

¹³C NMR Spectroscopy

from chapter _____ in the recommended text

A. Introduction

B. Fundamental Physics Of NMR (Nuclear Magnetic Resonance)

Nuclear spin

flipping these spins between aligned and counter-aligned states by applying a radiofrequency low energy range of the electromagnetic spectrum, ie low frequency and high $\frac{1}{2}$, and for ^{12}C the nuclear spin is 0.

high, but that of ^{13}C is low (1.1

averaged over multiple scans to increase both these parameters.

less than those between vibrational states in IR, and less are sensitive to large external magnetic fields zero

larger the energy gap between nuclear spin states.

both these parameters.

are sensitive to the electron density and proximal NMR active nuclei in the same molecule, hence these nuclei in different parts of the molecule flip when different

“shield each other

deshielded relative to

C. Chemical Shifts In General

SiMe₄.

δ on this scale reflects how much less the frequency is for an NMR active nuclei to flip, or resonate,

$$\frac{\text{frequency of } 0 \text{ on scale} - \text{frequency for nucleus}}{\text{frequency of } 0 \text{ on scale}}$$

positive.

deshielded

the operating frequency of the machine

200,000,000 Hz.

200 so on

200, ie 200 Hz.

on a 250 MHz machine, 1 ppm corresponds to 250 Hz in proton NMR spectra

on a 400 MHz machine, 1 ppm corresponds to 400 Hz in proton NMR spectra

on an 800 MHz machine, 10 ppm corresponds to 8000 Hz in proton NMR spectra

25 Hz.

difference of 0.1 ppm.

0.1 ppm.

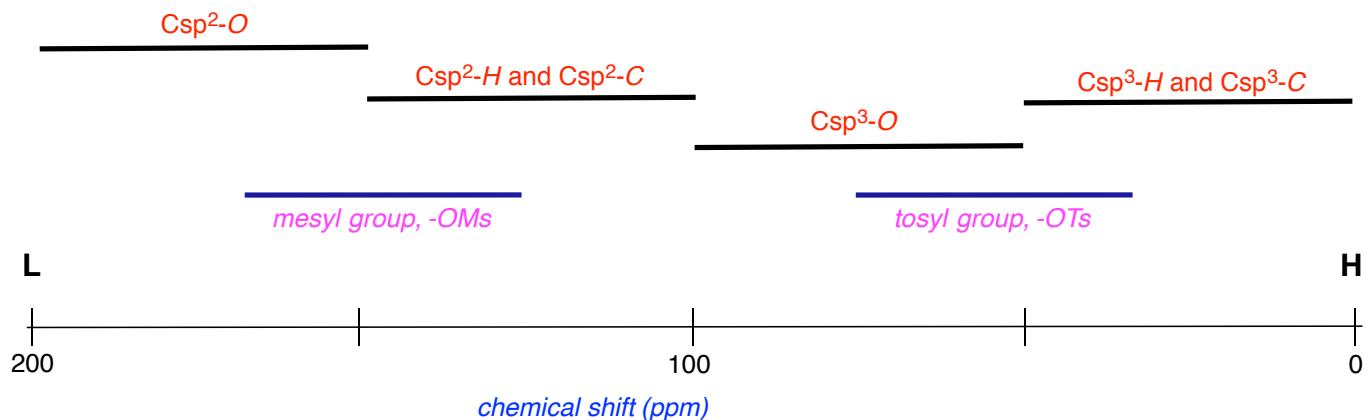
greater on a 60 MHz

greater on a 100 MHz

less as the operating frequency

D. Chemical Shifts In ^{13}C Spectra

upfield region and corresponds to shielded



downfield region and corresponds to deshielded

attract electron density tend to deshield

deshield

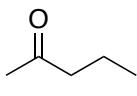
less shielded

inequivalent except

the same chemical shifts, and inequivalent ones usually resonate at different

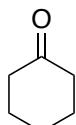
the same as

NOTE FROM KB: it is difficult to be sure about exactly which chemical shift range for some of these carbons, in other words some are borderline. When the book is re-printed I will make the ranges broader.



