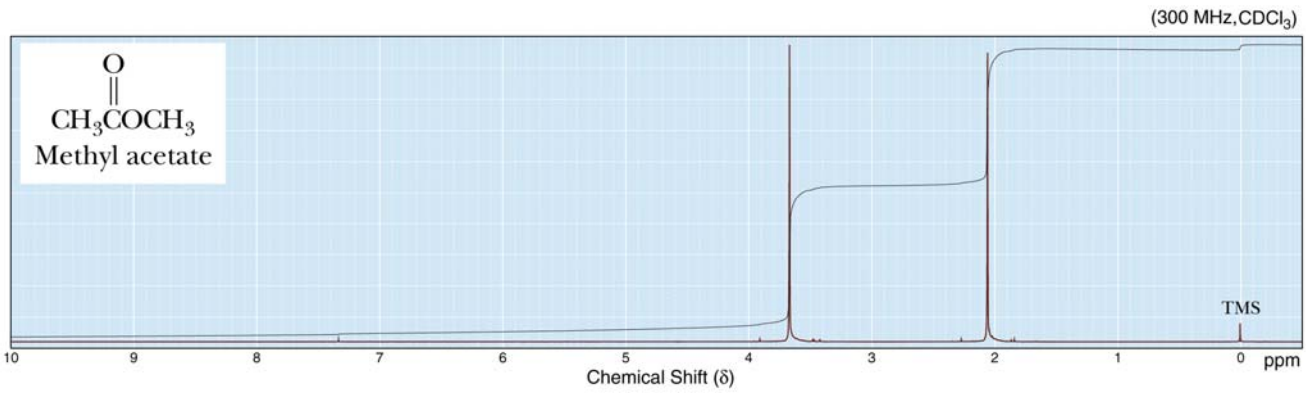
11. Proton NMR (text 12.6 – 12.9, 12.11, 12.12)

A. Proton Signals

- Like ^{13}C, ^{1}H atoms have spins of ±½, and when they are placed in a very strong magnetic field, they absorb radiofrequency radiation to give an NMR absorption peak.
- Like carbon NMR, non-equivalent protons in a molecule will absorb radiation of a different frequency. The peaks are plotted as a chemical shift (δ, ppm) relative to the single location of the single H in tetramethylsilane (TMS, set to 0).



- In the above spectrum of methyl acetate, we see two peaks downfield (to the left) of TMS. δ ranges from 0 – 13 ppm.
- δ values depend on the type, electronegativity, and hybridization of the atom that the H is bonded to
- In methyl acetate, the peak at 3.7 ppm is due to the three H's bonded to the CH_3O, while the 2.0 ppm peak is due to the three H's bonded to the acyl CH_3 (next to the carbonyl).

- Textbook Table 12.1 (provided on exams) has δ values.

TABLE 12.1 Average Values of Chemical Shifts of Representative Types of Hydrogens

