

THE SADTLER GUIDE TO NMR SPECTRA

By
W. W. SIMONS
and
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INTRODUCTION

This volume is intended for the chemist with an understanding of the principles of Proton Magnetic Resonance, but who wishes to acquire a ready familiarity with the characteristic appearance of the basic proton types. In working with this text, he will be able to develop a "feel" for the correlation of structural features with the resulting proton absorbance patterns. Normally, this skill is gained only by observing many thousands of random spectra, over a period of years.

Comprised of twelve sections, the volume is a systematic presentation of interpreted NMR spectra, arranged by proton type. In this arrangement, which is similar to that which is employed in many Organic Chemistry textbooks, the alkanes comprise the first group; they are then followed by the cycloalkanes, acetylenes, alkenes, cycloalkenes, benzenes, heteroaromatics and aldehydes. Representative examples of each type of compound have been included to illustrate the general appearance of the NMR spectra of each group, and to depict the effects of substitution on the proton absorbance patterns.

Each section is preceded by a short introduction in which chemical shifts, coupling constants and special features of the group are discussed. Each spectrum is accompanied by pertinent commentary concerning significant features of the absorbance patterns of the samples analyzed.

The spectra in this book have been selected from the Sadtler catalog of NMR Standard Spectra, either because they represent examples of characteristic absorbance patterns, or because they are commonly-encountered organic compounds.

Special indices have been prepared to aid the user in locating the compound, pattern or proton group in which he is interested. Indices by spin system, coupling constants and exchangeable proton types are provided, in addition to the standard alphabetical listing. A special table of chemical shifts has been included for about 130 compounds which produce NMR spectra consisting of only a single peak.

Our intention in preparing this book has been to fill the gap between textbooks with only a few spectra, and catalogs of spectra without explanatory comments. The Sadtler Guide to NMR Spectra may be used for individual study, as an illustrated text, or as a unique reference source for the characterization of unknown NMR spectra.

Definitions

Chemical Equivalence -- See Equivalence

Chemical Shift -- Chemical shift is the relative position of an absorbance band in reference to a standard. Tetramethylsilane (TMS) is the generally accepted internal standard for proton spectra. The part per million (ppm) delta scale has become the most widely used scale for describing chemical shifts. TMS is designated as 0.00 ppm delta and each 60 Hz of separation from the TMS band on a 60 MHz spectrometer is designated as 1.00 ppm. Most protons resonate in the chemical shift range from 0 to 10 ppm delta (0 - 600 Hz downfield from TMS).

Coupling -- Spin-spin coupling is a magnetic interaction between two or more nuclei which results in peak multiplicity. In order for nuclei to couple, they must possess a spin quantum number which is greater than zero. Hydrogen may thus couple with hydrogen ($I = \frac{1}{2}$), fluorine ($I = \frac{1}{2}$), phosphorus ($I = \frac{1}{2}$), and nitrogen ($I = 1$), but not with Tin¹¹⁸ ($I = 0$), carbon¹² ($I = 0$) nor oxygen¹⁶ ($I = 0$). In the special case of

First Order Coupling, the number of peaks in the resulting multiplets is equal to $(n+1)$ where (n) represents the number of nuclei to which the group is coupled. In order to apply the $n+1$ rule, all J values (**coupling constants**) involved in the interaction must be the same.

Coupling Constant -- The separation (in Hertz) between the peaks of a spin-spin multiplet is defined as the coupling constant. It is designated by the letter J . When two nuclei are spin coupled to each other, the peaks of each multiplet will be separated by this J value. The magnitude of the coupling constant is independent of the field strength of the spectrometer and is relatively insensitive to solvent changes. The J values for a specific type of coupling (geminal, vicinal, cis, trans, ortho, meta, etc.) usually only vary over a fairly narrow range of values. In general, the magnitude of coupling constants decreases as the number of intervening bonds between the coupled nuclei increases.

