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Chapter 14: NMR Spectroscopy

A. Introduction

- MS and IR can provide MW and a few other details, but we generally need *way* more info to fully determine a structure.
- Nuclear magnetic resonance (NMR) spectroscopy is a very powerful technique for structure determination.
- ^{1}H NMR ("proton NMR") provides details about the number, types, and relationships of H atoms in a molecule.
- ^{13}C NMR provides details about the number and types of C atoms in a molecule.
- NMR involves an effect on *nuclei* that occurs when molecules are exposed to radiofrequency energy while in a magnetic field...

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B. The NMR Effect

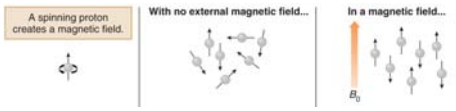
All nuclei are charged, and have a spin quantum number ("I") that can be 0, ½ , 1, etc. depending on the type of nucleus.

If I ≠ 0, the nucleus has a net spin. For ^{1}H, the value is ½.

When a charged particle (like a ^{1}H nucleus, i.e., a proton) spins, it creates a tiny magnetic field, making it like a tiny bar magnet.

Normally, these are randomly oriented in space.

However, in an external magnetic field (B_0), they become aligned "with" or "against" this applied field.



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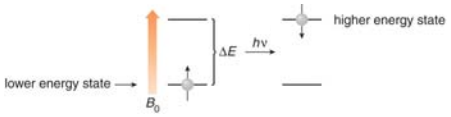
- This creates two possible energy states for each ^{1}H: alignment *with* B_0 is lower in energy, but only by a bit (< 0.1 cal), so the populations of the states are similar.
- If energy that matches the ΔE between these two states is applied, it is absorbed by lower energy nuclei, causing them to excite or "flip" to the higher E orientation.



- The value of ΔE needed lies in the radiofrequency (RF) range.
- At the appropriate ΔE for a given B_0, such excitation occurs, placing the nuclei in energetic "resonance" (not our usual definition of resonance…)

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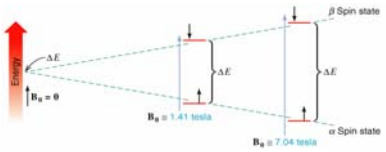
C. Resonance Frequency

- The stronger the B_0 (in tesla; T) , the larger the ΔE, and the higher the RF energy needed for resonance (in megahertz; MHz).
- *Very* powerful (superconducting!) magnets are needed to create large enough B_0 (and ΔE) to make the experiment most useful.



- NMR spectrometers are classified according to the RF energy value needed for ^1H resonance (e.g., 300 MHz, 500 MHz, etc.)
- The magnet strength (B_0) is chosen to give these round numbers, e.g., if B_0 = 7.04 T, ^1H frequency = 300 MHz

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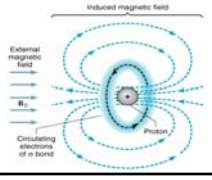
D. Chemical Shift

- A key element of the usefulness of NMR lies in the fact that environmental differences cause slight differences in the *exact* frequencies at which individual nuclei resonate.
- This phenomenon is called "chemical shift" (δ).
- These differences are on the order of parts-per-million (ppm); most ^1H NMR absorptions appear within a 10 ppm window.

Q: Why does the environment of a nucleus affect its resonating frequency?

A: The e^- nearby are *also* charged and affected by B_0.

- Their circulation leads to a contribution opposed to B_0 (in the vicinity of the nucleus)



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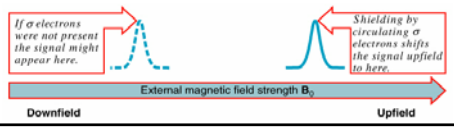
- The H experiences a lower effective B, thereby increasing the *external* B needed for resonance (to compensate) and increasing the frequency (ΔE) needed, as well.
- Key, net result: The signal for the ^1H is "shifted" to higher field.
- *Magnitude* of effect depends on e^- density around the nucleus…
- As e^- density increases, nuclei are said to become more shielded. (Resonance frequency at higher magnetic field; more "upfield").
- As e^- density decreases, nuclei are increasingly deshielded. (Resonance at lower field; further "downfield").



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- e^- density, in turn, depends on chemical environment (e.g., nearby functional groups, electronegativity of attached atoms, π e^- density in the area, resonance effects, etc.)

Consider these 3 examples (showing electronegativity effects):

CH_3CH_2Cl (H_a, H_b) — H_b's have less e^- density than H_a's due to Cl → more deshielded → more downfield than H_a's

$BrCH_2CH_2F$ (H_a, H_b) — H_b's have less e^- density than H_a's (F vs. Br) → more deshielded → more downfield than H_a's

$ClCH_2CHCl_2$ (H_a, H_b) — H_b's have less e^- density than H_a's (2 Cl vs. 1 Cl) → more deshielded → more downfield than H_a's

We've seen halide substituents reduce e^- density before, e.g., recall the effects of replacing H's with halides on pK_a of CH_3COOH…

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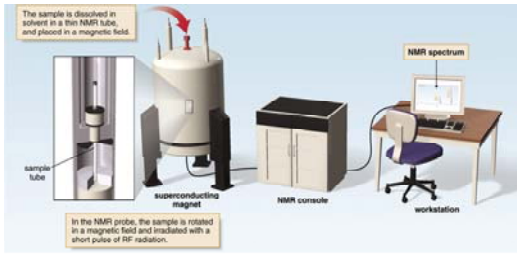
E. A Modern NMR Spectrometer



- A pulse of energy is applied to a solution of a compound to achieve simultaneous resonance of all its ^1H's.
- After this energy "pulse", nuclei return to their equilibrium distribution--the instrument detects the emitted energy to generate a spectrum that shows the individual "resonances".

