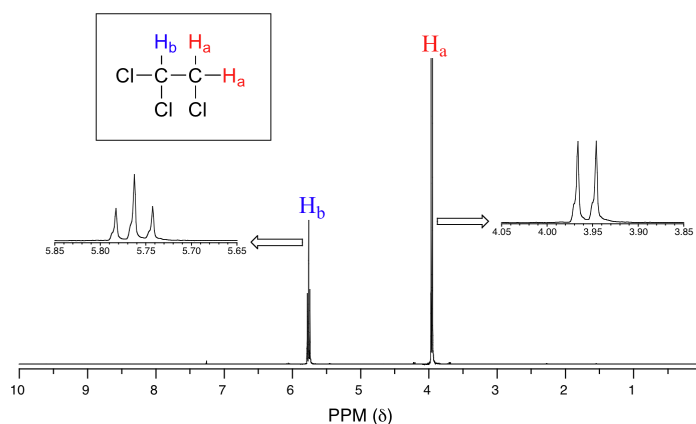# 14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra
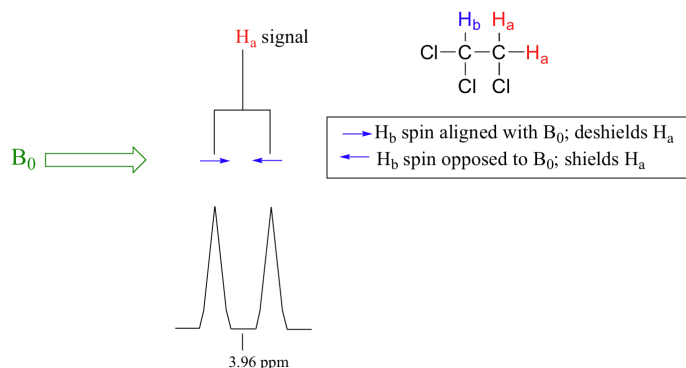
## 5.5A: The source of spin-spin coupling

The $^1$H-NMR spectra that we have seen so far (of methyl acetate and *para*-xylene) are somewhat unusual in the sense that in both of these molecules, each set of protons generates a single NMR signal. In fact, the $^1$H-NMR spectra of most organic molecules contain proton signals that are 'split' into two or more sub-peaks. Rather than being a complication, however, this splitting behavior actually provides us with more information about our sample molecule.

Consider the spectrum for 1,1,2-trichloroethane. In this and in many spectra to follow, we show enlargements of individual signals so that the signal splitting patterns are recognizable.
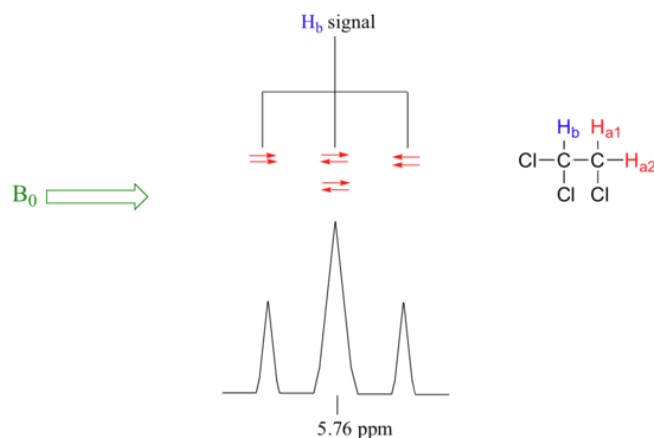


