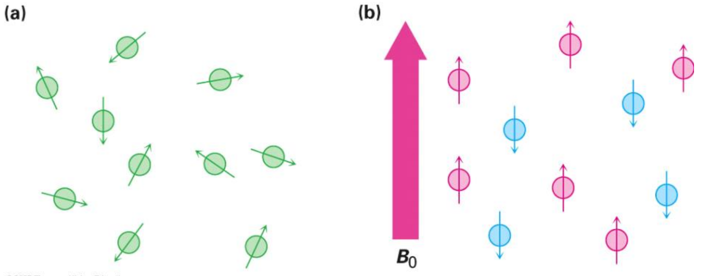
Chapter 13: Nuclear magnetic resonance spectroscopy

<u>NMR</u> is the most valuable spectroscopic technique for organic chemists because it maps the carbon-hydrogen framework of a molecule.

^{1}H and ^{13}C nuclei (and others) align in two directions in a strong magnetic field.



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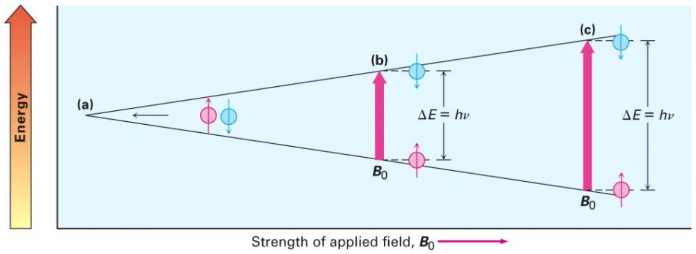
The lower-energy parallel orientation can be flipped to the higher-energy anti-parallel orientation by an applied radio frequency pulse.



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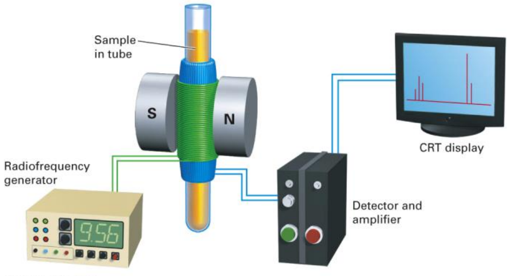
The stronger the external magnetic field, the higher energy the RF pulse must be.

13.2 The nature of NMR absorptions

Not all nuclei require the same amount of RF energy to spin-flip. Their electronic environment determines how strongly the external magnetic field affects them.



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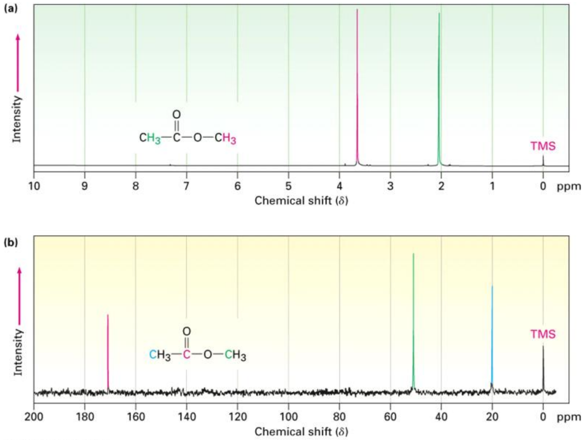
Chemically equivalent nuclei show a single absorption.



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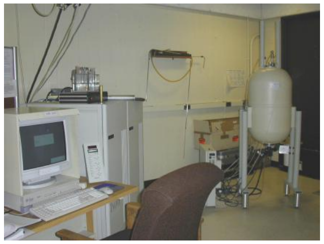
13.3 Chemical shifts

The horizontal axis of an NMR spectrum is called chemical shift (δ) with the unit of ppm.

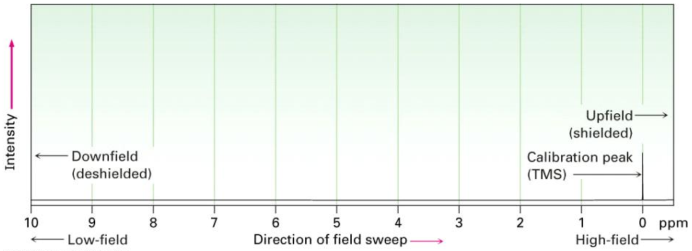
If the protons in a reference peak (usually tetramethyl silane, TMS) go into resonance at 200 MHz, typical organic molecules will have protons that vary by no more than 0.001% of that frequency (or 10 ppm).
Different size NMR spectrometers have different frequencies, so chemical shift is given in ppm so the scale is standard.



300 MHz NMR

900 MHz NMR

Most organic molecules have nuclei more exposed (deshielded) than TMS.



