

## $^{13}\text{C}$ NMR

The  $^{13}\text{C}$  NMR is generated in the same fundamental way as proton NMR spectrum. Only 1.1 % of naturally occurring carbon is  $^{13}\text{C}$  and actually an advantage because of less coupling.

**Requirement for NMR:** Spin quantum # (I)  $\neq 0$  Meaning  $\rightarrow$  must be an odd number and/or neutrons. Ex.  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , etc... (“Thinkbook”)

How do we find this? Look at the atomic number.

The  $^{13}\text{C}$  NMR is **directly** about the carbon skeleton not just the proton attached to it.

- The **number of signals** tell us how many different carbons or set of equivalent carbons
- The **splitting of a signal** tells us how many hydrogens are attached to each carbon. (N+1 rule)
- The **chemical shift** tells us the hybridization ( $\text{sp}^3$ ,  $\text{sp}^2$ ,  $\text{sp}$ ) of each carbon.
- Integration: Not useful for  $^{13}\text{C}$  NMR

**Proton-coupled spectrum** shows splitting of the carbon signal only by protons attached to *that carbon itself*.

$^{13}\text{C}$ -H coupling not  $^{13}\text{C}$ - $^{13}\text{C}$ -H or not  $^{13}\text{C}$ - $^{13}\text{C}$ - $^{13}\text{C}$ -H or not  $^{12}\text{C}$ - $^{13}\text{C}$   
coupling occurs but very low due to low abundance 1.1 % x 1.11% (“Thinkbook”)      No coupling  $^{12}\text{C}$  I=0 (“Thinkbook”)

Thus, for each carbon the multiplicity of the signal depends upon how many protons are attached to it.

**Note:** Due to low natural abundance,  $^{13}\text{C}$  NMR spectra do not ordinarily show carbon-carbon splitting two  $^{13}\text{C}$  being next to other is 1.1 % x 1.1% = 0.012 % (because  $^{12}\text{C}$  does not have a magnetic moment, it cannot split the signal of an adjacent  $^{13}\text{C}$ ), and are thus enormously simplified. (“Thinkbook”)

**Proton-Decoupled Spectrum** shows no splitting at all; it consists of a set of single peaks, one for each carbon or each set of equivalent carbons in a molecule. Even for very complicated molecules, such a spectrum is amazingly simple (because overlapping multiplets very difficult to interpret)-most commonly run spectrum for structural analysis; and will list the multiplicity of the peaks in the upper left-hand corner. (*Bruice*)

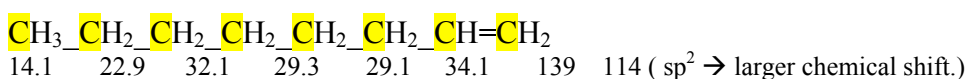
**Chemical Shift** in  $^{13}\text{C}$  NMR spectrum arises in the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied fields strength.

- ❖ Electronegative atoms and pi bonds cause downfield shifts (“Thinkbook”)
- ❖  $^{13}\text{C}$  chemical shift range 0-250 ppm (“Thinkbook”)

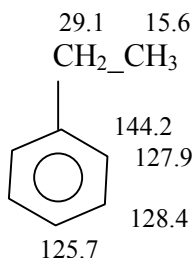
In  $^{13}\text{C}$  NMR spectrum, the more electronegative group bonded to carbon atom  $\rightarrow$  deshielding increases. This table demonstrates this effect.

	I	Br	Cl	F
Electronegativity (Pauling Scale)	2.5	2.8	3.0	4.0
Sp <sup>3</sup> hybrid carbon	$\text{CH}_3\text{I}$	$\text{CH}_3\text{Br}$	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{F}$
Chemical shift (ppm)	9.6	25.6	49.9	71.6

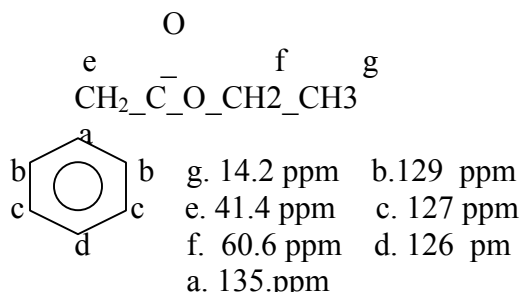
How many signals are in the  $^{13}\text{C}$  NMR spectrum?



