

¹³C-NMR spectroscopy

Proton magnetic resonance HNMR is the most type of NMR, but it is also possible to observe other nuclei which have ($I \neq 0$). The nuclei of C^{13} has spin quantum number $I=1/2$, the same as proton, so that when placed in magnetic field, two possible orientations with respect to the field one of lower energy and one of higher energy. Absorption of energy at the resonance frequency causes nuclei in the lower energy level transition to the higher energy level. There are significant difference between a ^{13}C -NMR and 1H -NMR

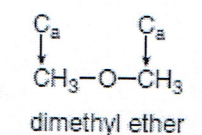
- 1- 1H is the major isotope of hydrogen (99.985% natural abundance), while ^{13}C is only a minor isotope (1.1%) HNMR is quantitative:
- 2- the area under the peak tells us the number of hydrogen nuclei, while ^{13}C NMR may give strong or weak peaks from the same number of ^{13}C nuclei
- 3- Protons interact magnetically ('couple') to reveal the connectivity of the structure, while ^{13}C is too rare for coupling between ^{13}C nuclei to be seen
- 4- 1H NMR shifts give a more reliable indication of the local chemistry than that given by ^{13}C spectra
- 5- ^{13}C -NMR have great range in chemical shift ≈ 0 -250 ppm compared to 0-10 ppm for 1H so it is possible to know exactly how many nonequivalent carbon there.

The important of ^{13}C -NMR spectrum in compound identification
there are three important things taken from ^{13}C -NMR spectra it will be used to identification of the compounds

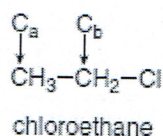
1- The number of signals

The number of signals in ^{13}C -NMR spectroscopy refer to the number of different carbon in the molecule. equivalent carbons are carbons that are in the same environment, and they must be identical in every way. Therefore, we can determine how many sets of equivalent carbons there are in a molecule by looking at the number of signals in its ^{13}C -NMR spectrum. There for bromoethane (CH_3CH_2Br) with two nonequivalent C's gives two ^{13}C NMR signals and 1-bromopropane ($CH_3CH_2CH_2Br$) with three nonequivalent C's gives three signals. Also the ^{13}C NMR spectra of dimethyl ether, chloroethane, and methyl acetate exhibit one,

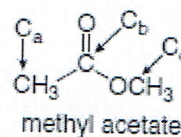
two, and three lines, respectively, because these compounds contain one, two, and three different types of carbon atoms.



1 ^{13}C NMR signal

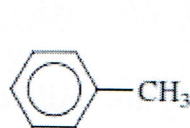


2 ^{13}C NMR signals

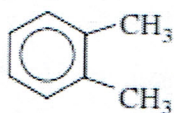


3 ^{13}C NMR signals

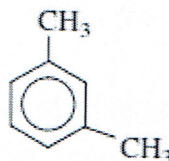
Ex : how many signals would you expect for the following compounds



