

^{13}C NMR Spectroscopy

^1H and ^{13}C NMR compared:

Both give information about the number of **chemically nonequivalent** nuclei (*nonequivalent hydrogens or nonequivalent carbons*)

Both give information about the environment of the nuclei (hybridization state, attached atoms, etc.)

FT-NMR techniques are standard practice for ^{13}C NMR

^1H and ^{13}C NMR compared:

^{13}C requires FT-NMR because the signal for a carbon atom is 10^{-4} times weaker than the signal for a hydrogen atom

A signal for a ^{13}C nucleus is only about 1% as intense as that for ^1H because of the magnetic properties of the nuclei, and

The "natural abundance" level is only 1.1% of all the C atoms in a sample are ^{13}C (most are ^{12}C)

^1H and ^{13}C NMR compared:

^{13}C signals are spread over a much wider range than ^1H signals making it easier to identify and count individual nuclei

Figure #1 shows the ^1H NMR spectrum of 1-chloropentane; Figure #2 shows the ^{13}C spectrum. It is much easier to identify the compound as 1-chloropentane by its ^{13}C spectrum than by its ^1H spectrum.

Figure #1

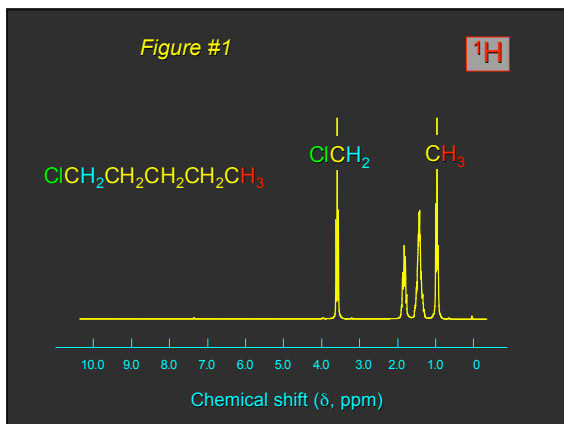
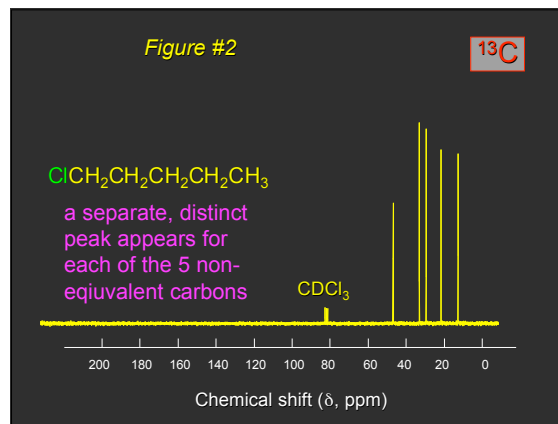


Figure #2

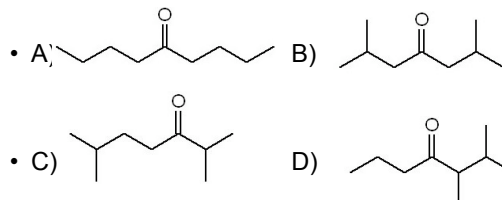


Question

- How many signals would you expect to see in the ^{13}C -NMR spectrum of *m*-chloroanisole?
- A) 4
- B) 5
- C) 6
- D) 7

Question

- Which compound has the most signals in its ^{13}C -NMR spectrum?



^{13}C Chemical Shifts

are measured in ppm (δ)
from the carbons of TMS

^{13}C Chemical Shifts are Most Affected By:

- Electronegativity of groups attached to carbon
- Hybridization state of carbon

Electronegativity has an even greater effect on ^{13}C chemical shifts than it does on ^1H chemical shifts.

Types of Carbons

	Classification	Chemical shift, δ	
		^1H	^{13}C
CH_4		0.2	-2
CH_3CH_3	primary	0.9	8
$\text{CH}_3\text{CH}_2\text{CH}_3$	secondary	1.3	16
$(\text{CH}_3)_3\text{CH}$	tertiary	1.7	25
$(\text{CH}_3)_4\text{C}$	quaternary		28

Replacing H with C (more electronegative) deshields C to which it is attached.

Electronegativity Effects on CH_3

	Chemical shift, δ	
	^1H	^{13}C
CH_4	0.2	-2
CH_3NH_2	2.5	27
CH_3OH	3.4	50
CH_3F	4.3	75

Electronegativity Effects and Chain Length

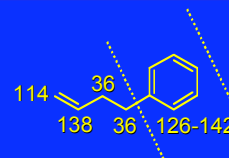


Chemical shift, δ	45	33	29	22	14
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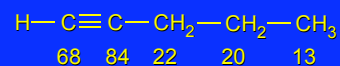
Deshielding effect of Cl decreases as number of bonds between Cl and C increases.