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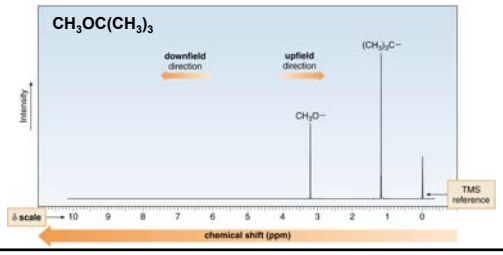
F. ^1H NMR Spectra

- An NMR spectrum is a plot of peak intensity vs. chemical shift (δ) in ppm "downfield" relative to a standard reference (tetramethylsilane; TMS) set by convention as 0 ppm.
- TMS was chosen for many reasons, but because it is upfield of most organics, shift numbers increase from right to left.



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- The chemical shift of an NMR resonance (or "signal"), in ppm, is measured according to the following equation:

$$\text{chemical shift (in ppm on the } \delta \text{ scale)} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\nu \text{ of the NMR spectrometer (in MHz)}}$$

- Because shift of a signal is reported as a fraction (i.e., in ppm) of whatever NMR operating frequency is being used, it is a constant for a given sample.
- However, in a 300-MHz (i.e., 300 million Hz) spectrum, 1 ppm = 300 Hz. In a 600-MHz spectrum, 1 ppm = 600 Hz.
- Thus, signals will be more spread out at 600-MHz, making fortuitous, confusing overlap of different signals less likely.

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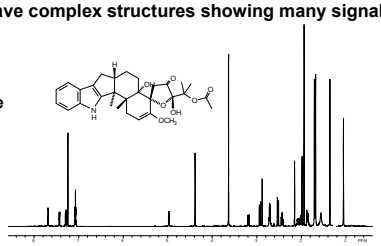
Superconducting magnets are really expensive, but this begins to explain why we care about going to higher frequencies…

It improves both resolution of the signals and sensitivity.

This is *most* important for real-world samples that are limited in quantity and/or have complex structures showing many signals.

A 600-MHz ^{1}H NMR spectrum of a more complex molecule:



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G. Types of Structural Info Provided by ^{1}H NMR Spectra

- Number of signals: indicates the number of "different types of H" (i.e., different environments of H's) in a molecule.
- Position of signals: helps sort out what types of H the molecule contains.
- Intensity (peak area) of signals: indicates the relative amounts (how many) of each kind of H.
- Shape (spin-spin coupling/splitting/multiplicity) of a signal: gives info about *neighboring* H's in the molecule.

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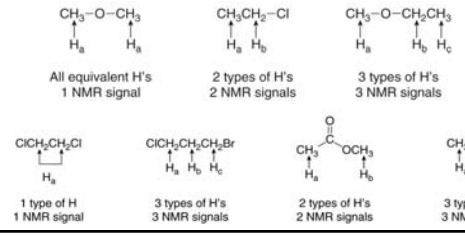
1. Number of Signals

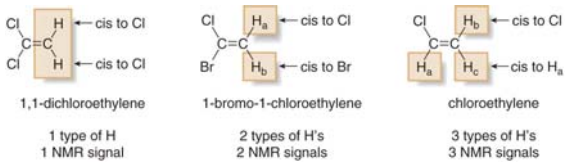
- ^{1}H's in different environments give different NMR signals.
- ^{1}H's in equivalent environments collectively give one NMR signal.
- The number of signals equals the number of different types of ^{1}H in a compound (unless signals fortuitously overlap…).



14-14

a. Alkenes—issues introduced by C=C geometry…

- In comparing two H atoms on a C=C (or a ring…), two H's are equivalent only if they are *cis* (or *trans*) to the same groups.



- This shows that it is possible for two H's *on the same C* to be *different*....

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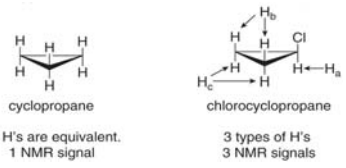
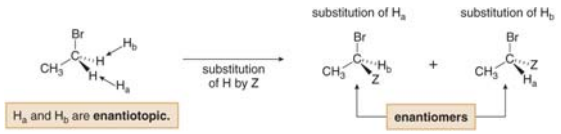
b. Substituted Cycloalkanes

- To determine whether two H's in a cycloalkane (or an alkene) are equivalent, consider whether or not the H's in question are *cis* (or *trans*) to the same groups.



c. Enantiotopic Protons

- If H_a below were replaced by "Z", we'd get a different enantiomer than we would if H_b were replaced by Z.
- These two H's are considered enantiotopic, and are chemical-shift equivalent (i.e., they will give one ^{1}H NMR signal).