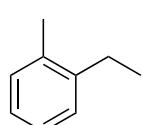
5
inequivalent C

number of resonances (ppm):
 0 - 50 4
 50 - 100 0
 100 - 150 0
 above 150 1



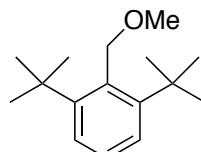
4
inequivalent C

number of resonances (ppm):
 0 - 50 3
 50 - 100 0
 100 - 150 0
 above 150 1



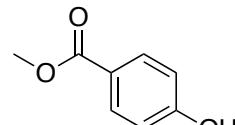
9
inequivalent C

number of resonances (ppm):
 0 - 50 3
 50 - 100 0
 100 - 150 6
 above 150 0



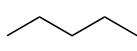
8
inequivalent C

number of resonances (ppm):
 0 - 50 2
 50 - 100 2
 100 - 150 4
 above 150 0



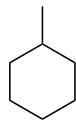
6
inequivalent C

number of resonances (ppm):
 0 - 40 0
 40 - 100 1
 100 - 150 3
 above 150 2



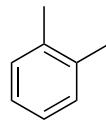
3
inequivalent C

number of resonances (ppm):
 0 - 50 3
 50 - 100 0
 100 - 150 0
 above 150 0



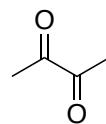
5
inequivalent C

number of resonances (ppm):
 0 - 50 5
 50 - 100 0
 100 - 150 0
 above 150 0



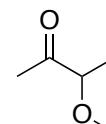
4
inequivalent C

number of resonances (ppm):
 0 - 50 1
 50 - 100 0
 100 - 150 3
 above 150 0



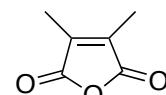
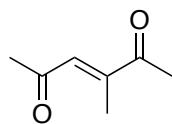
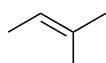
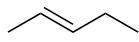
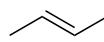
2
inequivalent C

number of resonances (ppm):
 0 - 50 1
 50 - 100 0
 100 - 150 0
 above 150 1



5
inequivalent C

number of resonances (ppm):
 0 - 50 2
 50 - 100 2
 100 - 150 0
 above 150 1



2
inequivalent C

number of resonances (ppm):
 0 - 50 1
 50 - 100 0
 100 - 150 1
 above 150 0

5
inequivalent C

number of resonances (ppm):
 0 - 50 3
 50 - 100 0
 100 - 150 2
 above 150 0

5
inequivalent C

number of resonances (ppm):
 0 - 50 3
 50 - 100 0
 100 - 150 2
 above 150 0

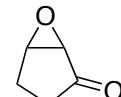
7
inequivalent C

number of resonances (ppm):
 0 - 50 3
 50 - 100 0
 100 - 150 2
 above 150 2

3
inequivalent C

number of resonances (ppm):
 0 - 50 1
 50 - 100 0
 100 - 150 1
 above 150 1

NOTE FROM KB: it is difficult to be sure about exactly which chemical shift range for some of these carbons, in other words some are borderline. When the book is re-printed I will make the ranges broader. HOWEVER the number of inequivalent C have been checked several times. They are right I believe, but sometimes the symmetry of the molecules is hard to see. Look out for planes of symmetry, C2 axes, and diastereotopic groups.



1
inequivalent C

number of resonances (ppm):
0 - 50 1
50 - 100 0
100 - 150 0
above 150 0

3
inequivalent C

number of resonances (ppm):
0 - 50 3
50 - 100 0
100 - 150 0
above 150 0

6
inequivalent C

number of resonances (ppm):
0 - 50 2
50 - 100 0
100 - 150 4
above 150 0

8
inequivalent C

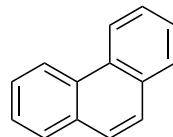
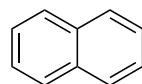
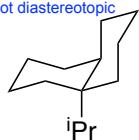
number of resonances (ppm):
0 - 50 4
50 - 100 0
100 - 150 4
above 150 0

5
inequivalent C

number of resonances (ppm):
0 - 40 2
40 - 100 2
100 - 150 0
above 150 1



flipping of cis-decalins
is fast on the 13C NMR
time scale, so iPr Me groups
are not diastereotopic



6
inequivalent C

number of resonances (ppm):
0 - 50 4
50 - 100 2
100 - 150 0
above 150 0

12
inequivalent C

number of resonances (ppm):
0 - 50 9
50 - 100 3
100 - 150 0
above 150 0

8
inequivalent C

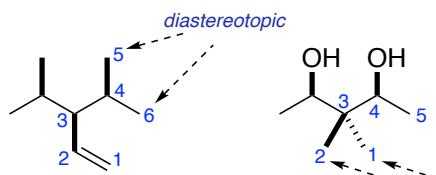
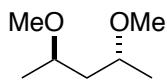
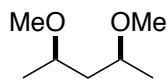
number of resonances (ppm):
0 - 50 8
50 - 100 0
100 - 150 0
above 150 0