Hybridization Effects

sp^3 hybridized carbon is more shielded than sp^2 .



sp hybridized carbon is more shielded than sp^2 , but less shielded than sp^3 .



Carbonyl Carbons are Especially Deshielded

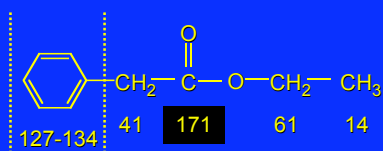


Table 1

Type of carbon	Chemical shift (δ), ppm
RCH_3	0-35
R_2CH_2	15-40
R_3CH	25-50
R_4C	30-40

Table 2



Type of carbon	Chemical shift (δ), ppm	Type of carbon	Chemical shift (δ), ppm
RCH_3	0-35	$\text{RC}\equiv\text{CR}$	65-90
R_2CH_2	15-40	$\text{R}_2\text{C}=\text{CR}_2$	100-150
R_3CH	25-50		110-175
R_4C	30-40		

Table 3

Type of carbon	Chemical shift (δ), ppm
RCH_2Br	20-40
RCH_2Cl	25-50
RCH_2NH_2	35-50
RCH_2OH	50-65
RCH_2OR	50-65

Table 4

Type of carbon	Chemical shift (δ), ppm	Type of carbon	Chemical shift (δ), ppm
RCH_2Br	20-40	$\begin{array}{c} O \\ \\ R-C-O-R \end{array}$	160-185
RCH_2Cl	25-50	$\begin{array}{c} O \\ \\ R-C-R \end{array}$	190-220
RCH_2NH_2	35-50		
RCH_2OH	50-65		
RCH_2OR	50-65		

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C-I$	0-40
$R-CH_3$	8-35	$C-Br$	25-65
$R-CH_2-R$	15-50	$C-Cl$	35-80
$\begin{array}{c} R \\ \\ R-CH-R \end{array}$	20-60	$C-N$	40-60
$\begin{array}{c} R \\ \\ R-C-R \\ \\ R \end{array}$	30-40	$C-O$	50-80
$=C$	65-85	$\begin{array}{c} R \\ \\ -N-C=O \end{array}$	165-175
$-C$	100-150	$\begin{array}{c} R \\ \\ RO-C=O \end{array}$	165-175
	110-170	$\begin{array}{c} R \\ \\ HO-C=O \end{array}$	175-185
		$\begin{array}{c} R \\ \\ H-C=O \end{array}$	190-200
		$\begin{array}{c} R \\ \\ R-C=O \end{array}$	205-220

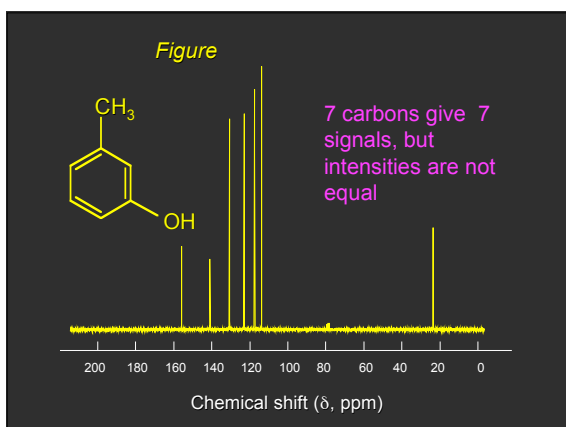
Question

• In the ^{13}C -NMR spectrum 1,2,3,5-tetramethylbenzene, how many peaks are **more shielded** than δ 80 ppm?

- A) 1
- B) 2
- C) 3
- D) 4

^{13}C NMR and Peak Intensities

Pulse-FT NMR distorts intensities of signals. Therefore, peak heights and areas can be deceptive.



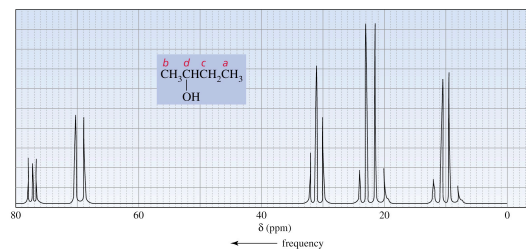
$^{13}C-H$ Coupling

Peaks in a ^{13}C NMR spectrum

^{13}C — ^{13}C splitting is not seen because the probability of two ^{13}C nuclei being in the same molecule is very small.

^{13}C — ^1H splitting occurs but is not seen when measured under conditions that suppress this splitting (*broadband decoupling*).