The signal at 3.96 ppm, corresponding to the two $H_a$ protons, is split into two subpeaks of equal height (and area) – this is referred to as a **doublet**. The $H_b$ signal at 5.76 ppm, on the other hand, is split into three sub-peaks, with the middle peak higher than the two outside peaks - if we were to integrate each subpeak, we would see that the area under the middle peak is twice that of each of the outside peaks. This is called a **triplet**.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei. In our 1,1,2 trichloromethane example, the $H_a$ and $H_b$ protons are spin-coupled to each other. Here's how it works, looking first at the $H_a$ signal: in addition to being shielded by nearby valence electrons, each of the $H_a$ protons is also influenced by the small magnetic field generated by $H_b$ next door (remember, each spinning proton is like a tiny magnet). The magnetic moment of $H_b$ will be aligned *with* $B_0$ in (slightly more than) half of the molecules in the sample, while in the remaining half of the molecules it will be opposed to $B_0$. The $B_{eff}$ 'felt' by $H_a$ is a slightly weaker if $H_b$ is aligned against $B_0$, or slightly stronger if $H_b$ is aligned with $B_0$. In other words, in half of the molecules $H_a$ is *shielded* by $H_b$ (thus the NMR signal is shifted slightly upfield) and in the other half $H_a$ is *deshielded* by $H_b$(and the NMR signal shifted slightly downfield). What would otherwise be a single $H_a$ peak has been split into two sub-peaks (a doublet), one upfield and one downfield of the original signal. These ideas an be illustrated by a **splitting diagram**, as shown below.
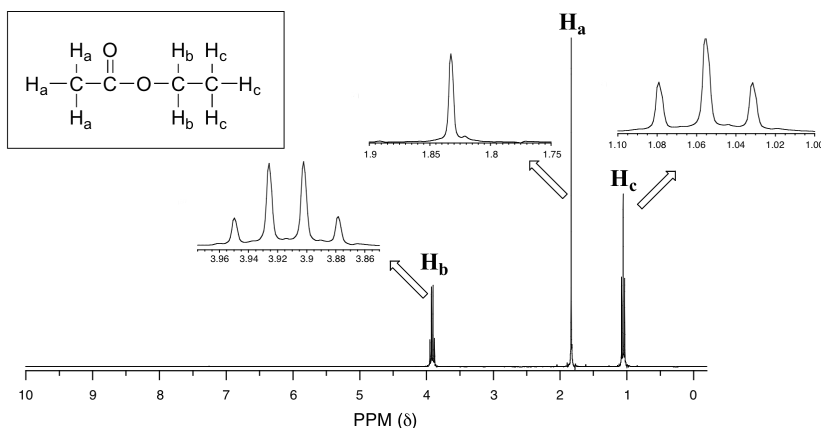


Now, let's think about the $H_b$signal. The magnetic environment experienced by $H_b$ is influenced by the fields of both neighboring $H_a$ protons, which we will call $H_{a1}$ and $H_{a2}$. There are four possibilities here, each of which is equally probable. First, the magnetic

fields of both $H_{a1}$ and $H_{a2}$ could be aligned with $B_0$, which would deshield $H_b$, shifting its NMR signal slightly downfield. Second, both the $H_{a1}$ and $H_{a2}$ magnetic fields could be aligned opposed to $B_0$, which would shield $H_b$, shifting its resonance signal slightly upfield. Third and fourth, $H_{a1}$ could be with $B_0$ and $H_{a2}$ opposed, or $H_{a1}$ opposed to $B_0$ and $H_{a2}$ with $B_0$. In each of the last two cases, the shielding effect of one $H_a$ proton would cancel the deshielding effect of the other, and the chemical shift of $H_b$ would be unchanged.



So in the end, the signal for $H_b$ is a **triplet**, with the middle peak twice as large as the two outer peaks because there are *two* ways that $H_{a1}$ and $H_{a2}$ can cancel each other out.

Now, consider the spectrum for ethyl acetate:



We see an unsplit **'singlet'** peak at 1.833 ppm that corresponds to the acetyl ($H_a$) hydrogens – this is similar to the signal for the acetate hydrogens in methyl acetate that we considered earlier. This signal is unsplit because there are no adjacent hydrogens on the molecule. The signal at 1.055 ppm for the $H_c$ hydrogens is split into a triplet by the two $H_b$ hydrogens next door. The explanation here is the same as the explanation for the triplet peak we saw previously for 1,1,2-trichloroethane.