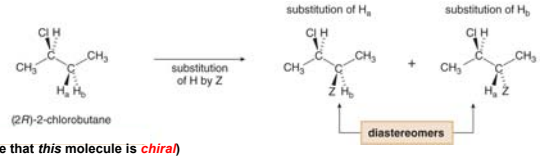


(Note that this molecule is *achiral*)

- It may seem obvious that two H's on the same sp^3 C would be equivalent, but look at the next case…

d. Diastereotopic Protons

- If H_a below were replaced by "Z", we'd get a different *diastereomer* than we would if H_b were replaced by Z.
- *Thus, these* two H's are *diastereotopic*, and are chemical-shift *inequivalent* (i.e., they will each give *different* ^{1}H NMR signals!).

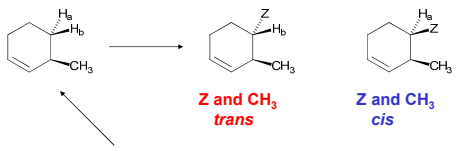


(Note that *this* molecule is *chiral*)

Why? H_a & H_b will always be in different environments; this can be seen if you look at any Newman projection along the C2-C3 bond.

This may be easier to see in a cyclic case:

- If H_a below were replaced by "Z", we'd get a *trans* isomer; if H_b were replaced by Z, we'd get a *cis* isomer--different *diastereomers*, so H_a and H_b are *diastereotopic.*



- Note how H_a will always be *trans* to the CH_3, while H_b will always be *cis* to it---different *environments → different shifts*
- The other CH_2's in this thing are all diastereotopic pairs, too!

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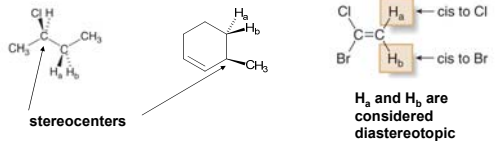
Q: What is it about a molecule that make it's CH_2's diastereotopic?

A: Generally, this occurs for any molecule with one or more *stereocenters*, but monosubstituted cycloalkanes and unsymmetrical 1,1-disubstituted alkenes also qualify



H_a and H_b are considered diastereotopic

This can complicate ^{1}H NMR spectra significantly. We will see an example on slide 42; the ^{1}H NMR spectrum of $H_3C-CH(Cl)-CH_2Cl$

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2. Position of Signals--Characteristic Chemical Shifts

^{1}H's of a given type will absorb in a *somewhat* predictable region:

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
sp^3 C–H	0.9–2	sp^2 C=C–H	4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7	Ar–H	6.5–8
Z–C–C–H Z = C, O, N	1.5–2.5	R(C=O)H	9–10
–C≡C–H	~2.5	R(C=O)OH	10–12
sp^3 Z–C–H Z = N, O, X	2.5–4	RO–H or R–N–H	1–5

Some differences can be explained by electronegativity, but not all….

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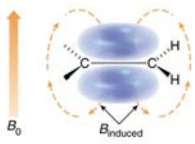
a. Alkenes: why are C=C-H's relatively downfield?

- **sp^2 = "more electronegative" than sp^3, but that's only part of it.**
- **In a magnetic field, the loosely held π e^- of the C=C circulate to create their own small, induced magnetic field, which *reinforces* B_0 in the vicinity of the H's.**



This moves the ^{1}H signals somewhat *downfield* (to ~4.5-6.5 ppm).

- **This is an "anisotropic" effect—the degree and direction of the shift depend on the location of the H's within the induced field.**
- **The alkene H's are in the "deshielding region" of the C=C.**

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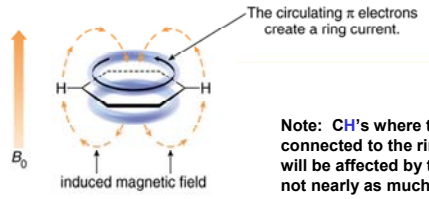
b. Aromatics? A similar story…

- In a magnetic field, the π e⁻ in benzene circulate around the ring creating a "ring current"—a particularly strong effect.
- The induced field again reinforces B_0 in the vicinity of the H's.
- Thus, the ^{1}H's again experience a downfield anisotropic effect—often even more so than alkene CH's (to ~ 6-8 ppm).

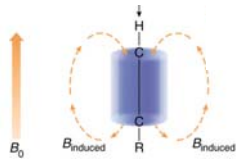


Note: CH's where the C is connected to the ring (or C=C) will be affected by this, too, but not nearly as much.

14-23

c. Alkynes?

- The π e⁻ of a C≡C also circulate in a magnetic field, but in *this* case, the induced field *opposes* B_0 in the vicinity of the C≡C-H.
- Alkyne ^{1}H's thus absorb *relatively* upfield (~ 2.5 ppm).

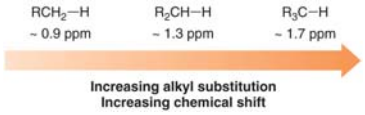


- Note, however, that hybridization is also a factor—sp orbitals are more electronegative than sp^2 or sp^3, so there is a *downfield* effect mixed in there, too…

14-24

d. Other "Anisotropic" Effects

- The chemical shift of almost any kind of C–H usually increases with increasing alkyl substitution.



Q: Hmm—this seems counterintuitive? R-groups are e⁻-*donating*, right? Shouldn't that *increase* shielding as we go to the right here? What's the deal?

A: σ e⁻ circulate, too! The associated fields are weaker, but there are a lot of them. Their effects, together with typical geometric relationships among them, cause this general trend.