Proton-Coupled ^{13}C NMR of 2-Butanol

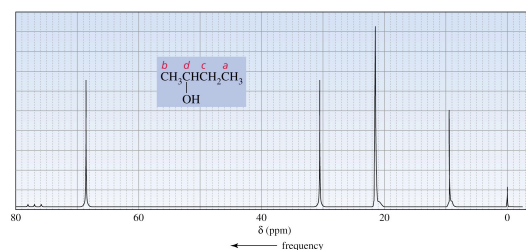


Question

- Which compound has four signals in its ^{13}C -NMR spectrum (^{13}C - ^1H coupled): a singlet, a doublet, a triplet, and a quartet.

- A) HOCH2CH2CH2COOH B) HOOCCH2CH2COOH
- C) CH3CH2CH(OH)COOH D) CH3C(=O)CH2COOH

Proton-Decoupled ^{13}C NMR of 2-Butanol



Using DEPT to Count the Hydrogens
Attached to ^{13}C

Distortionless Enhancement
of Polarization Transfer
(De-coupling)

Measuring a ^{13}C NMR spectrum involves

- Equilibration of the nuclei between the lower and higher spin states under the influence of a magnetic field
- Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state
- Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restored
- Mathematical manipulation (Fourier transform) of the data to plot a spectrum

Measuring a ^{13}C NMR spectrum involves

Steps 2 and 3 can be repeated hundreds of times to enhance the signal-noise ratio

2. Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state
3. Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restored

Measuring a ^{13}C NMR spectrum involves

In DEPT, a second transmitter irradiates ^1H during the sequence, which affects the appearance of the ^{13}C spectrum.

- some ^{13}C signals stay the same
- some ^{13}C signals disappear
- some ^{13}C signals are inverted

Figure #3

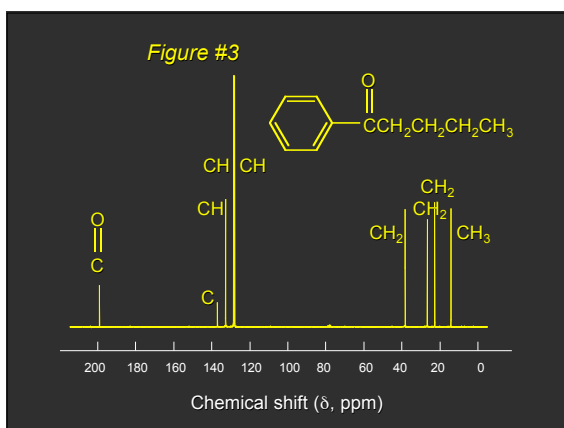


Figure #4

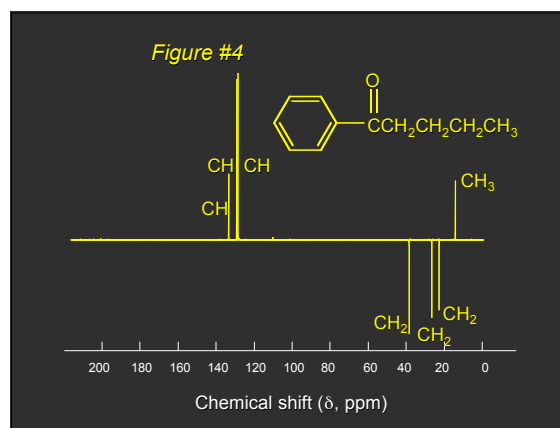
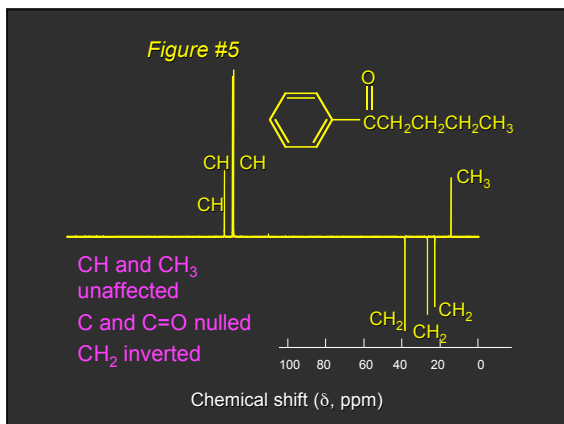
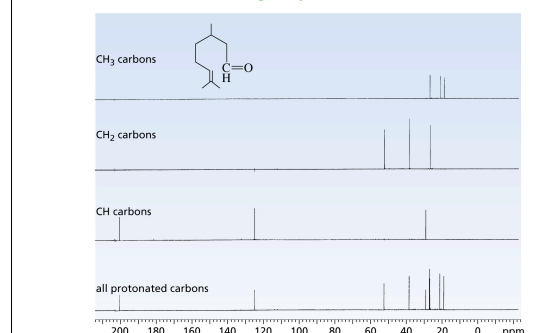