Eight signals,  
no equivalent carbons



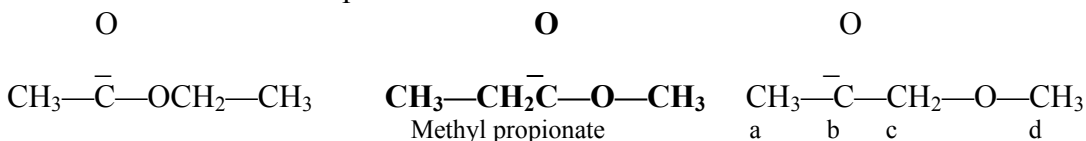
Equivalent carbons  
On benzene ring (6 signals)



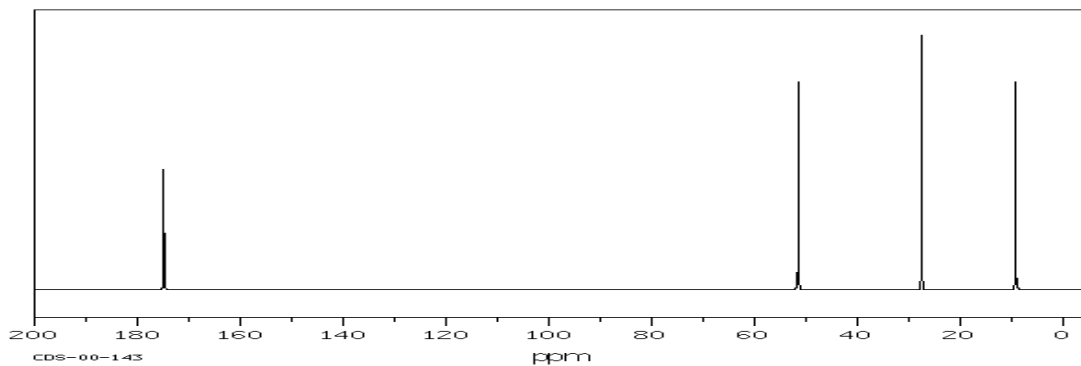
Note: there are two methyl groups and one corresponding to -CH<sub>2</sub> downfield (60.6 ppm) is attached to O cause deshielded  
Benzyl CH<sub>2</sub> (41.1 ppm). Aromatic ring carbons have resonance over range from 126 ppm to 135 ppm.

Determine the structure from this formula  $\text{C}_4\text{H}_8\text{O}_2$  in  $^{13}\text{C}$  spectrum  $\rightarrow$  179.9 ppm (triplet) 51.5 ppm (quartet), 27.5 ppm (triplet) and 9.2 ppm (quartet) ('Thinkbook PP#12')  
179.9 ppm corresponding to ester or ketone carbonyl group; 51.5 ppm is downfield must be close to carbonyl or oxygen (OCH<sub>3</sub>); 27.5 ppm (CH<sub>2</sub>) and 9.2 ppm (quartet) -CH<sub>3</sub> group further away from carbonyl group in upfield region.

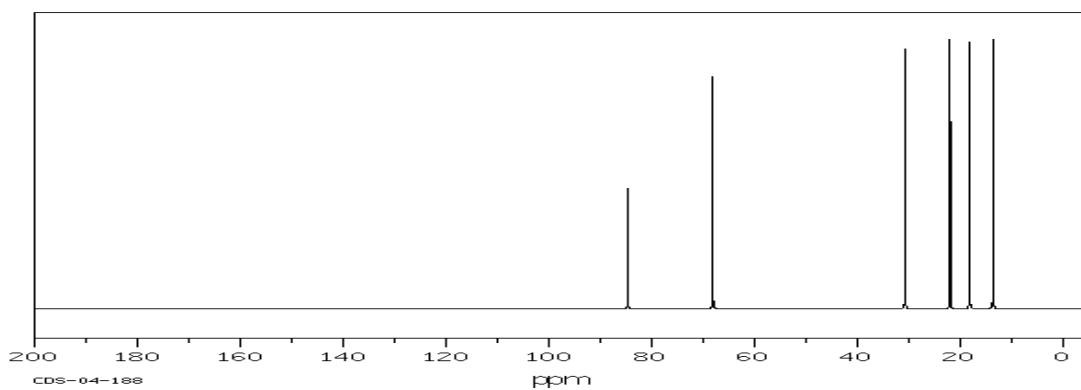
These are three structures possibilities:



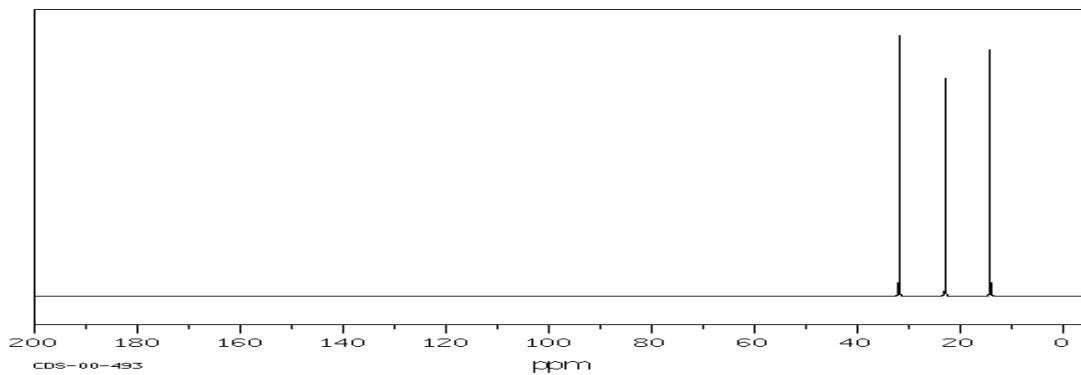
Note: b. this C must downfield and probably over 200 ppm.