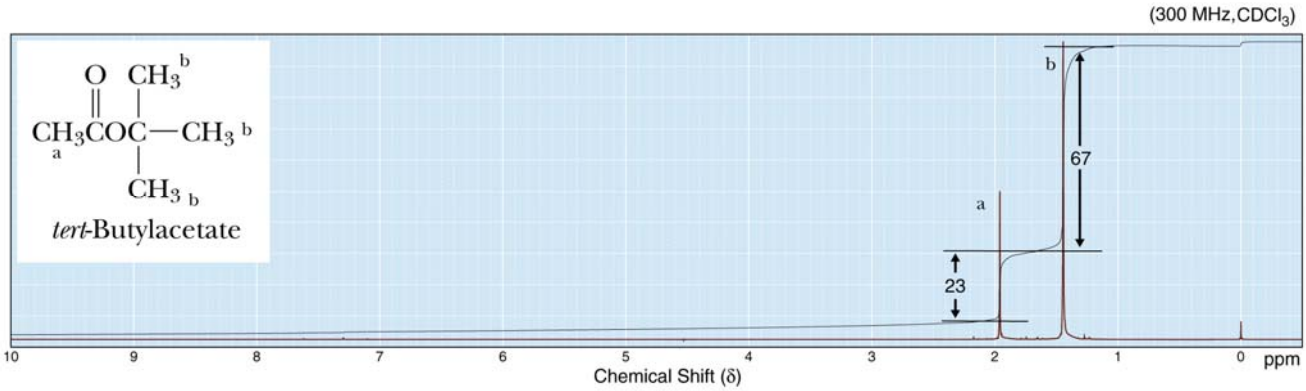
Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
$(CH_3)_4Si$	0 (by definition)	$R\overset{O}{\overset{\|}{C}}OCH_3$	3.7–3.9
RCH_3	0.8–1.0	$R\overset{O}{\overset{\|}{C}}OCH_2R$	4.1–4.7
RCH_2R	1.2–1.4	RCH_2I	3.1–3.3
R_3CH	1.4–1.7	RCH_2Br	3.4–3.6
$R_2C{=}CRCHR_2$	1.6–2.6	RCH_2Cl	3.6–3.8
$RC{\equiv}CH$	2.0–3.0	RCH_2F	4.4–4.5
$ArCH_3$	2.2–2.5	$ArOH$	4.5–4.7
$ArCH_2R$	2.3–2.8	$R_2C{=}CH_2$	4.6–5.0
ROH	0.5–6.0	$R_2C{=}CHR$	5.0–5.7
RCH_2OH	3.4–4.0	ArH	6.5–8.5
RCH_2OR	3.3–4.0	$R\overset{O}{\overset{\|}{C}}H$	9.5–10.1
R_2NH	0.5–5.0	$R\overset{O}{\overset{\|}{C}}OH$	10–13
$R\overset{O}{\overset{\|}{C}}CH_3$	2.1–2.3		
$R\overset{O}{\overset{\|}{C}}CH_2R$	2.2–2.6		

*Values are approximate. Other atoms within the molecule may cause the signal to appear outside these ranges.

- Proton chemical shifts give us the same sort of structural information for H atoms that ^{13}C shifts do for C. However, ^{1}H NMR has two features that make it a much more valuable structural probe: signal area and signal splitting.

B. Signal Area

- In proton NMR, the area under a signal peak is directly proportional to the number of H's contributing to that peak.
- NMR instruments have an integrator that displays the area of a peak as a vertical line superimposed on the spectrum. The amount of vertical displacement is proportional to area.
- In methyl acetate (p. 1), the displacement is the same for both peaks, as they both have the same area (3 H each). Thus, we can conclude that there are two different types of proton environments, and since the formula is $C_3H_6O_2$, the molecule must contain two methyl groups.
- The ratios of the peaks give information that is invaluable in the determination of molecular structure; e.*g.* $C_6H_{12}O_2$.



- The peak near 1.5 ppm (peak **b**) is for alkyl H atoms at higher field than the alkyl atoms at 1.9 ppm (peak **a**).
- The areas of the peaks are 67 (**b**) and 23 (a), so the ratio of peaks **b**:**a** are 2.91:1 = 3:1.
- This means that there are three times as many **b** protons.

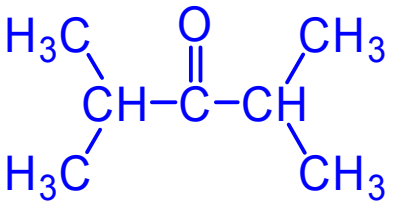
- So what does this mean? The molecular formula tells us that there are 12 H. Thus, peak **b** must correspond to 9 H, and peak **a** to 3 H.

- By combining the NMR data with the molecular formula and the IR spectrum (IR of esters later), we can conclude that the molecule must be *t*-butyl acetate.

- Proton NMR data is often written in a shorthand notation that includes the chemical shift and the number of H atoms in each signal, given in brackets. For *t*-butyl acetate:

  o $C_6H_{12}O_2$ δ 1.95 (3H) and 1.44 (9H)

- Sample question: Propose a possible structure for a ketone of formula $C_7H_{14}O$ that has two signals in its proton NMR with a ratio of 6:1.