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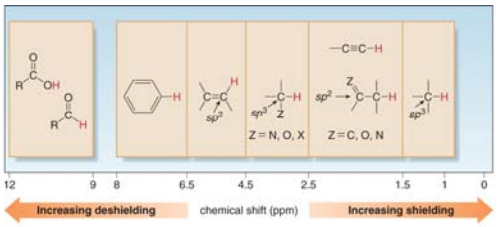
Overview of General ^{1}H NMR Spectral Regions



Effects are additive, so these are just *approximate* ranges.

E.g., the CH_2O in CH_2=CHCH_2OH would be a bit further downfield than the one in $CH_3CH_2CH_2OH$.

And, generally, δ for CH > CH_2 > CH_3, given identical substituents.

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3. Intensity of ^{1}H NMR Signals

- **The *area* of an ^{1}H NMR signal/peak is proportional to the number of ^{1}H's associated with it.**
- **"Integration" of the peak areas is often plotted as a stepped curve (an integral) above the spectrum.**
- **The height of each "step" is proportional to the area under the peak, which is proportional to the number of ^{1}H's for that signal.**

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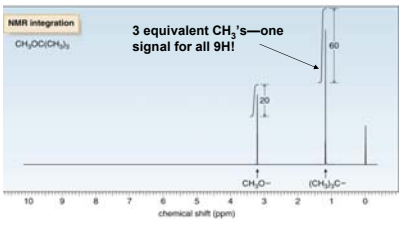
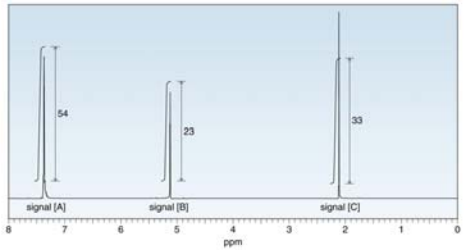
- **NMR data systems calculate the value of each integral for you in arbitrary units (or you could just measure with a ruler…).**
- **The ratio of these values gives info about how many ^{1}H's of each type are represented by the various signals.**
- **This is a *ratio*—not the absolute number—of ^{1}H's—but if you know the molecular formula, you can figure out the numbers.**



Ratio of signals is 3:1, but knowing formula ($C_5H_{12}O$), this must translate to 9H:3H

If you *didn't* know the formula, this'd be tricky to figure out…

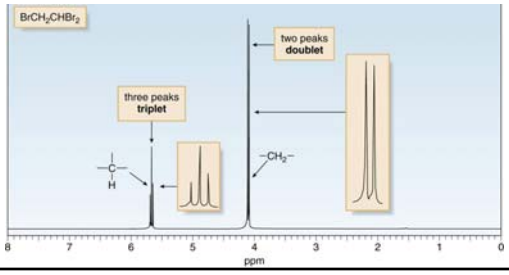
The text gives another example ($C_9H_{10}O_2$; below), but makes things look more complicated than they need to be…



- Their integrals are messed up (e.g., *size* of integral for A is clearly not more than twice that for B…??), but…
- Just eyeballing the ***numbers*** shown, with an available total of 10H, makes it pretty clear that the ratio must be 5:2:3…

4. Signal *Shape*: Spin-Spin Coupling/Splitting in ^{1}H NMR

- The simple sample spectra that we have seen up to now have included only single-peak absorptions called singlets.
- However, signals for individual ^{1}H types often show more complex shapes, i.e., they are split into more than one peak.



The reason? Spin-spin coupling (= splitting) generally occurs between non-equivalent ^{1}H's on the same C or adjacent C's.

Q: *Why* does the CH_2 in $BrCH_2CHBr_2$ occur as a *doublet*?

- When exposed to B_0, the ***adjacent*** ^{1}H ($CHBr_2$) can be aligned with (↑) or against (↓) B_0.
- Thus, the CH_2 can experience two slightly different net magnetic fields caused by this ^{1}H's own little field—one slightly larger than B_0, and one slightly smaller than B_0 (~50:50 chance)
- The corresponding CH_2's absorb at two different frequencies, so the absorption gets split into a 1:1 doublet.
- As we will soon see, the CH_2 will also split the CH signal…

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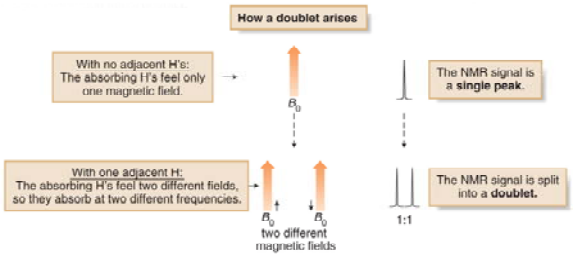
a. Coupling Constants

When two ^{1}H's split each other, they are said to be *coupled*.

The frequency difference, in Hz, between the two peaks of the doublet is called the coupling constant, *J*. This "*J*-value" is a constant and is independent of the B_0 being used.



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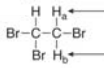
Ok, fine. But why is the CHBr$_2$ signal a *3*-line thing (a triplet)?

- When in B_0, the adjacent CH_2 protons H_a and H_b can *each* be aligned with (↑) or against (↓) B_0.



- Thus, a CHBr$_2$ proton could experience one of three slightly different net magnetic fields:
  - one slightly larger than B_0 (when the CH_2 spins are ↑↑)
  - one slightly smaller than B_0 (the ↓↓ case)
  - one the same strength as B_0 (the ↓↑ and ↑↓ cases)
- Because the CHBr$_2$ ^{1}H's can experience 3 different net magnetic effects, subsets of the population appear at 3 slightly different frequencies, resulting in a triplet.