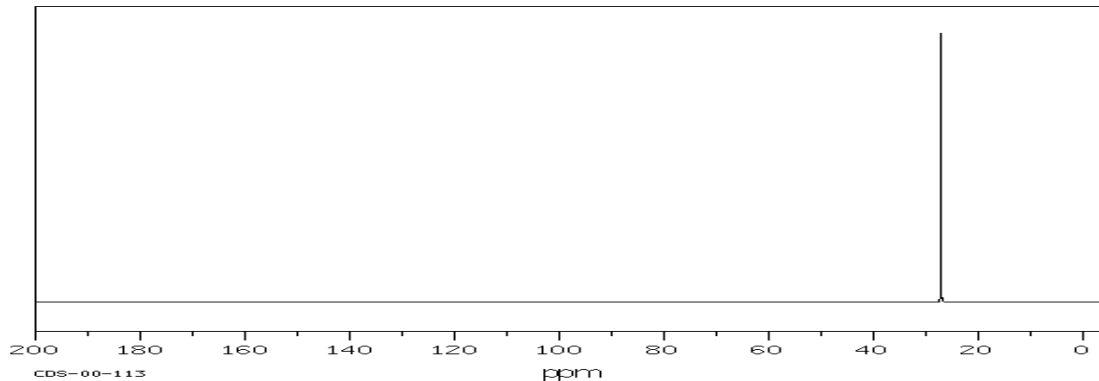
Actual structure = Methyl Propionate ( $^{13}\text{C}$  spectrum above)



$\text{CH}_3$   $\text{CH}_2$   $\text{CH}_2$   $\text{CH}_2$   $\text{C}$   $\text{CH}$   
 13.7 22.1 30.9 18.3 84.5 68.4  
 Six signals (no equivalent carbons)



$\text{CH}_3$   $\text{CH}_2$   $\text{CH}_2$   $\text{CH}_2$   $\text{CH}_2$   $\text{CH}_3$  (note: there are **six** carbons but  $^{13}\text{C}$   
 a a b b c c NMR showed only 3 signals  
 a. 14.16ppm b. 31.87 ppm c. 22.89 ppm due to molecular symmetry)



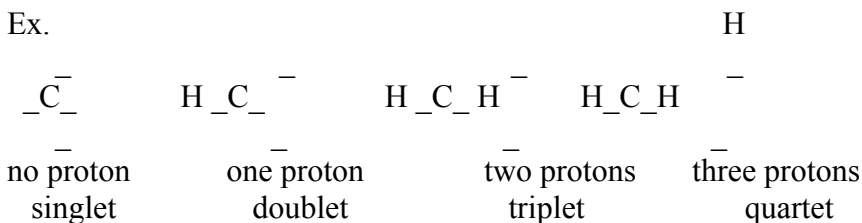
**Cyclohexane** has **one** signal because all carbons on the ring are equivalent carbons

**Note:** Enantiomers and resonance contributors have identical spectra but diastereomers spectra are NOT identical.

### Typical $^{13}\text{C}$ NMR Chemical Shift ranges

ppm	Hybridization	Kinds of compounds
0-70	$\text{Sp}^3$	Alkane ( $\text{CH}_3$ )
70-100	$\text{Sp}^3$ and sp	C-O and C-N
100-160	$\text{Sp}^2$	Aromatic C and C=C
160-210	$\text{Sp}^2$	Aldehydes and ketone carbonyl ( $\text{C}=\text{O}$ )

**Splitting Pattern** ( $N+1$  rule): for each carbon the multiplicity of the signal depends upon how many protons are attached to it.



2D- NMR: Interaction of nuclear spins plotted in two dimensions.

Correlation Spectroscopy (COSY)

- ❖ Two axes correspond to the single isotope (*Thinkbook*)
- ❖ The interaction indicates with H's are coupled  $\rightarrow$  gives better understanding of structure. (*Thinkbook*)

### **Heteronuclear Multiple-Quantum Coherence (HMQC)**

- ❖ 2 axes correspond to 2 different isotopes (usually  $^{13}\text{C}$  and  $^1\text{H}$ )
- ❖ Interaction indicates H's coupling to nuclei other than H

### **Magnetic Resonance Imaging (MRI)**

- ❖  $^1\text{H}$  NMR spectroscopy has been applied to diagnostic medicine.
- ❖ The relaxation times of hydrogen atoms in different environments (ex. brain vs. bone)
- ❖ The rate of relaxation is related to the extent of binding of water to the surface of biological molecules.

*Note: These  $^{13}\text{C}$  spectra obtained from National Institute of Advanced Science and Technology (AIST) website:<http://www.aist.go.jp/>*