C. Signal Splitting

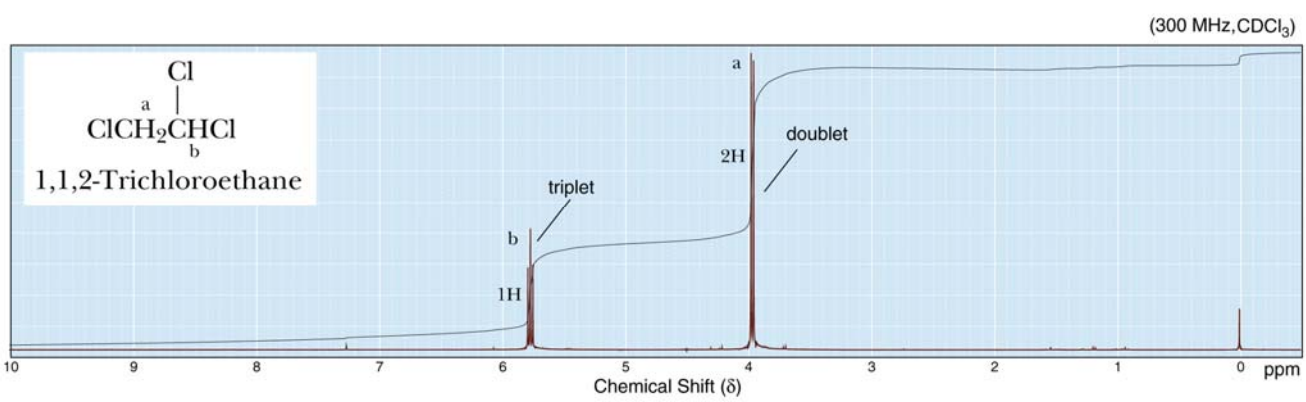
- Proton spectra have another feature that provides important structural information. This is called signal (or spin-spin) splitting. This effect is caused by the effect of a proton's magnetic field on that of another nearby proton.

- Suppose we have a compound where the two H's are non-equivalent. If they did not affect each other, we would get the simple spectrum shown below, with unsplit signals.

- However, in reality, the two spins of H_a perturb the total magnetic field around H_b. When the magnetic moment of H_a is aligned with the applied external field, H_b experiences a slightly higher total field. Similarly, when the magnetic moment of H_a is opposed to the external field, H_b experiences a slightly reduced total field.

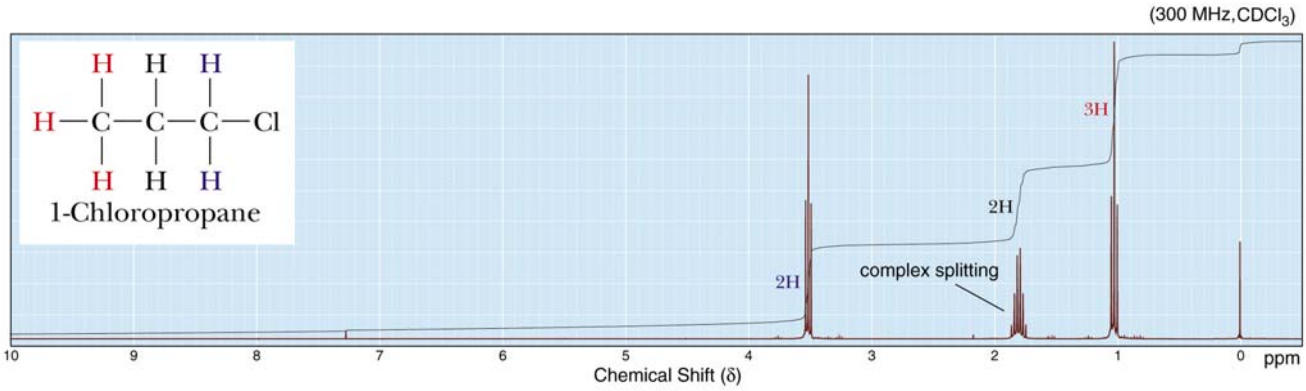
- This means that H_b will absorb radiation of two slightly different energies. So, they appear as two equal peaks in the spectrum. By the same argument, H_b will split the signal for H_a into two peaks.

