**13 C-NMR spectroscopy**

Proton magnetic resonance HNMR is the most type of NMR, but it is also possible to observe other nuclei which have ( I ≠0 ) .The nuclei of C13 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 different between a 13C-NMR and 1H-NMR

**1-** 1H is the major isotope of hydrogen (99.985% natural abundance), while 13C is only a minor isotope (1.1%)H NMR is quantitative:

**2-** the area under the peak tells us the number of hydrogen nuclei, while 13C NMR may give strong or weak peaks from the same number of  13C nuclei

**3-** Protons interact magnetically (‘couple’) to reveal the connectivity of the structure, while 13C is too rare for coupling between 13C nuclei to be seen

**4-** 1H NMR shifts give a more reliable indication of the local chemistry

than that given by 13C spectra

**5-** 13C –NMR have great rang 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.

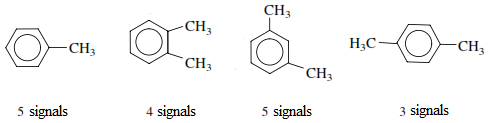
**The important of 13C-NMR spectrum in compound identification** there are three important thinks taken from 13C-NMR spectra it will be used to identification of the compounds

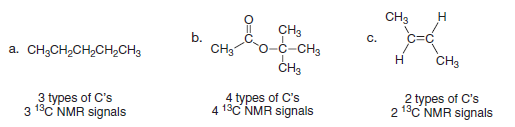
**1- The number of signals**

The number of signals in 13C-NMR spectroscopy refer to the number of deferent 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 13C -NMR spectrum. There for bromoethane ( CH3CH2Br) with two nonequivalent C's gives two 13C NMR signals and 1-bromopropane ( CH3CH2 CH2Br) with three nonequivalent C's gives three signals. Also the 13C 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.



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



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**2- 13C-NMR position of signals**

The positions of the signals in an 13C- NMR spectrum give information about the kind of carbons and there chemical shift. Just as chemical shifts in 1H NMR are measured relative to the protons of TMS, chemical shifts in 13C 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 13C NMR depend on the same effects as the chemical shifts of protons in 1H NMR:

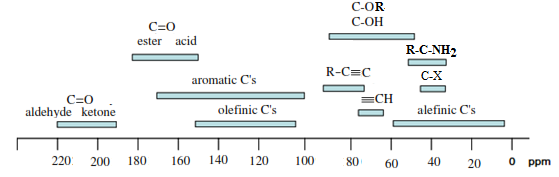
**•** The *sp*3 hybridized C atoms of alkyl groups are shielded and absorb upfield.

**•** Electronegative elements like halogen, nitrogen, and oxygen shift absorptions downfield.

**•** The *sp*2 hybridized C atoms of alkenes and benzene rings absorb downfield.

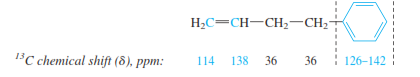
**•** Carbonyl carbons are highly deshielded, and absorb farther downfield than other carbon types.

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

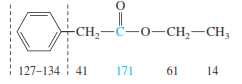
H NMR. As illustrated by 4-phenyl-1-butene, sp3 -hybridized carbons are more shielded than sp2-hybridized ones.

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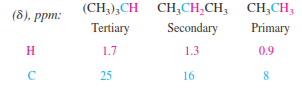
the sp2-hybridized carbons, C-1 is the most shielded because it is bonded to only one other carbon. The least shielded carbon is the ring carbon to which the side chain is attached. It is the only sp2-hybridized carbon connected to three others. Acetylenes are anomalous in 13C, as in H NMR. sp-Hybridized carbons are less shielded than sp3-hybridized ones, but more shielded than sp2 -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 13C NMR spectrum.

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**Electro negativity Effects**. Electronegative substituents affect 13C chemical shifts in the same way as they affect 1H chemical shifts, by withdrawing electrons. For H NMR, recall that because carbon is more electronegative than hydrogen, the protons in methane (CH4) are more shielded than primary hydrogens (RCH3), primary hydrogens are more shielded than secondary (R2CH2), and secondary more shielded than tertiary (R3CH). The same holds true for carbons in 13C NMR, but the effects can be 10–20 times greater.



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



different functional groups affect the chemical shifts of C atoms compear with δ values for unsubstituted compounds. This is 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 NR2, while they all have greater effects than CH3 consistent with the order of relative electronegativities O > N > C , and the effect of a halogen on δ values decreases in the electronegativity order F > Cl > Br > I , that based on their actual electronegativity values.

**Ex: Explain why the carbonyl carbon of an aldehyde or ketone absorbs farther downfi eld than the carbonyl carbon of an ester in a**

**13C NMR spectrum.**

**Ex:** **Which of the indicated carbon atoms in each molecule absorbs farther downfi eld?**

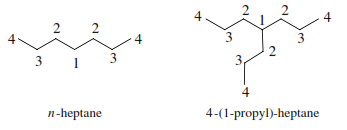
a. CH3CH2OCH2CH3 b. BrCH2CHBr2 c. HCOOCH3 d. CH3CH=CH2

**Ex: pridict the number signals and the postion of signals in 13CNMR spectrum of the following compound**

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**3-The intensity of  13C-NMR signals**

The intensity of  13C-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  13C-NMR spectra, but it is not bossible to determine if the ratio of defferent carbon types is 1:2:2:2 as expected for *n*-heptane or 1:3:3:3 expected for branh compound.

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**4- 13C-NMR splitting of the signals ( multiplicity )**

the number of splitting in the signals in 13C-NMR spectra refer to the number of protons that is directly attached to carbon. Thus quanternary carbons (R4C) are singlate, methine carbons (R3CH) are doublets, methylene carbons ( R2CH2) are triplets, and methyl carbons (RCH3) are quartets.

For example the 13C-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 dublate and the other is triblate because there are 1H and 2H directly attached to these carbon atoms respectively, same thinks happen with each epoxide carbon atoms , both methylene carbon atoms are triplets because there are 2 H directly attached .