The $H_b$ hydrogens give rise to a **quartet** signal at 3.915 ppm – notice that the two middle peaks are taller then the two outside peaks. This splitting pattern results from the spin-coupling effect of the *three* $H_c$ hydrogens next door, and can be explained by an analysis similar to that which we used to explain the doublet and triplet patterns.
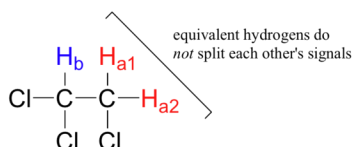
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### Example 5.6

a. Explain, using left and right arrows to illustrate the possible combinations of nuclear spin states for the $H_c$ hydrogens, why the $H_b$ signal in ethyl acetate is split into a quartet.

b. The integration ratio of doublets is 1:1, and of triplets is 1:2:1. What is the integration ratio of the $H_b$ quartet in ethyl acetate? (Hint – use the illustration that you drew in part a to answer this question.)
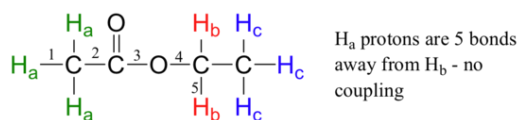
Solution

By now, you probably have recognized the pattern which is usually referred to as the **n + 1 rule**: if a set of hydrogens has *n* neighboring, non-equivalent hydrogens, it will be split into *n* + 1 subpeaks. Thus the two $H_b$ hydrogens in ethyl acetate split the $H_c$ signal into a triplet, and the three $H_c$ hydrogens split the $H_b$ signal into a quartet. This is very useful information if we are trying to determine the structure of an unknown molecule: if we see a triplet signal, we know that the corresponding hydrogen or set of hydrogens has two `neighbors`. When we begin to determine structures of unknown compounds using $^1$H-NMR spectral data, it will become more apparent how this kind of information can be used.

Three important points need to be emphasized here. First, signal splitting only occurs between non-equivalent hydrogens – in other words, $H_{a1}$ in 1,1,2-trichloroethane is *not* split by $H_{a2}$, and vice-versa.
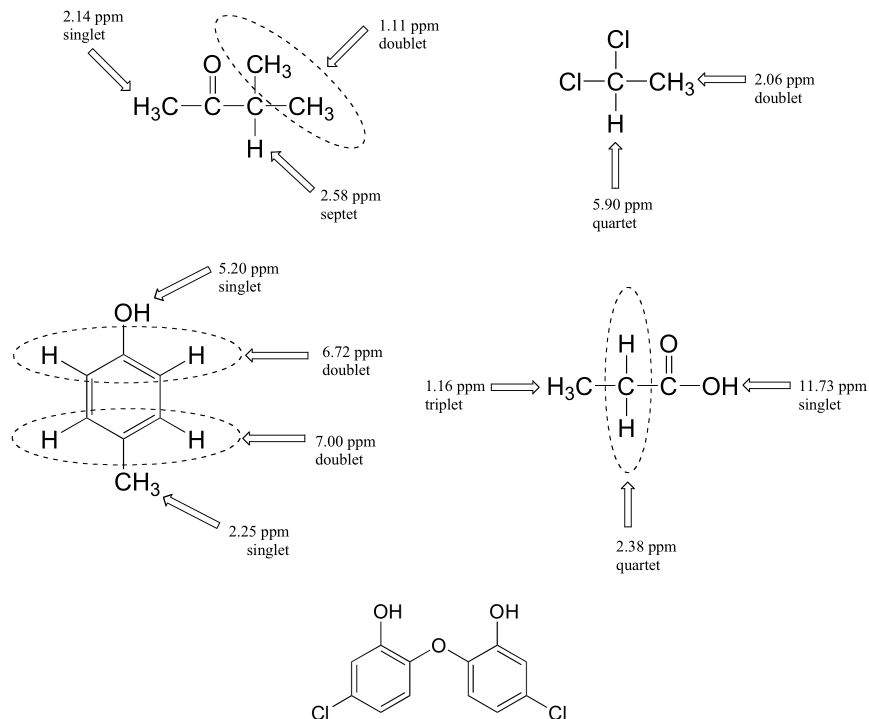


Second, splitting occurs primarily between hydrogens that are separated by three bonds. This is why the $H_a$ hydrogens in ethyl acetate form a singlet– the nearest hydrogen neighbors are five bonds away, too far for coupling to occur.