- This type of signal splitting is normal for all H atoms bonded to adjacent atoms. The effect of *one* H atom on its neighbouring H is to split the NMR signal into two signals, as in the example above.
- We also find that two equivalent H atoms will split a neighbouring H atom into three peaks. Likewise, three equivalent H will split a neighbouring H into 4 peaks.
- General rule: A proton signal with *n* equivalent H atoms on a neighbouring atom is split into *n+1* peaks
- There is also terminology for peak splitting:
  - A signal that appears as a single peak is a singlet
  - A signal that is split into two is called a doublet
  - A signal that is split into three is called a triplet
  - A signal that is split into four is called a quartet
  - A signal that is split into five or more is a multiplet
- It is important to recognize that all peaks in a split signal below to one H atom (or one group of magnetically equivalent H atoms), as shown in 1,1,2-trichloroethane:



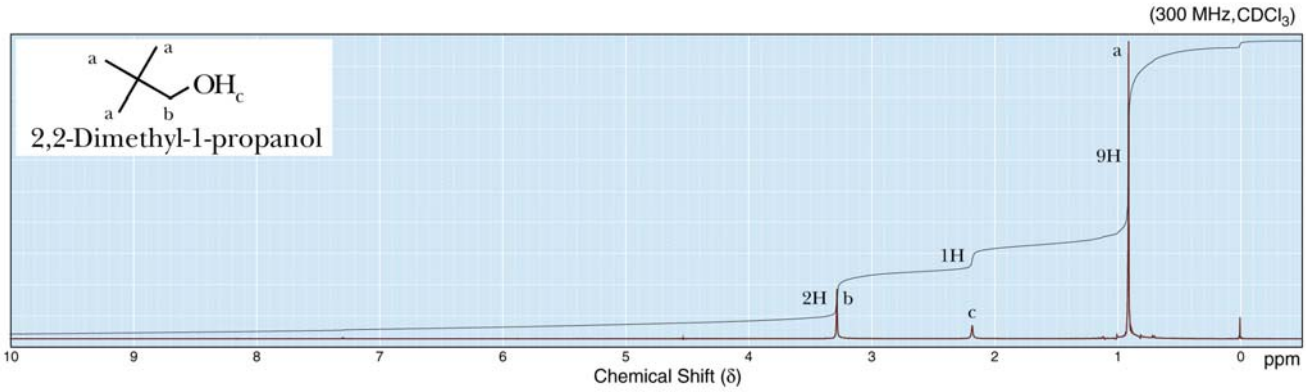
- Two equivalent protons (**a**) appear at 3.96 ppm and they are split into a doublet by a single proton neighbour (**b**)
- The single proton (**b**) is at 5.77 ppm and is split into a triplet by its two neighbouring protons (**a**)
    - This tells us which H atoms are on adjacent atoms, and how many H atoms are on the adjacent atom.

- 1-chloropropane is another example:



- The protons on carbons 1, 2, and 3 respectively appear at 3.52, 1.76, and 1.05, and respectively integrate to 2, 2, 3.
- The three protons on C3 are split into a triplet by the two H's on C2, as are the two protons on C1.
- The two protons on C2 are split into a quartet by the three H on C3, and each signal of the quartet is further split into a triplet by the two H on C1. All peaks of the resulting **complex multiplet** at 1.76 are difficult to resolve.

- Exception: Hydrogen-bonded H-atoms, such as those in amines and alcohols, do not split the signal of adjacent hydrogens, nor are they split themselves. Below, both the hydroxyl H (**c**) and the adjacent CH_2 H's (**b**) are singlets.