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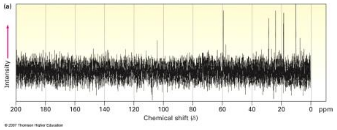
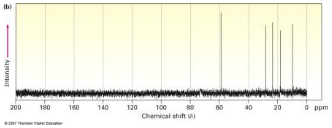
13.4-5 ^{13}C NMR spectroscopy

^{12}C has no magnetic spin, so ^{13}C must be used. It's only 1.1% of all carbon, so many scans must be used to amplify the signal.

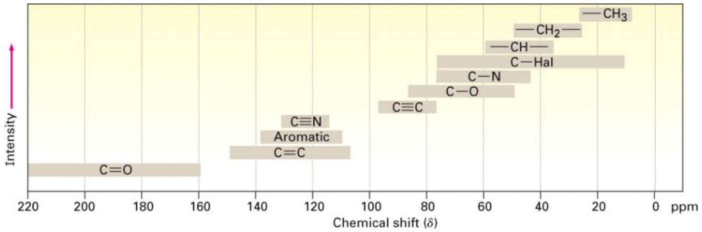


1 scan



200 scans

Carbons can vary up to ~200 ppm from the reference.
Carbons attached to electronegative atoms are the most "deshielded" and will show the highest δ.



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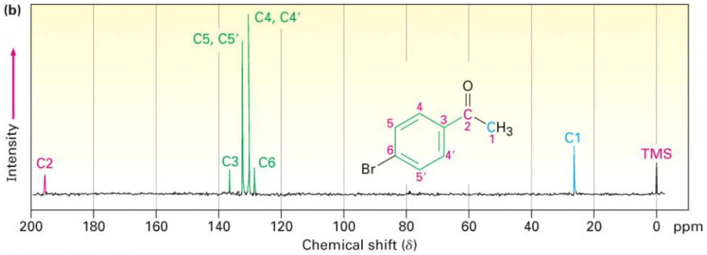

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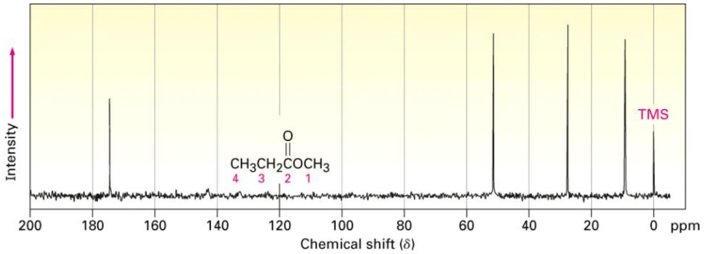
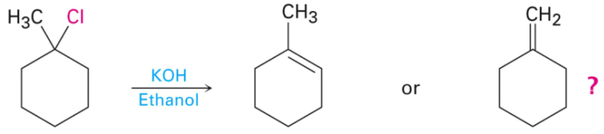
The carbons on either side of the ring are equivalent by symmetry.

13.7 Uses of ^{13}C NMR spectroscopy

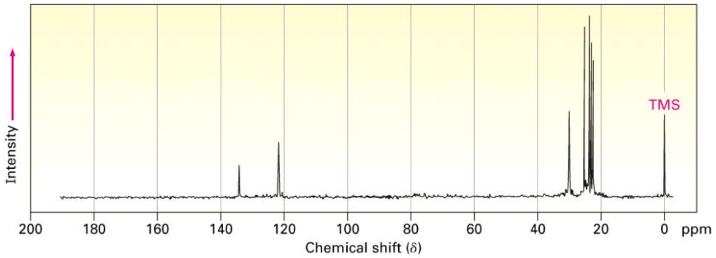


Note the differences in peak height. Hybridization is a factor but typically the intensity of ^{13}C peaks is ignored.

Important chemical insights can come from ^{13}C NMR spectroscopy. Zaitsev's rule can be verified:

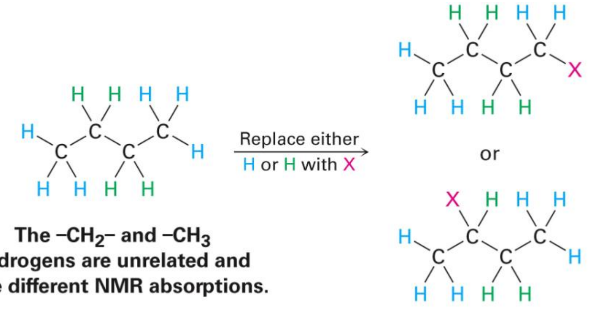


1-Chloro-1-methylcyclohexane **1-Methylcyclohexene** **Methylenecyclohexane**



13.8 ^{1}H NMR spectroscopy and proton equivalence

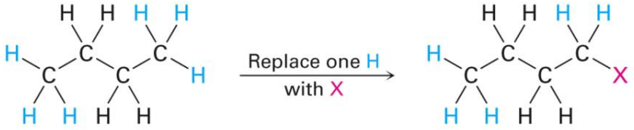
Like ^{13}C nuclei, protons (^{1}H) only show different resonances for chemically distinct protons.