3
inequivalent C

number of resonances (ppm):
0 - 50 0
50 - 100 0
100 - 150 3
above 150 0

7
inequivalent C

number of resonances (ppm):
0 - 50 0
50 - 100 0
100 - 150 7
above 150 0



4
inequivalent C

number of resonances (ppm):
0 - 50 2
50 - 100 2
100 - 150 0
above 150 0

4
inequivalent C

number of resonances (ppm):
0 - 50 2
50 - 100 2
100 - 150 0
above 150 0

6
inequivalent C

number of resonances (ppm):
0 - 50 3
50 - 100 0
100 - 150 2
above 150 0

5
inequivalent C

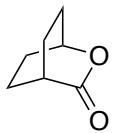
number of resonances (ppm):
0 - 50 3
50 - 100 1
100 - 150 0
above 150 0

4
inequivalent C

number of resonances (ppm):
0 - 50 3
50 - 100 1
100 - 150 0
above 150 0



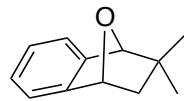
2 inequivalent C
number of resonances (ppm):
0 - 50 2
50 - 100 0
100 - 150 0
above 150 0



5 inequivalent C
number of resonances (ppm):
0 - 50 3
50 - 100 1
100 - 150 0
above 150 1



3 inequivalent C
number of resonances (ppm):
0 - 50 3
50 - 100 0
100 - 150 0
above 150 0



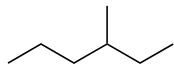
12 inequivalent C
number of resonances (ppm):
0 - 50 4
50 - 100 2
100 - 150 6
above 150 0



5 inequivalent C
number of resonances (ppm):
0 - 50 3
50 - 100 0
100 - 150 2
above 150 0

1 ^{13}C resonances.

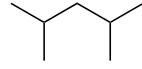
cannot be



7 inequivalent C



4 inequivalent C



3 inequivalent C

E. Coupling In ^{13}C NMR

^{13}CH Spin Systems

The ^1H nucleus is

different to

into two peaks of almost equal intensity; this is called a doublet.

The chemical shift of that carbon is exactly at the center of

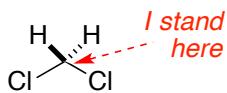
coupling with protons

doublet and a singlet, respectively.

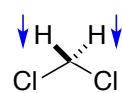
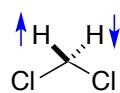
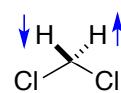
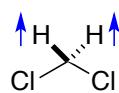
In that experiment it would

$^{13}\text{CH}_2$ Spin Systems

the same



and experience.....



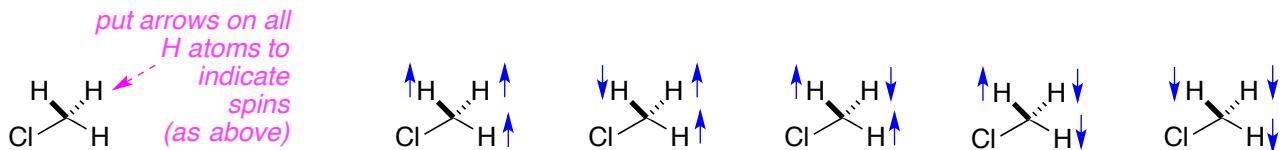
magnetic effect feels same

3 different magentic field strengths influence that ^{13}C , ratio 1:2:1

three different magnetic fields and the relative probability is 1:2:1.
triplet for the carbon and it could

^{13}C Spin Systems

quartet for the carbon and it could



4 different magnetic field strengths influence that ^{13}C , ratio 1:3:3:1

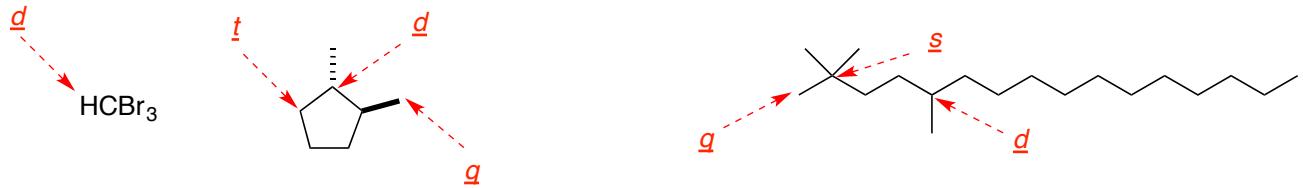
The relative probabilities for finding the spins in a or o states is 1:3:3:1.

n + 1 peaks.
doing the splitting and not those being observed.

follows Pascal's triangle.

rare and can be ignored.