Occasionally we will see four-bond and even 5-bond splitting, but in these cases the magnetic influence of one set of hydrogens on the other set is much more subtle than what we typically see in three-bond splitting (more details about how we quantify coupling interactions is provided in section 5.5B). Finally, splitting is most noticeable with hydrogens bonded to carbon. Hydrogens that are bonded to heteroatoms (alcohol or amino hydrogens, for example) are coupled weakly - or not at all - to their neighbors. This has to do with the fact that these protons exchange rapidly with solvent or other sample molecules.

Below are a few more examples of chemical shift and splitting pattern information for some relatively simple organic molecules.
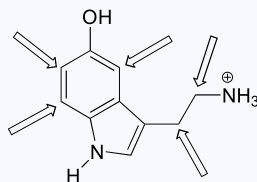


## Example 5.7

a. How many proton signals would you expect to see in the $^1$H-NMR spectrum of triclosan (a common antimicrobial agent found in detergents)? For each of the proton signals, predict the splitting pattern. Assume that you see only 3-bond coupling.
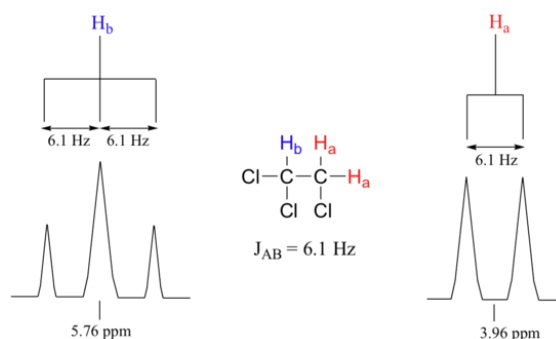
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Solution

## Example 5.8

Predict the splitting pattern for the $^1$H-NMR signals corresponding to the protons at the locations indicated by arrows (the structure is that of the neurotransmitter serotonin).
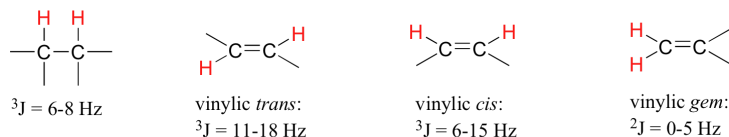


Solution

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## 5.5B: Coupling constants

Chemists quantify the spin-spin coupling effect using something called the **coupling constant**, which is abbreviated with the capital letter *J*. The coupling constant is simply the difference, expressed in Hz, between two adjacent sub-peaks in a split signal. For our doublet in the 1,1,2-trichloroethane spectrum, for example, the two subpeaks are separated by 6.1 Hz, and thus we write $^3J_{a-b} = 6.1$ Hz.
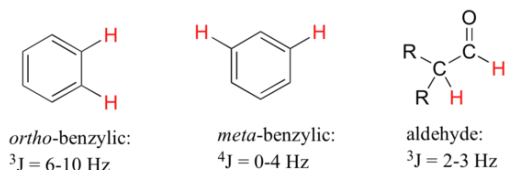


The superscript 3 tells us that this is a three-bond coupling interaction, and the a-b subscript tells us that we are talking about coupling between $H_a$ and $H_b$. Unlike the chemical shift value, *the coupling constant, expressed in Hz, is the same regardless of the applied field strength of the NMR magnet*. This is because the strength of the magnetic moment of a neighboring proton, which is the source of the spin-spin coupling phenomenon, does *not* depend on the applied field strength.

When we look closely at the triplet signal in 1,1,2-trichloroethane, we see that the coupling constant - the `gap` between subpeaks - is 6.1 Hz, the same as for the doublet. This is an important concept! The coupling constant $^3J_{a-b}$ quantifies the magnetic interaction between the $H_a$ and $H_b$ hydrogen sets, and *this interaction is of the same magnitude in either direction*. In other words, $H_a$ influences $H_b$ to the same extent that $H_b$ influences $H_a$. When looking at more complex NMR spectra, this idea of **reciprocal coupling constants** can be very helpful in identifying the coupling relationships between proton sets.