Deshielding -- Unsaturated bonds, certain elements and functional groups can reduce the electron density around a proton to which they are proximally attached. The result is a "deshielding" of the affected proton so that it comes into resonance at lower field strength. The deshielding effect of substituents varies with the type of hydrogen which is being affected.

Substituent	Deshielding Effect on Aliphatics	Deshielding on Aromatics
-C(=O)-OH	weak	strong
-NO ₂	strong	strong
-I	moderate	strong
-Cl	strong	weak
-OH	strong	(shielding)

Equivalence -- There are two basic types of equivalence. Two protons are magnetically equivalent when they are in identical magnetic environments, i.e. they are structurally identical, and couple to all other protons in the same way. Two protons are chemically equivalent when they are chemically indistinguishable and occupy identical structural environments. Chemically equivalent nuclei are not necessarily magnetically equivalent. Chemical equivalence is exemplified by the two alpha protons of thiophene. In that molecule, H-2 and H-5 are chemically equivalent but not magnetically equivalent because they do not couple equally to each of the two beta protons.

Exchangeable Proton -- Hydrogen atoms attached to electronegative elements such as oxygen, nitrogen, sulfur and chlorine are very active protons which readily exchange with each other, with the protons of water, and with mineral acids and bases. When two different types of hydrogens are in rapid exchange, they display an averaged chemical shift. The chemical shifts of the exchangeable protons are widely variable because they are sensitive to pH, temperature, and concentration. Protons bonded directly to carbon, silicon, tin and phosphorus are generally not exchangeable.

Exchange Rate -- Two types of exchange rates are observed in NMR. Conformational exchange is observed when a given nucleus is capable of existing in two or more conformations. The rapid interconversion of axial and equatorial protons of cyclohexane is an example of conformational exchange. Positional exchange involves actual bond cleavage in which a proton breaks a bond to one nucleus and attaches itself to another ($R-O-H_a + H_b-O-H \rightarrow R-O-H_b + H_a-O-H$). In both types of exchange, the rate of interchange determines the appearance of the resultant absorbance band in the NMR spectrum. If the exchange rate is considerably faster than the difference in the resonance frequencies of the two forms, then only a single, well-resolved resonance will be observed. If the exchange rate is slower than the frequency difference, then two separate absorption bands will be observed. Intermediate exchange rates often produce broad, poorly-resolved bands, such as those commonly observed for the -OH group of alcohols. These peaks become quite sharp upon the addition of acid or base to the sample solution, because the acid base greatly increase the rate of exchange of the exchangeable protons.

First Order -- See Coupling

Geminal Coupling -- Coupling between two nuclei attached to the same carbon is termed geminal coupling. This coupling occurs through two bonds and is often designated as 2J coupling. Geminal coupling between methylene protons ($H-C-H$), when observed, is usually large with J values on the order of 10 to 20 Hz. Geminal coupling between vinyl protons ($H_2C=C$) is usually quite small with J values ranging from 1 to 4 Hz.

High Field -- At constant frequency, NMR spectra are usually scanned from left (lower field) to right (higher field). The designation **high field** is applied to bands which resonate near TMS at the right-hand part of the spectrogram. The absorbance bands of aliphatic protons appear in the range from 0.5 to 4 ppm and are often referred to as "high field" bands. Any proton which resonates at a smaller delta value than another proton is said to resonate at "higher field".

Higher Order -- Higher order (or second order) multiplets occur when two proton groups are strongly coupled, i.e. the difference in chemical shift between the bands is small in comparison to their coupling constant. Higher order multiplets do not follow the $n+1$ rule because they usually display additional splitting and, thus, cannot be analyzed by first order principles. Strictly speaking, all proton-proton couplings produce higher order patterns, however, as long as the difference in chemical shift is 6-10 times larger than the J value ($\Delta \nu/J$), the multiplets are usually interpreted as first order patterns. The A_2X_2 pattern of Spectrum 69 is considered first order ($\Delta \nu/J = 7.4$), while the analogous A_2B_2 pattern of Spectrum 68 is considered higher order ($\Delta \nu/J = 5.7$).