Differentiating CH, CH₂, And CH₃ In ^{13}C Spectra



coupling constant and it is expressed in Hz.
different on machines operating at different field strengths, so they are never

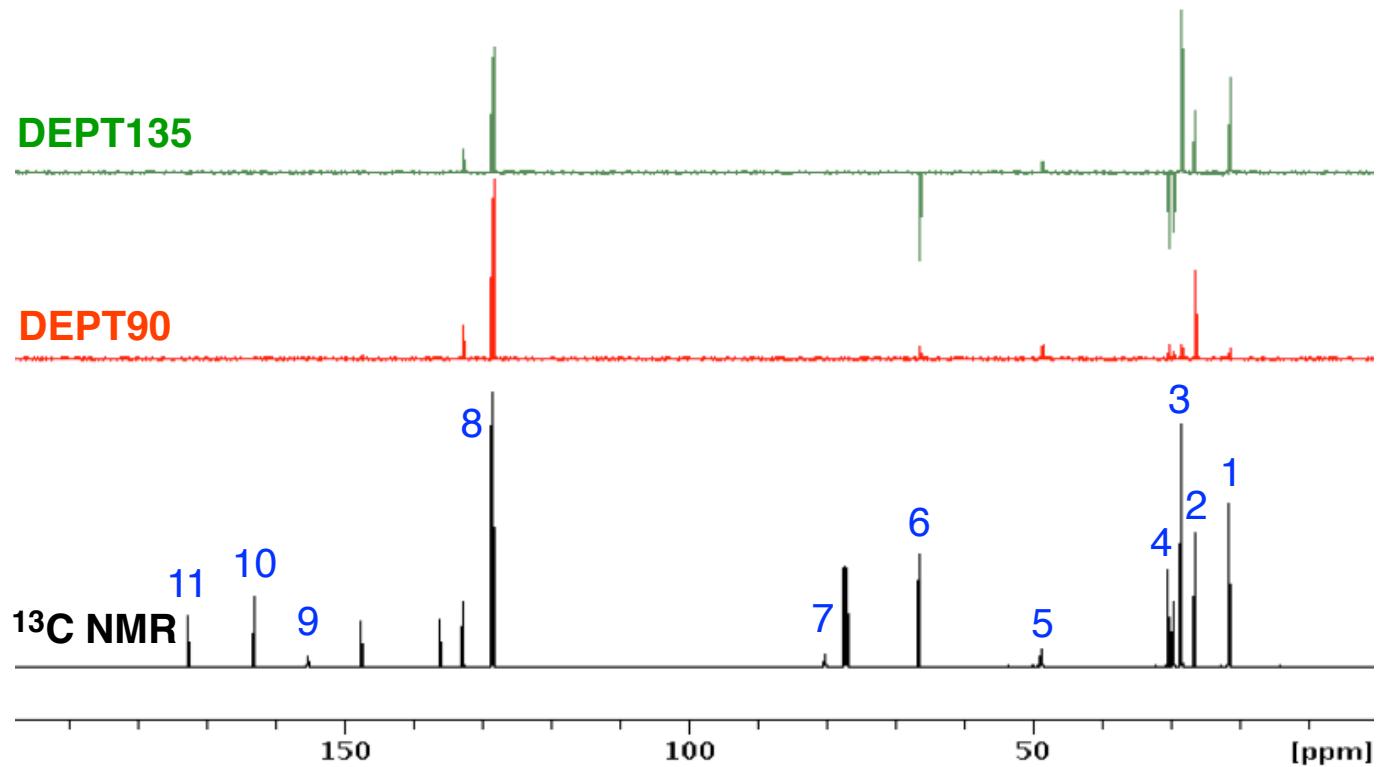
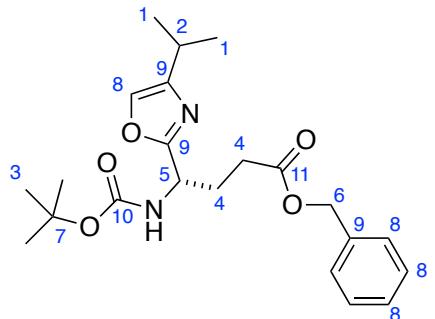
DEPT Spectra To Differentiate Quaternary, Methine-, Methylene-, and Methyl-Carbons
quaternary, do not
positive peaks, and resonances for CH₂ carbons negative.

CH peaks.

can

more

(Some inequivalent carbon atoms are given the same number if they are indistinguishable in the spectra, eg C⁴, C⁸ and C⁹). This will be made clear in the next edition.



nearly always shown.

¹H-NMR signals of the protons attached to them.