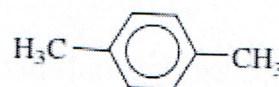
5 signals



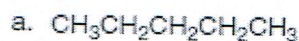
4 signals



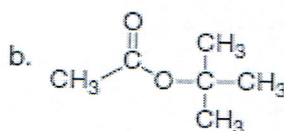
5 signals



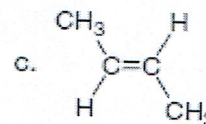
3 signals



3 types of C's
3 ^{13}C NMR signals



4 types of C's
4 ^{13}C NMR signals



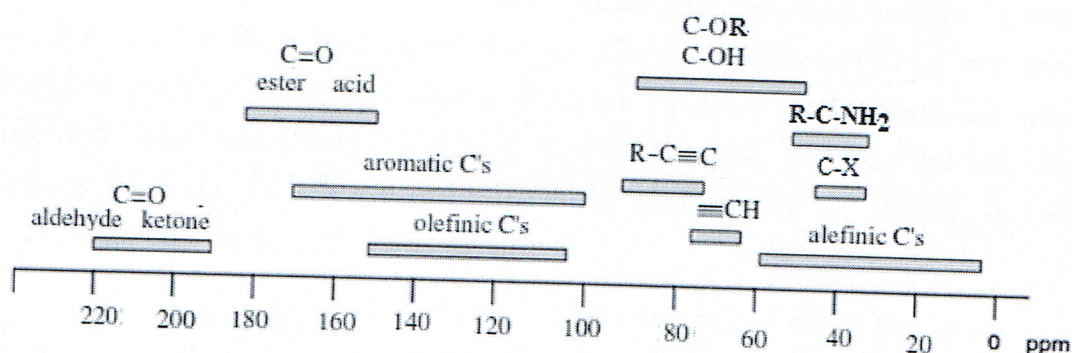
2 types of C's
2 ^{13}C NMR signals

2- ^{13}C -NMR position of signals

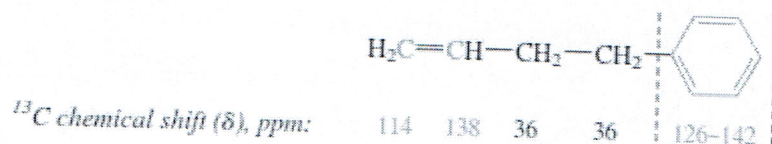
The positions of the signals in an ^{13}C -NMR spectrum give information about the kind of carbons and their chemical shift. Just as chemical shifts in ^1H NMR are measured relative to the protons of TMS, chemical shifts in ^{13}C NMR are measured relative to the carbons of tetramethylsilane TMS as the reference signal at 0 ppm. Also the chemical shifts of carbon atoms in ^{13}C NMR depend on the same effects as the chemical shifts of protons in ^1H NMR:

- The sp^3 hybridized C atoms of alkyl groups are shielded and absorb upfield.
- Electronegative elements like halogen, nitrogen, and oxygen shift absorptions downfield.
- The sp^2 hybridized C atoms of alkenes and benzene rings absorb downfield.
- Carbonyl carbons are highly deshielded, and absorb farther downfield than other carbon types.

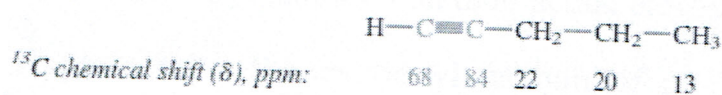
The following chart lists typical chemical-shift ranges for some representative types of carbon atoms.



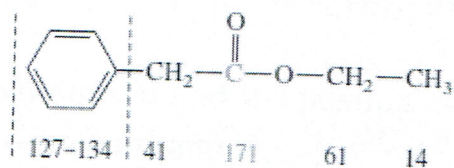
Hybridization Effects. Here again, the effects are similar to those seen in H NMR. As illustrated by 4-phenyl-1-butene, sp^3 -hybridized carbons are more shielded than sp^2 -hybridized ones.



the sp^2 -hybridized carbons, C-1 is the most shielded because it is bonded to only one other carbon. The least shielded carbon is the ring carbon to which the side chain is attached. It is the only sp^2 -hybridized carbon connected to three others. Acetylenes are anomalous in ^{13}C , as in H NMR. sp -Hybridized carbons are less shielded than sp^3 -hybridized ones, but more shielded than sp^2 -hybridized ones.



Electronegativity and hybridization effects combine to make the carbon of a carbonyl group especially deshielded. Normally, the carbon of $C=O$ is the least shielded one in a ^{13}C NMR spectrum.



Electronegativity Effects. Electronegative substituents affect ^{13}C chemical shifts in the same way as they affect ^1H chemical shifts, by withdrawing electrons. For ^1H NMR, recall that because carbon is more electronegative than hydrogen, the protons in methane (CH_4) are more shielded than primary hydrogens (RCH_3), primary hydrogens are more shielded than secondary (R_2CH_2), and secondary more shielded than tertiary (R_3CH). The same holds true for carbons in ^{13}C NMR, but the effects can be 10–20 times greater.