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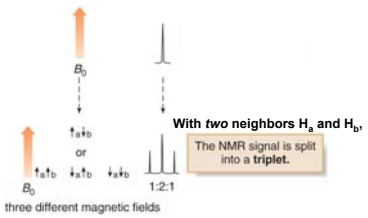
- Because there are *two* ways to align one ^{1}H with B_0, and one against B_0 (i.e., $\uparrow_a\downarrow_b$ and $\downarrow_a\uparrow_b$), the middle peak of the triplet is twice as intense as the two outer peaks.
- This makes the ratio of the areas under the three peaks 1:2:1.
- The distance in Hz between each peak in a simple "multiplet" like this (i.e., the *J*-value) will be the same.



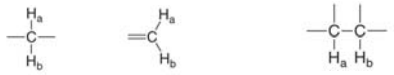
b. Splitting Patterns

- Some general rules describe splitting patterns commonly seen in ^{1}H NMR spectra of organic compounds.

[1] Equivalent protons do not split each other.

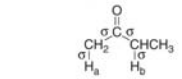
[2] A set of *n* equivalent *neighboring* ^{1}H's will split the signal for a nearby ^{1}H type into n + 1 peaks.

[3] Splitting is usually observed between non-equivalent ^{1}H's on the same C (geminal H's) or adjacent C's (vicinal H's).



geminal H's vicinal H's

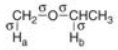
[4] Splitting is not generally observed between ^{1}H's separated by more than three σ bonds.



2-butanone

H_a and H_b are separated by four σ bonds.

no splitting between H_a and H_b



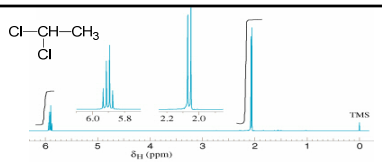
ethyl methyl ether

H_a and H_b are separated by four σ bonds.

no splitting between H_a and H_b

Four-bond couplings can sometimes be seen through π-systems, but even these are usually relatively small.

Another example:



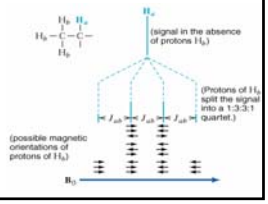
$\underline{CH_3}$: 3 identical ^{1}H split by 1 adjacent ^{1}H; n + 1 = 2 peaks ⇒ doublet

$\underline{CH}$: 1 ^{1}H split by 3 identical adjacent ^{1}H; n + 1 = 4 peaks ⇒ "quartet"

Quartet is 1:3:3:1 because each ^{1}H of the CH_3 ^{1}H's could have ↑ or ↓ spin.

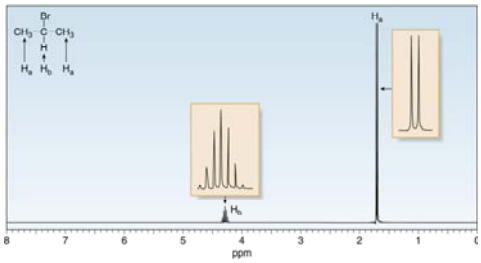
All possible combinations will occur, in statistically expected 1:3:3:1 ratio.

Often not *perfect* (as above), but this is the expected ratio.



14-37

^{1}H NMR Spectrum of 2-Bromopropane



- This is a characteristic pattern for an isopropyl group.
- The 6 H_a protons are split by the one H_b to give a doublet.
- H_b is split by 6 equivalent H_a protons to yield a *septet* (n + 1 = 7). Relative ratios? From all possible spin combos: 1:6:15:20:15:6:1

14-38

Some other common ^{1}H NMR splitting patterns…

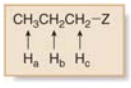
Example	Pattern	Example	Pattern
—C—C— (H_a H_b)	H_a H_b	—CH_2CH_3 (H_a H_b)	H_a H_b
—C—CH_2— (H_a H_b)	H_a H_b	—C—CH_3 (H_a H_b)	H_a H_b
—CH_2CH_2— (H_a H_b)	H_a H_b		

Keep in mind the difference between multiplicity and *integration*…

14-39

c. More Complex Splitting Patterns

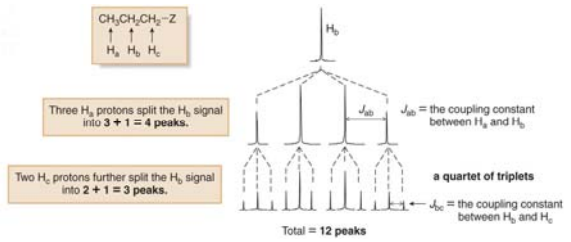
- When two *different* sets of adjacent ^{1}H's are coupled to a given ^{1}H (n ^{1}H's on one adjacent C and m ^{1}H's on another), things can get more complicated…
- If the *J* with n = the *J* with m; the number of peaks in an NMR multiplet will = (m + n) + 1, as you might have expected.
- However, if the *J* with n ≠ the *J* with m, you could see a much messier multiplet; it could have (m + 1) x (n + 1) lines!
  - Let's consider these possible scenarios using an *n*-propyl group as an example



Consider the signal for the H_2 labelled below as "b":