The $-CH_2-$ and $-CH_3$ hydrogens are unrelated and have different NMR absorptions.

The two replacement products are constitutional isomers.

Protons on the same carbon are equivalent (as long as the molecule is achiral) - protons on different carbons can also be equivalent by symmetry.



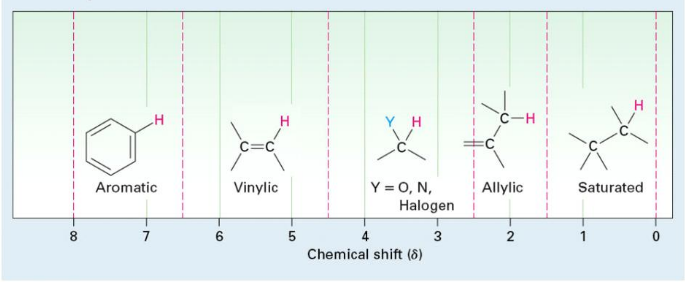
The 6 $-CH_3$ hydrogens are *homotopic* and have the same NMR absorptions.

Only one replacement product is possible.

13.9 Chemical shifts and ^{1}H NMR spectroscopy

Chemical shifts for normal organic protons vary from 0-12 ppm or so. Again, more electron-withdrawing groups shift the protons downfield (to the left).

Table 13.2 Regions of the ^{1}H NMR Spectrum



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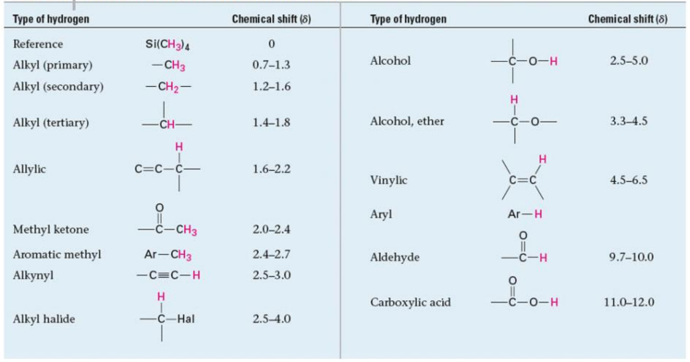
Hydrogens on benzene are deshielded because of a special magnetic effect with the pi electrons in the ring.

Table 13.3 Correlation of ^{1}H Chemical Shift with Environment



Type of hydrogen		Chemical shift (δ)	Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0	Alcohol	—C—O—H	2.5–5.0
Alkyl (primary)	$—CH_3$	0.7–1.3	Alcohol, ether	H—C—O—	3.3–4.5
Alkyl (secondary)	$—CH_2—$	1.2–1.6	Vinylic	C=C—H	4.5–6.5
Alkyl (tertiary)	—CH—	1.4–1.8	Aryl	Ar—H	
Allylic	C=C—C—H	1.6–2.2	Aldehyde	$—C(=O)—H$	9.7–10.0
Methyl ketone	$—C(=O)—CH_3$	2.0–2.4	Carboxylic acid	$—C(=O)—O—H$	11.0–12.0
Aromatic methyl	$Ar—CH_3$	2.4–2.7			
Alkynyl	—C≡C—H	2.5–3.0			
Alkyl halide	H—C—Hal	2.5–4.0			

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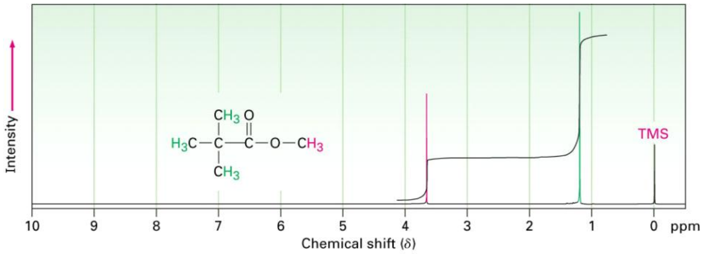
13.10 Integration of ^{1}H NMR absorptions: proton counting

Peak height on ^{1}H NMR is not particularly useful, but **area** under the peak is proportional to the number of protons in that resonance.

This is indicated by an **integration curve** superimposed on the spectrum. The relative height of the "stair steps" is proportional to the ratio of protons in each resonance.