Coupling constants between proton sets on neighboring sp$^3$-hybridized carbons is typically in the region of 6-8 Hz. With protons bound to sp$^2$-hybridized carbons, coupling constants can range from 0 Hz (no coupling at all) to 18 Hz, depending on the bonding arrangement.
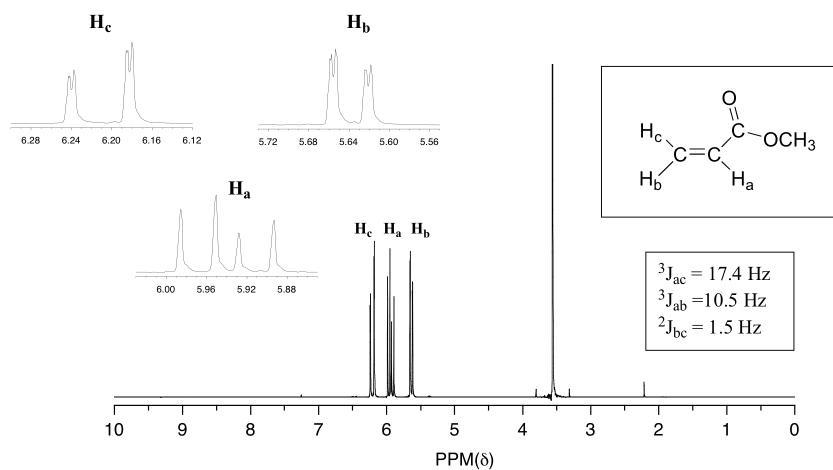


For vinylic hydrogens in a *trans* configuration, we see coupling constants in the range of $^3J = 11$-18 Hz, while *cis* hydrogens couple in the $^3J = 6$-15 Hz range. The 2-bond coupling between hydrogens bound to the same alkene carbon (referred to as geminal hydrogens) is very fine, generally 5 Hz or lower. *Ortho* hydrogens on a benzene ring couple at 6-10 Hz, while 4-bond coupling of up to 4 Hz is sometimes seen between *meta* hydrogens.
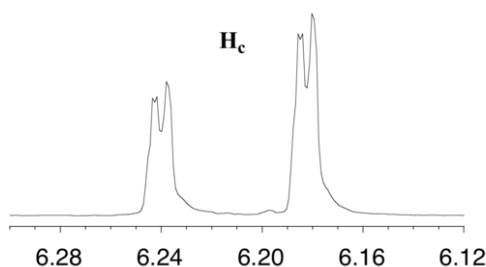
*ortho*-benzylic:
$^3J = 6\text{-}10$ Hz

*meta*-benzylic:
$^4J = 0\text{-}4$ Hz

aldehyde:
$^3J = 2\text{-}3$ Hz

Fine (2-3 Hz) coupling is often seen between an aldehyde proton and a three-bond neighbor. Table 4 lists typical constant values.
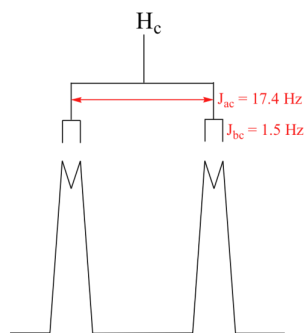
## 5.5C: Complex coupling

In all of the examples of spin-spin coupling that we have seen so far, the observed splitting has resulted from the coupling of one set of hydrogens to *just one* neighboring set of hydrogens. When a set of hydrogens is coupled to *two or more* sets of nonequivalent neighbors, the result is a phenomenon called **complex coupling**. A good illustration is provided by the $^1$H-NMR spectrum of methyl acrylate:



$^3J_{ac} = 17.4$ Hz
$^3J_{ab} = 10.5$ Hz
$^2J_{bc} = 1.5$ Hz

First, let's first consider the $H_c$ signal, which is centered at 6.21 ppm. Here is a closer look:
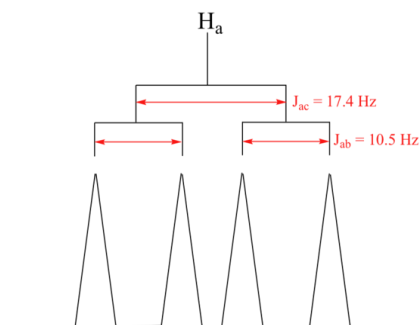


With this enlargement, it becomes evident that the Hc signal is actually composed of four sub-peaks. Why is this? $H_c$ is coupled to both $H_a$ and $H_b$ , but with *two different coupling constants*. Once again, a splitting diagram can help us to understand what we are seeing. $H_a$ is *trans* to $H_c$ across the double bond, and splits the $H_c$ signal into a doublet with a coupling constant of $^3J_{ac} = 17.4$ Hz. In addition, each of these $H_c$ doublet sub-peaks is split again by $H_b$ (*geminal* coupling) into two more doublets, each with a much smaller coupling constant of $^2J_{bc} = 1.5$ Hz.
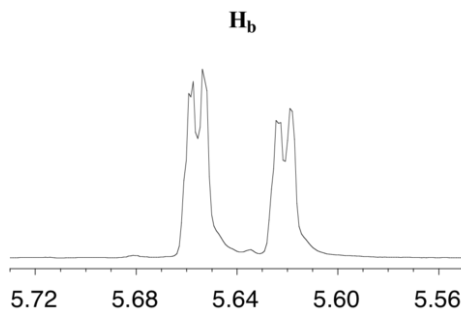
$H_c$



The result of this `double splitting` is a pattern referred to as a **doublet of doublets**, abbreviated `dd`.

The signal for $H_a$ at 5.95 ppm is also a doublet of doublets, with coupling constants $^3J_{ac}$= 17.4 Hz and $^3J_{ab}$ = 10.5 Hz.

$H_a$



The signal for $H_b$ at 5.64 ppm is split into a doublet by $H_a$, a *cis* coupling with $^3J_{ab}$ = 10.4 Hz. Each of the resulting sub-peaks is split again by $H_c$, with the same *geminal* coupling constant $^2J_{bc}$ = 1.5 Hz that we saw previously when we looked at the $H_c$ signal. The overall result is again a doublet of doublets, this time with the two `sub-doublets` spaced slightly closer due to the smaller coupling constant for the *cis* interaction. Here is a blow-up of the actual $H_b$signal:
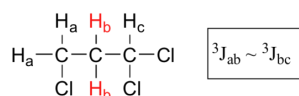
**$H_b$**



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### Example 5.9

Construct a splitting diagram for the $H_b$ signal in the $^1$H-NMR spectrum of methyl acrylate. Show the chemical shift value for each sub-peak, expressed in Hz (assume that the resonance frequency of TMS is exactly 300 MHz).
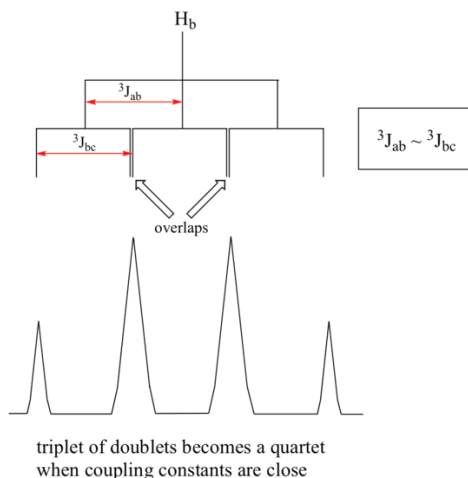
Solution