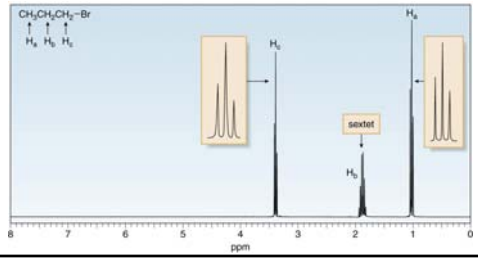
If $J_{ab} = J_{bc}$ (or if $J_{ab} \approx J_{bc}$), we'd expect 5 + 1 = 6 peaks/lines for this H_2 signal. (We will see this on the next slide…)

But…what if J_{ab} is *different* from J_{bc}? Just for kicks, let's say $J_{ab} >> J_{bc}$…in *that* case, we could get 12 lines for that H_2 signal!

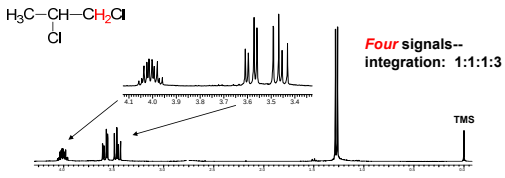


The Actual ^{1}H NMR Spectrum of 1-Bromopropane:

- **The H_c's and H_a's are not equivalent, so we can't *necessarily* just add them together and use the *n* + 1 rule, *but*…**
- **J_{ab} and J_{bc} tend to be very similar in an open-chain system like this, so the *n* + 1 "rule" *does* work here--the H_b signal is a sextet.**



But here's one where we *do* see some different vicinal *J*-values:



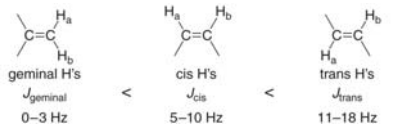
The CH_2 ^{1}H's are *diastereotopic* (see slides 17-19), so they are inequivalent, and appear as two one-H signals (δ 3.46 and 3.58).

This also makes the CH and CH_2 multiplets more complicated!

This is a very common phenomenon among compounds that have one or more *stereocenters*…

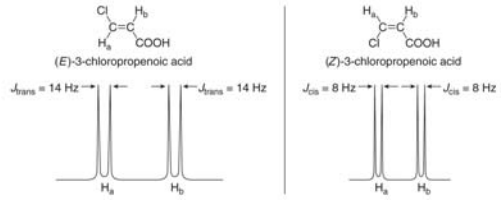
d. Alkene *J*-values

- ^{1}H's on C=C's often give characteristic splitting patterns. Consider the three possible disubstituted C=C's…
- When the ^{1}H's on the C=C are different (usually the case unless the thing is symmetrical), each ^{1}H splits the signal of the other so that each appears as a doublet (a "d").
- The magnitude of the *J* depends on the arrangement of the H's:

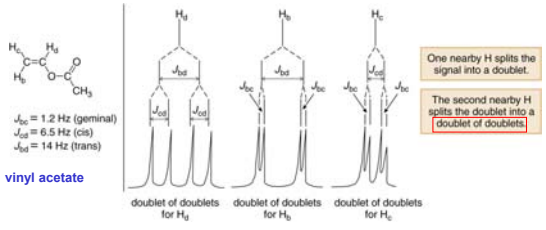


This gives us an *easy* way to tell which kind of system we have!

Cis vs. *trans* isomers can easily be distinguished!



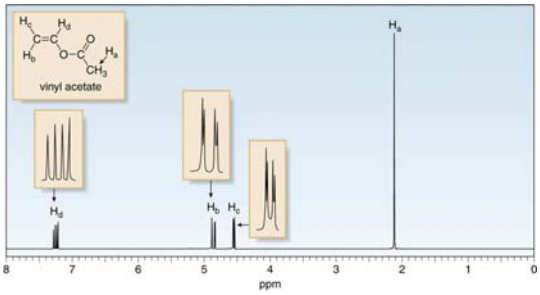
Consider a vinyl group (-CH=CH$_2$). All three H's are different, and all three possible couplings show up:



And the *shifts* are surprisingly different →

14-46

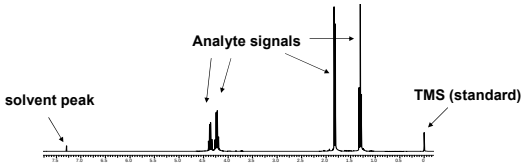
^{1}H NMR Spectrum of Vinyl Acetate



14-47

e. NMR Solvents

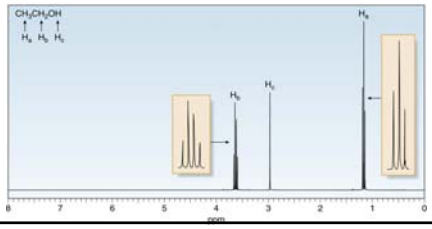
- NMR spectra are usually collected using dilute solutions.
- Regular solvents pose a problem--so much more abundant than the *analyte* that they would give giant masking signals…
- Solution: *deuterated* solvents—classic example = $CDCl_3$ (as opposed to $CHCl_3$). D (= ^{2}H) does not show a ^{1}H NMR signal!
- Could still see a small $CHCl_3$ signal (~7.26 ppm), but it is due to trace residual $CHCl_3$, not the $CDCl_3$.