Lean -- See Tenting

Long Range Coupling -- Normally, the only couplings which are large enough to be observed on a 500 Hz sweep width spectrum are those which take place through three bonds or less. On occasion, the geometry of the molecule or the presence of unsaturated bonds leads to observable coupling through more than three bonds. Such couplings are referred to as **long range**. Allyl groups display long range coupling between the methylene group and the terminal olefinic hydrogens ($CH_2-C=C-H_2$). Coupling through five bonds is observed in pyridines ($J_{2,5}$) in addition to coupling through four bonds ($J_{2,4}$). **Long range coupling** is most often observed in unsaturated systems.

Low Field -- Low field is a term applied to bands which occur far removed from TMS (0.00 ppm delta). A peak which appears at a larger delta value than another band is said to absorb at lower field. Aromatic protons absorb at lower field (6 to 10 ppm) than aliphatic protons (0.5 to 4 ppm).

Magnetic Equivalence -- See Equivalence

Multiplets -- Spin-spin interaction between one nucleus and one or more other magnetic nuclei results in a splitting of the resonance band into two or more peaks which are displaced symmetrically about the original resonance frequency. Typical $n+1$ multiplets which are commonly observed in NMR spectra are described below.

Singlet: A single resonance peak arises from the presence of an isolated, uncoupled proton group. Isolated methyl groups (Spectrum 10), disubstituted methanes (Spectrum 291) and t-butyl groups appear as sharp singlets.

Doublet: A doublet usually appears as a pair of peaks of approximately the same height, separated by from 1 to 20 Hz. The appearance of a doublet indicates that the band is due to a proton group coupled to one other hydrogen (or other nucleus with a spin of $\frac{1}{2}$). The separation between the peaks of a doublet is not significantly affected by solvent changes. Spectrum 43 contains an isopropyl doublet.

Triplet: Triplet multiplicity is observed as three equally spaced peaks with peak heights in the ratio of 1:2:1. A triplet originates from the coupling of a proton group with two other nuclei by the same J value. Each proton produces a doublet and the centerpeak of the triplet represents the overlap of one peak of each doublet. Spectrum 69 contains two triplets.

Quartet: A quartet arises from coupling to three other nuclei by the same coupling constant. The three doublets overlap to form four evenly spaced peaks with relative intensities of 1:3:3:1. Spectrum 17 contains an ethyl quartet and a triplet.

Pentet, Sextet, Heptet: These multiplets arise from coupling with four, five and six nuclei respectively. The outer peaks become progressively smaller in comparison to those in the center of the pattern and are often lost in the baseline noise. The relative intensities of a pentet are 1:4:6:4:1, a sextet are 1:5:10:10:5:1 and those of a heptet are 1:6:15:20:15:6:1. Spectrum 75 contains a pentet at about 1.78 ppm, Spectrum 56 contains a sextet at about 4.43 ppm and Spectrum 43 contains a heptet at 4.11 ppm.

Doublet of Doublets: A doublet of doublets is observed when a proton is coupled to one nucleus with a large J value and to a second nucleus with a much smaller J value. The spacing between the peaks is not necessarily equal. The peaks are normally of about the same intensity. The multiplet usually appears as two identical, well separated doublets. An aromatic proton which is simultaneously coupled to both an ortho and meta proton displays such a pattern. Spectrum 345 contains a doublet of doublets centered at about 7.21 ppm.

1:2:1 multiplet: This is a special type of doublet of doublets in which the two J values are similar in magnitude. The peaks are arranged so that they appear as a singlet, a doublet, and a singlet. Multiplets of this type are often observed in pyridine derivatives resulting from the coupling of H-3 with H-2 and H-4. Spectrum 437 contains a 1:2:1 multiplet at 8.49 ppm.

Doublet of triplets: A doublet of triplets arises from coupling to one nucleus by a large J value and to two other nuclei by a much smaller J value. It is essentially a large doublet in which each peak has been split into a smaller triplet. An aromatic proton which is coupled to one ortho hydrogen and two meta hydrogens displays this pattern. Spectrum 109 contains a clear doublet of triplets at 6.25 ppm due to coupling to three fluorine nuclei.