Figure #5



DEPT ^{13}C NMR distinguish among CH₃, CH₂, and CH groups



Question

- Which isomer of C_6H_{14} is consistent with the following ^{13}C -NMR spectrum data? δ 11.1
- (CH_3); δ 18.4 (CH_3); δ 29.1 (CH_2); δ 36.4 (CH)
- A) *n*-hexane
- B) 2,3-dimethylbutane
- C) 2-methylpentane
- D) 3-methylpentane

Question

- Identify the $C_4H_{10}O$ isomer on the basis of its ^{13}C -NMR spectrum data: δ 31.2 (CH_3 , 3C); δ 68.9 (C, 1C)
- A) 2-butanol
- B) 2-methyl-2-propanol
- C) 1-butanol
- D) $CH_3CH_2-O-CH_2CH_3$

2D NMR Methods:

COSY: Carbon Hydrogen Correlation Spectroscopy
HETCOR: Heteronuclear Chemical Shift Correlation
NOESY: Nuclear Overhauser Effects Spectroscopy
TROSY: Translation Relaxation Optimized Spectroscopy

2D NMR: COSY AND HETCOR

2D NMR Terminology

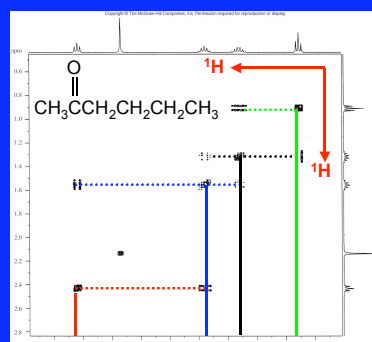
1D NMR = 1 frequency axis
2D NMR = 2 frequency axes

COSY = Correlated Spectroscopy

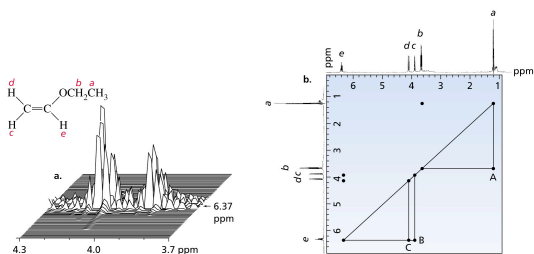
1H - 1H COSY provides connectivity information by allowing one to identify spin-coupled protons.

x,y-coordinates of cross peaks are spin-coupled protons

1H - 1H COSY

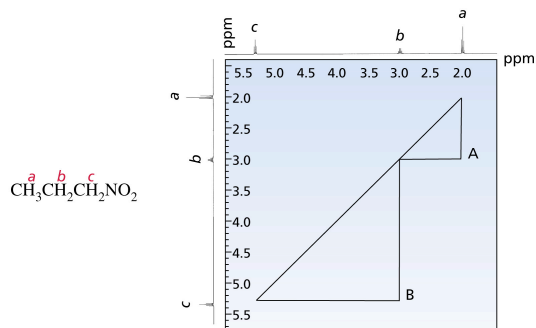


The COSY spectrum identifies protons that are coupled
 COSY: Carbon Hydrogen Correlation Spectroscopy



Cross peaks indicate pairs of protons that are coupled

COSY Spectrum of 1-Nitropropane

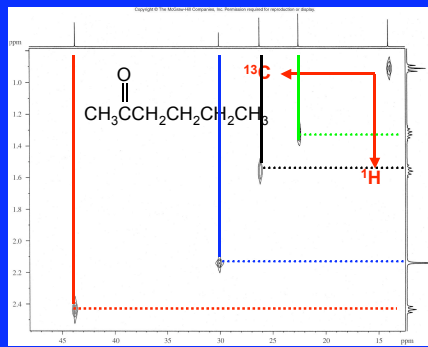


HETCOR

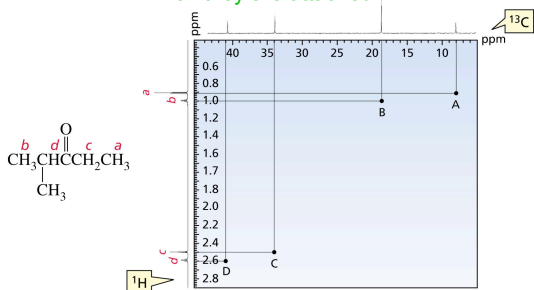
^1H and ^{13}C spectra plotted separately on two frequency axes.

Coordinates of cross peak connect signal of carbon to protons that are bonded to it.

^1H - ^{13}C HETCOR



The HETCOR spectrum of 2-methyl-3-pentanone indicates coupling between protons and the carbon to which they are attached



HETCOR: Heteronuclear Chemical Shift Correlation

Other Current 2D-NMR Methods

- NOESY: Nuclear Overhauser Effects Spectroscopy
- TROSY: Translation Relaxation Optimized Spectroscopy