8.1 Symmetry in NMR Spectra

Protons and other nuclei in NMR spectra can be classified as heterotopic, diastereotopic, enantiotopic and homotopic. Heterotopic and diastereotopic protons will have different chemical shifts and couplings to neighboring magnetic nuclei, enantiotopic and homotopic protons will have identical chemical shifts. They may or may not have identical couplings to other nuclei. Distinction can be made by the substitution test.

The Substitution Test for Equivalence of Protons

For a pair of protons to be tested, replace one and then the other with another group (one not present in the molecule). Compare the two structures formed. If they are identical, the protons are homotopic, if they are enantiomers, the protons are enantiotopic, if they are diastereomers then the protons are diastereotopic, if they are structural isomers, the protons are heterotopic.

Homotopic Protons:

\[
\begin{align*}
\text{A} & : \text{CH}_3 \text{CH}_3 \text{H} \text{Ph} \\
\text{B} & : \text{CH}_3 \text{CH}_3 \text{H} \text{Ph}
\end{align*}
\]

The structures A and B are identical, the two protons are homotopic.

Enantiotopic Protons:

Enantiotopic protons normally have identical chemical shifts. However, when the molecule is placed in a chiral environment (say with an optically active, solvent, cosolvent or Lewis acid) the the protons can become diastereotopic. This is in contrast to homotopic protons, which are always identical.

\[
\begin{align*}
\text{C} & : \text{CH}_3 \text{OH} \text{Ph} \\
\text{D} & : \text{CH}_3 \text{OH} \text{Ph}
\end{align*}
\]

The structures C and D are enantiomers, the two protons are enantiotopic.

Diastereotopic Protons:

The concept of diastereotopicity was first introduced during the early days of NMR spectroscopy, when certain kinds of molecules gave unexpectedly complex NMR spectra, leading to some confusion about the origins of this hitherto undetected phenomenon (Nair, P. M.; Roberts, J. D. J. Am. Chem. Soc., 1957, 79, 4565). A typical situation where diastereotopic protons are seen is a CH\textsubscript{2} group in a chiral molecule (one with an asymmetric center, or other types of asymmetry).

\[
\begin{align*}
\text{E} & : \text{CH}_3 \text{Cl} \text{O} \text{CH}_3 \text{H} \text{Ph} \\
\text{F} & : \text{CH}_3 \text{Cl} \text{O} \text{CH}_3 \text{H} \text{Ph}
\end{align*}
\]

The structures E and F are diastereomers, the two protons are diastereotopic.

A more subtle form of diastereotopism is demonstrated in the classical example of diethyl acetal below. Even though diethyl acetal has no asymmetric centers, the CH\textsubscript{2} group is diastereotopic. This can be shown by applying the substitution test, which creates a pair of diastereomers G and H (see Sect 5-HMR-13).

\[
\begin{align*}
\text{G} & : \text{CH}_3 \text{O} \text{CH}_3 \text{O} \text{CH}_3 \text{H} \text{D} \\
\text{H} & : \text{CH}_3 \text{O} \text{CH}_3 \text{O} \text{CH}_3 \text{H} \text{D}
\end{align*}
\]
Magnetic Equivalence

There is an additional element of symmetry which is important for NMR spectroscopy, the magnetic equivalence or inequivalence of nuclei. Protons that are enantiotopic or homotopic will have the same chemical shift, but they will not necessarily be magnetically equivalent. For two protons to be magnetically equivalent they not only have to have the same chemical shift, but they must also each have the same $J$ coupling to other magnetic nuclei in the molecule. This is easiest to see from some specific examples.

The two vinyl and two allylic protons in cyclopropene are each magnetically equivalent because each of the A protons is equally coupled to the two X protons. The spectrum consists of two identical triplets ($A_2X_2$ system).

On the other hand, the two pairs of equivalent protons in trans-dichlorocyclopropane are NOT magnetically equivalent, because each of the A protons is coupled differently to the two X protons (one is a trans coupling, the other a cis). We refer to this as an AA'XX' system, where A and A' refer to protons that are symmetry equivalent but not magnetically equivalent. The spectrum will be much more complicated than two triplets.

Two more examples are 1,1-difluoroallene, which is an $A_2X_2$ system, and 1,1-difluoroethylene, which is an AA'XX' system (see 5-HMR-14.2 for a spectrum).

In general any system which contains chemical shift equivalent but magnetically inequivalent nuclei of the AA' type will not give first order splitting patterns, although sometimes the spectra may appear to be first order ("deceptively simple" spectra). For example, X-CH$_2$-CH$_2$-Y systems are of the AA'XX' type, but the coupling constants $J_{AX}$ and $J_{AX'}$ are often close enough in size that apparent triplets are seen for each CH$_2$ group. See Section 5-HMR-14 for examples.