14-48

f. ^{1}H NMR Signals for OH Protons

- OH (and amine NH) protons behave differently from CH's, mainly because they undergo H-bonding and/or exchange.
- An OH might not show coupling with adjacent CH's (as below), but for another sample of the same compound, it might!
- Consider the spectrum of ethanol (CH_3CH_2OH) below:



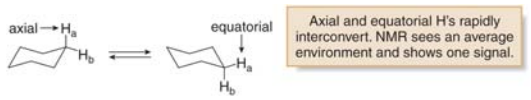
14-49

- The three-proton CH_3 signal is split by the CH_2 into a triplet.
- The two-proton CH_2 signal is split by the CH_3 into a quartet.
- But…the adjacent OH shows no coupling with the CH_2???
- OH's often undergo intermolecular exchange so rapidly that a given OH proton is not around long enough to exert mutual spin effects with the CH_2 → no coupling!
- If rate is *slowed* somehow (e.g., in very dilute solution), coupling can sometimes be seen, but this is hard to predict.
- Intermediate situations can occur where coupling is not observed, but the OH shows up as a broad lump…can even be so broad that you don't notice it!

14-50

g. Cyclohexane Conformers

- Cyclohexane conformers interconvert rapidly at room temperature. An NMR spectrum shows an *average* of these.
- Each C has two different types of H—one axial, one equatorial—but their rapid interconversion results in a single NMR signal due to the average environment that each H experiences.

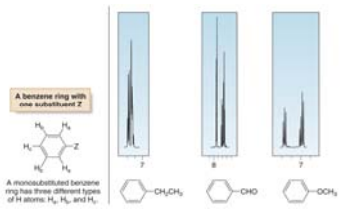


- Otoh, if a system has a strongly preferred conformer, e.g., due to a *t*-butyl substituent, then the ax and eq H's *would* be different.

14-51

h. Protons on Benzene Rings

- Benzene's ^1H's are equivalent, and give one peak at 7.27 ppm.
- Monosubstituted benzenes contain five ^1H's that are *not* all equivalent; the appearance of the signals varies, depending on what is attached.



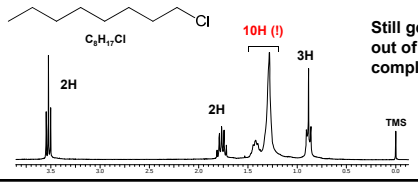
Think about why this might be—we'll revisit it when we talk more about benzenes…

Patterns for more highly substituted benzenes will be diagnostic because their *vicinal J*-values are larger (*ca.* 7.5 Hz) than others.

14-52

i. Overlapping signals

- Efforts (even counting signals) can be hampered by overlap of signals that have very similar chemical shifts.
- For example, technically, 1-chlorooctane (below) has eight different kinds of H. (This is what the *book* would say…)
- However, the environments of some of the CH_2's are so similar that they resonate at about the same place, giving a nearly uninterpretable blob with confusing integration…



Still get ***some*** useful info out of it, but this does complicate things…

14-53

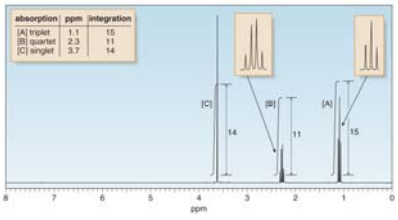
H. Use of ^{1}H NMR in Structure Determination

Some steps to consider are listed below. They do not have to be followed in this order. With practice, some will become intuitive.

1. Figure the number of unsaturations: #C – ½ #(H + X) + ½ #N + 1
2. Count the signals: try to determine the # of different types of H
3. Look at integration to tell how *many* of each type you have. This can tell you whether a signal = a CH_3 or a CH or CH_2. Think about possible symmetry issues.
4. Look at splitting to tell what's next to what. Look for diagnostic *patterns* (e.g., see slide 38).
5. Consider chemical shifts (and any other available information, such as IR) to decide what kind of functional groups you might have, and which H's they are near.

14-54

Example: $C_4H_8O_2$; IR says there's a C=O



1. Number of unsaturations = 4 – 4 + 1 = 1 (the C=O must be the only one!)
2. Number of different types of H? There are three (three signals).

14-55

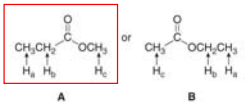
3. How many of each type (based on integration)? Ratio of 3:2:3 (and 3H + 2H + 3H = 8H; matches formula).

(Only 4 C → this must correspond to two CH_3's and a CH_2).

So…we have a C=O, two *different* CH_3's, a CH_2, and one more O. Not all that many possibilities….but let's keep going…

4. Splitting? CH_3 at 1.1 ppm and CH_2 split each other → an ethyl pattern, just like in ethanol. The *other* CH_3 is a singlet—it must have *no vicinal H neighbors*!

5. Shift—at this point, there are only two chemically reasonable structures, and shift distinguishes them:

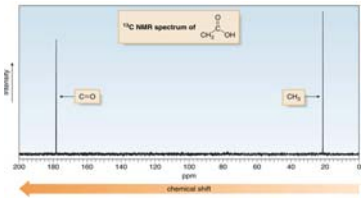


The only way the CH_3 singlet can be downfield of the CH_2 is to place it on the electronegative O

14-56

G. ^{13}C NMR Spectra

- ^{12}C is not NMR-active because its I value = 0.
- However, 1.1% of the carbon nuclei in nature are not ^{12}C—they are ^{13}C (remember that from the MS chapter?), and the I value for ^{13}C = ½, just like ^{1}H, so we *can* see *^{13}C's* by NMR!
- "Standard" ^{13}C NMR spectra are easier to analyze because the signals are not split; each type of C appears as a single peak.