Triplet of doublets: A triplet of doublets is produced by the coupling of a proton with two other nuclei by the same J value, and to a third nucleus by a smaller coupling constant. The overall appearance is that of a triplet with each of its peaks split into smaller doublets. It is most often observed for aromatic and heteroaromatic protons which are coupled to two ortho protons and one meta proton. Spectrum 427 contains a triplet of doublets at 7.46 ppm.

Offset -- Absorbance bands which occur at very low fields (below 8.3 ppm) will not be recorded during the normal 500 Hz spectrum sweep. In order to display these bands on the chart and determine their chemical shifts, the entire spectrum is moved to higher field until the band in question can be recorded. The offset in Hz which was required is then converted into ppm and is added to the apparent chemical shift of the band. For example, in Spectrum 462 the "e" proton was not recorded on the 500 Hz base scan. The spectrum was shifted 144 Hz to higher field and the peak was then recorded with an apparent chemical shift of 6.48 ppm. The offset in Hertz was converted into ppm by dividing it by the field strength of the spectrometer in MHz (60 in this case). This value was then added to the apparent chemical shift:

$$\frac{144 \text{ Hz}}{60} + 6.48 = 8.88 \text{ ppm}$$

In Spectrum 461, all of the bands were offset 54 Hz and thus, 0.90 ppm was added to their apparent chemical shifts in order to obtain the actual chemical shifts.

Proton Groups -- Proton groups are the various hydrogen-containing fragments which comprise a given molecule; i.e. methyl (CH_3); methylene ($-\text{CH}_2-$); methine ($-\text{CH}-$); hydroxyl ($-\text{OH}$); acetylenic ($-\text{C}\equiv\text{C}-\text{H}$); etc.

Restricted Rotation -- This is a phenomenon which is occasionally observed in NMR spectra, when rapid rotation about an apparent single bond does not occur. It usually results in the non-equivalence of the proton groups attached to one of the atoms of the bond. The classic example of restricted rotation is observed in the spectrum of N,N-dimethylformamide (Spectrum 475) in which the two methyl groups possess different chemical shifts due to restricted rotation about the $\text{O}=\text{C}-\text{N}$ bond. Spectrum 12 and Spectrum 23 also display the effects of restricted rotation.

"Roof-top" Structure - See Tenting

Shielding - The electrons which surround a resonating nucleus are said to "shield" the nucleus so that it does not experience the full effect of the applied magnetic field. As a result, a stronger than theoretical field will be required in order to bring the nuclei into resonance at a fixed frequency. The protons of TMS are among the most strongly shielded protons found in organic compounds. The shielding effect of various groups is not necessarily the same for all types of protons. For example, silicon strongly shields the aliphatic methyl groups of TMS but it deshields the olefinic protons of vinylsilanes. Although a hydroxyl group strongly shields aromatic protons, it deshields aliphatic groups.

Second Order - See Higher Order

Splitting - See Coupling

Spin Systems - A table of spin systems for the spectra in this book is provided on page 523. Spin system notations have been developed to indicate the type of multiplets which one would observe for a given group of spin coupled protons. Each different nucleus is assigned a letter and the number of magnetically equivalent nuclei in each group is indicated by a subscript number. Groups of nuclei which are far apart in chemical shift are assigned letters which are far apart in the alphabet (AM or AX). Nuclei which are close in chemical shift are assigned letters which are close in the alphabet (AB or XY). If two nuclei are chemically equivalent but magnetically non-equivalent, they are given the same letter but one is assigned a "prime" symbol (AA'). Several spin system designations are described below:

A₃X₂ This notation is used to describe the multiplicity an ethyl group (CH₃-CH₂) which produces "first order" multiplets. The letters A and X indicate that the methyl and methylene bands are well separated in chemical shift. Spectrum 24 contains a clear A₃X₂ spin system pattern.

