the magnetic nucleus is less shielded from the magnetic field and so it experiences more of the external magnetic field.

Adjacent magnetic nuclei add to/subtract from the force of the externally applied field, and therefore affect the amount of energy released when a nucleus goes back into alignment (In other words, they split the signal). If there is only one type of chemically different hydrogen neighbor, the **multiplicity is  $N + 1$** . **If there are two types of chemically different hydrogen neighbors, the multiplicity is  $(N + 1)$  for the first type of neighbor times  $(N + 1)$  for the second type of neighbor.**

Because NMR measures the environment that each magnetic nucleus experiences, it is used to identify nearby functional groups and also to determine the overall structure of the molecule.

To interpret  $^1\text{H}$  NMR spectra, you can:

1. Compare the actual number of hydrogens to the number that is expected based on the  $2N + 2$  rule. If there are fewer hydrogens than expected, it means the molecule includes double bonds and/or rings. If there are at least six fewer hydrogens than expected, it probably means the molecule has a benzene ring.
2. Look for signals in the 7–8 ppm range to determine whether the molecule has a substituted benzene ring, and if so, the characteristics of that ring. If the signal is a **Multiplet Mess**, it means the benzene ring is **Monosubstituted**. If it's a **Doublet of Doublets**, then the benzene ring is **Disubstituted with Different groups para** to each other. If it's a **Singlet at approximately Seven**, the ring is **Substituted with the Same group in a para configuration**.

3. Examine the number of signals. If there are fewer signals than expected, the structure has a carbonyl group, a *tert*-butyl group, an iso-branch and/or general symmetry.
4. Look at the locations of signals to determine nearby functional groups.
5. Look at the multiplicity of each signal to determine characteristics of immediate hydrogen neighbors.
6. Use integration data to determine the relative proportion of hydrogens that contributed to each signal.
7. Use coupling constants to determine which hydrogens are neighbors.

## **What You Need to Learn, Understand, and Apply**

1. The types of information that can be determined from NMR.
2. The general theory of NMR.
3. How to determine when hydrogens/carbons are chemically equivalent. Also, how to label hydrogens/carbons using the signal designations a, b, c, etc.
4. Approximate values of NMR chemical shifts for general classes of  $^1\text{H}$  nuclei.
5. What causes an NMR signal to split and how to use splitting patterns to help determine the structure of a compound.
6. How to interpret and use integration lines on an NMR plot to help determine the structure of a compound.
7. How the signal of a hydrogen attached to nitrogen or oxygen is affected if the sample is contaminated with trace amounts of either acid or base.
8. What NMR coupling constants are and what information they provide.
9. The advantages of using  $^{13}\text{C}$  NMR either alone or in addition to  $^1\text{H}$  NMR and some of the tools that can be used to interpret  $^{13}\text{C}$  NMR.
10. The principle of MRI.
11. The skills needed to apply the material and avoid common errors.