- Huh? Why should that be??
- Two reasons…

14-57

The ^{13}C's out there are randomly distributed among all possible positions within a molecule.

Due to its low natural abundance (1.1%), the chance of two ^{13}C's being bonded to each other is very small (0.011 x 0.011 = 0.0001%)

Thus, nearly all ^{13}C's will be attached to NMR-inactive ^{12}C, which does not cause splitting.

Q: But couldn't ^{13}C NMR signals be split by nearby ^{1}H's?

A: Yes, but standard ^{13}C NMR experiments employ a technique that "decouples" the ^{1}Hs from the ^{13}C's, so that every ^{13}C peak is simplified to a singlet.

This throws away coupling information, and prevents accurate integration, but makes the thing easier to interpret AND improves s/n (remember, we can only see 1% of the carbons in the sample…)

H. Types of Structural Info Provided by ^{13}C NMR Spectra

Since we don't see the coupling and can't integrate, there are only two features of a standard ^{13}C NMR spectrum that provide structural info:

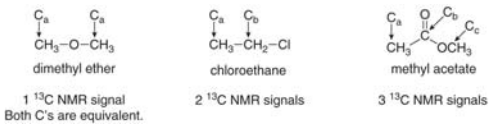
- Number of signals: indicates the number of "different types of C" (i.e., different environments of C's) in a molecule.
- Position of signals: shifts help sort out what types of C the molecule contains.

Re intensities: we can't accurately integrate ^{13}C NMR spectra, but signals that correspond to more than one identical C (e.g., the CH_3 in $(CH_3)_2CHOH$) *do* tend to be *somewhat* larger.

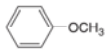
Also, C's with no H on them tend to give somewhat smaller signals than others.

1. Number of signals

Recognizing the # of different types of C has analogy to the spotting the # of different types of H.



However, must be wary of symmetry issues…e.g., the compound below would have only four ^{13}C NMR signals in the sp^2 region (plus the OCH_3 carbon in the sp^3 region):



2. Position—chemical shift range

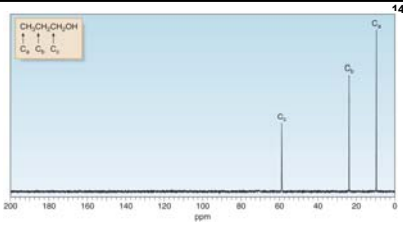
- ^{13}C NMR signals occur over a much broader chemical shift range than ^{1}H signals (*ca.* 0-220 ppm downfield from TMS).
- Why? C's can be hybridized differently—H cannot—and each C is bonded to more things than an H. There's just more variety….
- Chemical shift trends in ^{13}C NMR parallel those in ^{1}H NMR, because the same basic kinds of factors influence them.

Table 14.5 Common ^{13}C Chemical Shift Values

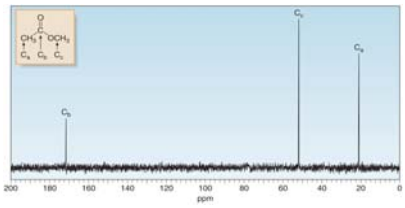
Type of carbon	Chemical shift (ppm)	Type of carbon	Chemical shift (ppm)
sp^3 C–H	5–45	C=C	100–140
sp^3 C–Z (Z = N, O, X)	30–80	C–	120–150
–C≡C–	65–100	C=O	160–210

14-61

^{13}C NMR Spectrum of 1-Propanol:



^{13}C NMR Spectrum of Methyl Acetate:

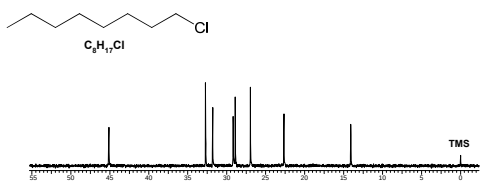


14-62

An advantage of the wide shift range and sharp signals is that ^{13}C NMR spectra tend to have less of an issue with overlap.

Remember that blobby ^{1}H NMR spectrum of 1-chlorooctane on slide 52?

The ^{13}C NMR spectrum clearly resolves all eight ^{13}C signals!



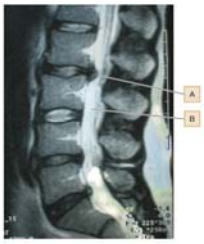
14-63

- Thus, ^{13}C NMR is a useful compliment to ^{1}H NMR in structure determination.
- Allows C-types to be counted, and shows signals for C's that do not have ^{1}H on them.
- e.g., ^{1}H NMR alone would not explicitly show you that you have a C=O, but ^{13}C NMR would...
- There are *many* other, more sophisticated NMR techniques available to help deal with more complicated structures, but they are beyond the scope of this course.

A Final NMR Note--Magnetic Resonance Imaging (MRI)

MRI—a valuable technique used in medicine for visualizing soft tissues not well resolved by x-rays—employs NMR technology, but note how they avoided using the term "nuclear"...

an MRI instrument



an image showing an area of compression (box A) in a spinal column