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When constructing a splitting diagram to analyze complex coupling patterns, it is usually easier to show the larger splitting first, followed by the finer splitting (although the reverse would give the same end result).
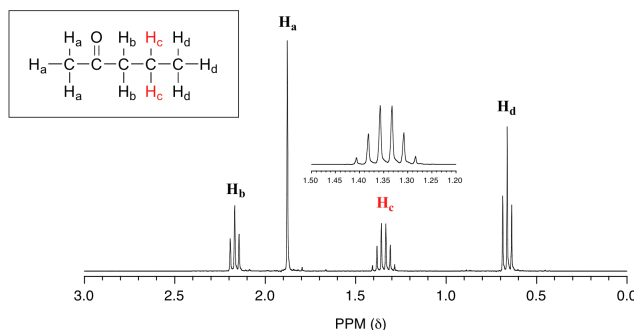
When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `n + 1 rule` of non-complex splitting. In the spectrum of 1,1,3-trichloropropane, for example, we would expect the signal for $H_b$ to be split into a triplet by $H_a$, and again into doublets by $H_c$, resulting in a 'triplet of doublets'.

$$^3J_{ab} \sim {}^3J_{bc}$$

$H_a$ and $H_c$ are not equivalent (their chemical shifts are different), but it turns out that $^3J_{ab}$ is very close to $^3J_{bc}$. If we perform a splitting diagram analysis for $H_b$, we see that, due to the overlap of sub-peaks, the signal appears to be a quartet, and for all intents and purposes follows the $n + 1$ rule.
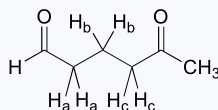


triplet of doublets becomes a quartet
when coupling constants are close

For similar reasons, the $H_c$ peak in the spectrum of 2-pentanone appears as a sextet, split by the five combined $H_b$ and $H_d$ protons. Technically, this 'sextet' could be considered to be a 'triplet of quartets' with overlapping sub-peaks.
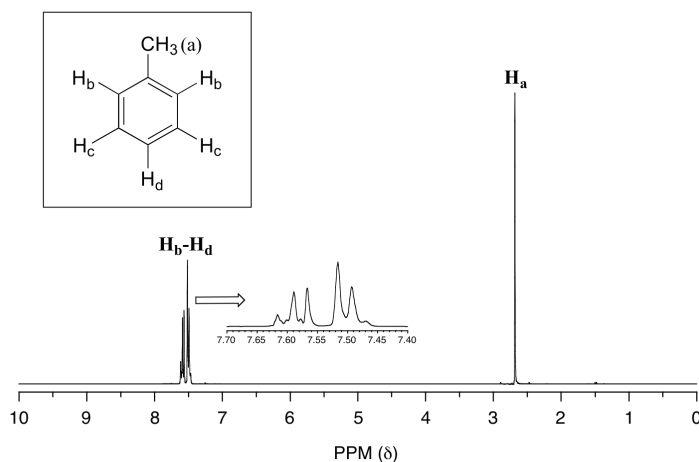


### Example 5.10

What splitting pattern would you expect for the signal coresponding to $H_b$ in the molecule below? Assume that $J_{ab} \sim J_{bc}$. Draw a splitting diagram for this signal, and determine the relative integration values of each subpeak.



Solution

In many cases, it is difficult to fully analyze a complex splitting pattern. In the spectrum of toluene, for example, if we consider only 3-bond coupling we would expect the signal for $H_b$ to be a doublet, $H_d$ a triplet, and $H_c$ a triplet.

In practice, however, all three aromatic proton groups have very similar chemical shifts and their signals overlap substantially, making such detailed analysis difficult. In this case, we would refer to the aromatic part of the spectrum as a **multiplet**.

When we start trying to analyze complex splitting patterns in larger molecules, we gain an appreciation for why scientists are willing to pay large sums of money (hundreds of thousands of dollars) for higher-field NMR instruments. Quite simply, the stronger our magnet is, the more resolution we get in our spectrum. In a 100 MHz instrument (with a magnet of approximately 2.4 Tesla field strength), the 12 ppm frequency 'window' in which we can observe proton signals is 1200 Hz wide. In a 500 MHz (~12 Tesla) instrument, however, the window is 6000 Hz - five times wider. In this sense, NMR instruments are like digital cameras and HDTVs: better resolution means more information and clearer pictures (and higher price tags!)

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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