Summary

- Proton NMR spectra often reveal so much structural information that a definitive molecular structure can be drawn for a molecule if only its molecular structure and proton NMR spectrum are known (*e.g.* 1-chloropropane).

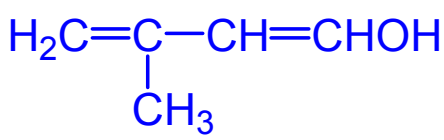
- We only examine the main features of proton NMR in this course, such as chemical shift, signal area, and signal splitting. We don't examine the magnitude of the splitting, the splitting by H atoms on non-adjacent atoms, or spectra that do not rigorously obey the predicted splitting patterns of "first order" spectra. Those interested should consider Chem 3370a/b, a spectroscopy course.

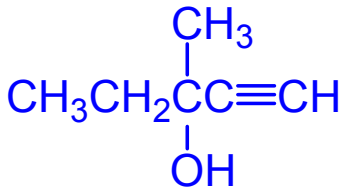
- To enhance your NMR skills, please study sections 12.11 (Interpreting NMR Spectra) and 12.12 (Solving NMR Problems) in your textbook. These two sections apply the basics of proton NMR to functional groups and compounds, and give examples of structure elucidation.

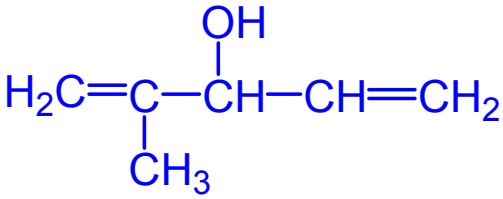
- Summary:
  - Pages covered: 334 – 342, 346 - 354
  - Problems: 8, 11, 13, 15, 18, 21, 30, 35, 35.
  - 2005: 34, 35, 37 2006: 32 – 34
    2007: 32 – 33 2008: 32 – 34

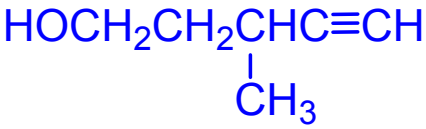
- Example question: What is the structure of the compound $C_6H_{10}O$? It decolourizes a solution of Br_2 in CCl_4. Its IR spectrum has a broad peak at 3500 cm^{-1} and a sharp peak at 3300 cm^{-1}. Its proton NMR spectrum consists of:

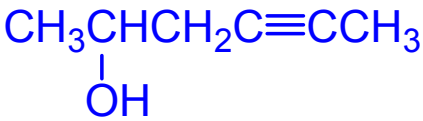
  - δ 3.4 (1H, singlet), 2.4 (1H, singlet), 1.6 (2H, quartet), 1.4 (3H, singlet), 1.0 (3H, triplet)



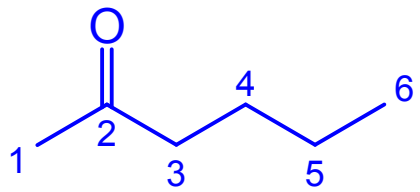








- MCAT: Use the structure to answer the questions that follow.



1. How many peaks appear in its proton NMR spectrum

   5 6 11 12

2. What is true about the peak that is produced by the hydrogens on C1 in the NMR spectrum?
   - The peak integrates as 2 and is split into a doublet
   - The peak integrates as 2 and is split into a triplet
   - The peak integrates as 1 and is split into a triplet
   - The peak integrates as 3 and is a singlet

3. What is true about the peak that is produced by the hydrogens on C3 in the NMR spectrum?
   - The peak integrates as 2 and is split into a doublet
   - The peak integrates as 2 and is split into a triplet
   - The peak integrates as 1 and is split into a triplet
   - The peak integrates as 3 and is a singlet

4. The peak that is farthest upfield in the NMR spectrum is a triplet. To which carbon are the hydrogens responsible for the peak attached?

   1 2 5 6 (furthest from the carbonyl)

5. Which of the following peaks (cm^{-1}) are present in its IR spectrum? 1680 2220 3200 3500