A₂B₂ This designation describes a higher order ethylene pattern (-CH₂-CH₂-) in which the two groups possess similar chemical shifts. Spectrum 68 contains the two distorted triplets which such a spin system may produce.

AMX Compounds which contain three coupled nuclei with quite different chemical shifts represent an AMX spin system. The nuclei are usually coupled to each other by three different J values. The AMX spin system usually appears as three doublets of doublets. The three vinyl protons of Spectrum 220 display AMX spin system multiplicity. In Spectrum 352, the three coupling constants are nearly identical, resulting in three well separated triplets for that AMX system.

AA'BB'
or
AA'XX'

These spin systems are observed in para substituted benzenes and unsubstituted five membered heterocycles. In each case, the two A protons are magnetically non-equivalent because they do not couple equally to each of the B protons. The "prime" designation is used to denote this magnetic non-equivalence. N-substituted pyrroles represent an AA'BB' system (Spectrum 410) producing, in this case, two deceptively simple triplets. The ortho doublets of Spectrum 328 represent an AA'XX' system in which the magnetic non-equivalence of the two sets of protons results in additional "splitting" at the base of each peak.

Tenting, Lean or "Roof-top" effect -- Tenting is a term applied to the distortion in the peak heights of spin-spin multiplets due to higher order effects. The outer peaks of two multiplets which are coupled to each other are usually reduced in intensity while the inner peaks increase in intensity. Such multiplets are said to "lean" towards each other. This distortion produces a "tent" or "roof-top" outline above the combined multiplet patterns. As the chemical shift between two multiplets decreases, the tenting effect becomes more pronounced. The triplet and quartet of Spectrum 301 display a moderate degree of tenting. The lowest field peak of the triplet is taller than the highest field peak. Similarly, the highest field peak of the quartet is taller than the lowest field peak. In a complex spectrum, tenting effects are helpful in determining whether a multiplet is coupled to a group at higher field or to one at lower field. In Spectrum 85, for example, the doublet at 1.58 ppm is leaning toward lower field (it is coupled to "d"), the quartet at 2.12 ppm is also leaning toward lower field (it is coupled to "c" and "d"), the triplet at 3.68 is leaning toward higher field (it is coupled to "b") and the sextet at 4.21 ppm is leaning toward higher field (it is coupled to "a" and "b").

Virtual Coupling -- Virtual coupling may be observed if two protons are coupled strongly (possess similar chemical shifts) and one of them is coupled to a third nucleus. The multiplet arising from the third nucleus often appears as if it were coupled to both of the other nuclei. Such multiplets often appear to be first order. The additional splitting can often lead to misinterpretation of the pattern.

Vicinal Coupling -- Vicinal coupling is the term applied to coupling between two nuclei (protons) attached to adjacent carbon atoms (H-C-C-H). The coupling occurs through three bonds and is often designated as 3_J coupling.

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THE ALKANES

Chemical Shifts

Because the alkanes possess no deshielding substituents nor unsaturated bands, their protons absorb in a narrow range at high field (0.7 to 2.0 ppm). The terminal methyl group of the normal alkanes appears as a distorted triplet near 0.9 ppm while the internal methylene groups form a complex multiplet near 1.3 ppm. A comparison of the integration values of the methyl and methylene absorbance bands may be used to calculate the approximate chain length of an unknown alkane. Determinations such as this are only accurate to about ± 1 carbon for the very long chain alkanes (C_{15} and over).

The branched alkanes also absorb at high field but produce more complex absorbance patterns. Three types of methyl groups may be observed; triplets (CH_3-CH_2), doublets (CH_3-CH) and singlets (CH_3-C). Many of the branched alkanes produce such complex patterns that it is often difficult to determine the site and type of branching which exists in the molecule. These patterns are useful as fingerprint patterns when spectra of known compounds are available for direct comparison.

Spin-Spin Coupling

Due to the small difference in chemical shift between the various protons of the alkanes, all of the observed patterns are of higher order. Because of this, it is usually not possible to measure the coupling constants of such compounds. It is assumed that they would be similar in magnitude to those of the substituted alkanes which are described in the next section.