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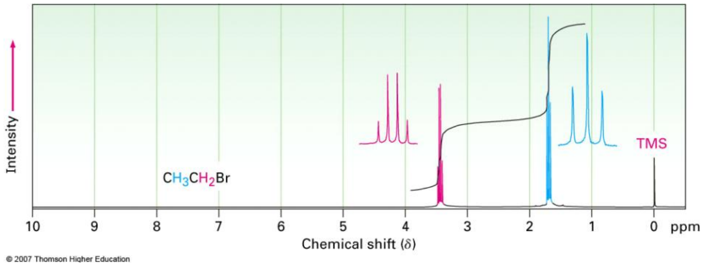
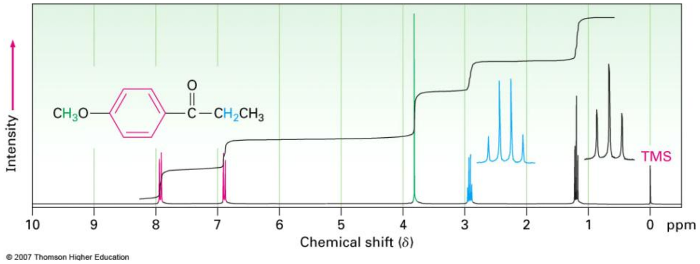
13.11 Spin-spin splitting in ^{1}H NMR spectra

Protons on **neighboring carbons** can have either a positive or negative effect on chemical shift. One neighboring proton will split the resonance you're looking at once, making a doublet.



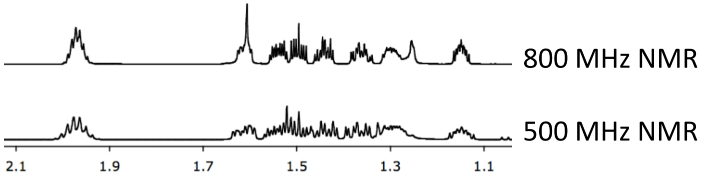
Splitting tree:

***n* + 1 rule**: if a proton has *n* protons on neighboring carbons, its resonance will show *n* + 1 peaks.



13.12 More complex spin-spin splitting patterns

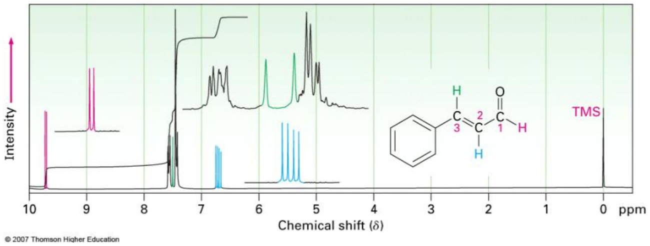
Hydrogens on free-rotating sp^3 carbons will normally split neighboring hydrogens by a 7 Hz **coupling constant** (regardless of the size of the NMR magnet).



Larger (higher-field) magnets will have fewer overlapping peaks as a result!

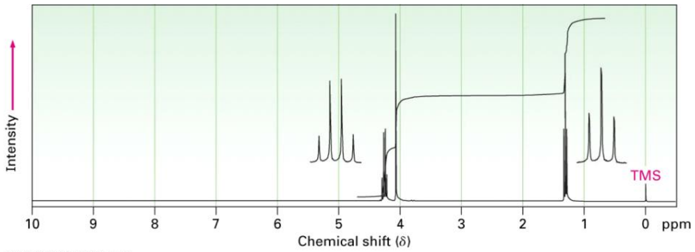
Hydrogens that are at a fixed angle from neighboring hydrogens will have a coupling constant related to that angle.

Hydrogens that are *trans* on a double bond will have a larger coupling constant than hydrogens *cis* on a double bond.



13.13 Uses of ^1H NMR spectroscopy

$C_4H_7O_2Cl$



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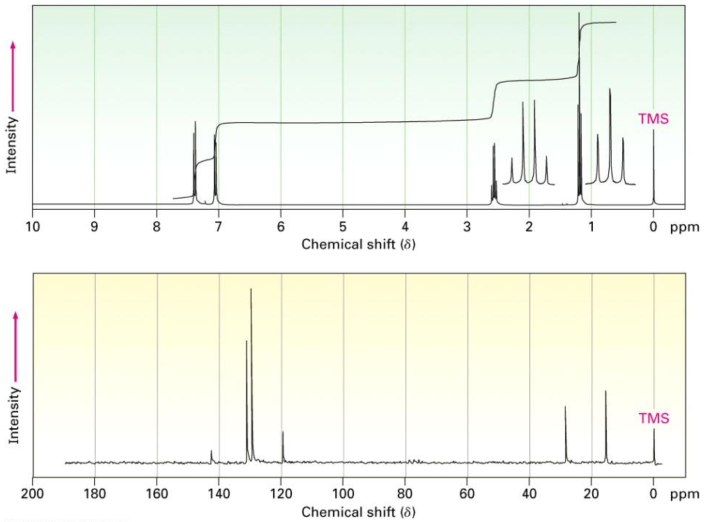
C_8H_9Br



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