(δ), ppm:	$(\text{CH}_3)_3\text{CH}$ Tertiary	$\text{CH}_3\text{CH}_2\text{CH}_3$ Secondary	CH_3CH_3 Primary
H	1.7	1.3	0.9
C	25	16	8

The shielding was increase by increasing the distance with electronegative atom.

	Cl	—CH ₂ —	CH ₂ —	CH ₂ —	CH ₂ —	CH ₃
(δ), ppm:	45	33	29	22	14	

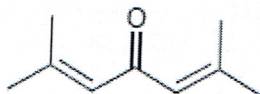
different functional groups affect the chemical shifts of C atoms compare with δ values for unsubstituted compounds. This depends on the electronegativity of the atom of that functional group directly bonded to the C skeleton. The effects of OH or OR are greater than those of NH, NHR, and NR_2 , while they all have greater effects than CH_3 , consistent with the order of relative electronegativities $\text{O} > \text{N} > \text{C}$, and the effect of a halogen on δ values decreases in the electronegativity order $\text{F} > \text{Cl} > \text{Br} > \text{I}$, that based on their actual electronegativity values.

Ex: Explain why the carbonyl carbon of an aldehyde or ketone absorbs farther downfield than the carbonyl carbon of an ester in a ^{13}C NMR spectrum.

Ex: Which of the indicated carbon atoms in each molecule absorbs farther downfield?

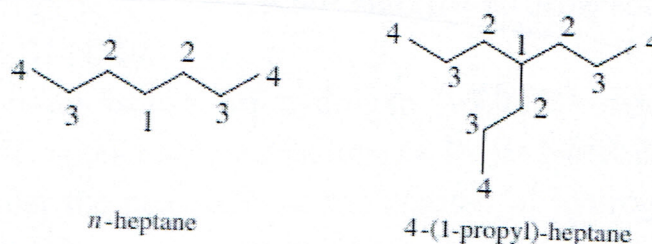
- a. $\underline{\text{CH}_3}\text{CH}_2\text{OCH}_2\text{CH}_3$ b. $\text{Br}\underline{\text{CH}_2}\underline{\text{CH}}\text{Br}_2$ c. $\text{H}\underline{\text{C}}\text{OO}\underline{\text{C}}\text{H}_3$
 d. $\underline{\text{CH}_3}\text{CH}=\underline{\text{CH}_2}$

Ex: predict the number signals and the position of signals in ^{13}C NMR spectrum of the following compound



3-The intensity of ^{13}C -NMR signals

The intensity of ^{13}C -NMR signals are not directly proportional to the number of carbons responsible for those signals. Thus both *n*-heptane and 4-(1-propyl) heptane have 4 signals in there ^{13}C -NMR spectra, but it is not possible to determine if the ratio of different carbon types is 1:2:2:2 as expected for *n*-heptane or 1:3:3:3 expected for branched compound.



4- ^{13}C -NMR splitting of the signals (multiplicity)

the number of splitting in the signals in ^{13}C -NMR spectra refer to the number of protons that is directly attached to carbon. Thus quaternary carbons (R_4C) are singlets, methine carbons (R_3CH) are doublets, methylene carbons (R_2CH_2) are triplets, and methyl carbons (RCH_3) are quartets.

For example the ^{13}C -NMR spectrum of 1,2-epoxy-5-hexene has 6 signals since there are 6 nonequivalent carbons. Olefinic carbons (≈ 115 and 138 ppm), epoxide carbons (≈ 47 and 52 ppm), methylene carbons (≈ 30 and 32 ppm). The multiplicity of these signals shown in the following figure below, one of olefinic carbon is doublet and the other is triplet because there are 1H and 2H directly attached to these carbon atoms respectively, same things happen with each epoxide carbon atoms, both methylene carbon atoms are triplets because there are 2 H directly attached.

