# B18OA1 $^{13}$C NMR Spectroscopy

## Introduction

You should be familiar with the idea that electrons have a property called 'spin'. There are two possible spin states for an electron, and electrons can be paired in an orbital if they have opposite (antiparallel) spin.

Like electrons, the protons and neutrons in an atom also have a spin with two possible quantum states: +½ and –½. In the nucleus protons can pair with other antiparallel protons in the same way that electrons pair in the orbitals surrounding the nucleus. Neutrons do the same. Whenever nuclei pair like this they have a net spin of zero ($^{12}$C, $^{16}$O). A nucleus with unpaired protons and/or neutrons, however, will have an overall spin. In this situation each unpaired particle contributes ½ to the overall nuclear spin quantum number, *I*. A nucleus with an overall spin has magnetic properties and can exist in 2 *I* + 1 magnetic states. So for *I* = ½ nuclei, as is the case for $^{1}$H and $^{13}$C, the nucleus can adopt 2 × ½ + 1 = 2 magnetic states. In the NMR technique we can observe nuclei switching between these states — by monitoring the energy absorbed when they change state. The nuclei of atoms like deuterium are rather more complicated. Deuterium, which has a nuclear spin quantum number *I* = 1, can adopt three magnetic states (since 2 *I* + 1 = 2 × 1 + 1 = 3).

We will only study $^{1}$H NMR and $^{13}$C NMR (say "proton NMR and carbon thirteen NMR") spectra in this course. Since $^{12}$C has a nuclear spin quantum number, *I*, of zero, it is not NMR-active. This means that carbon NMR spectra are measured by observing the small amount of $^{13}$C atoms that exist in organic molecules. Since the natural abundance of $^{13}$C is only 1.1%, recording $^{13}$C NMR spectra will take more time and/or more concentrated samples.

| Isotope | Spin quantum number *I* | Natural abundance (in %) | Sensitivity relative to $^{1}$H | Receptivity (= natural abundance × sensitivity) | Resonance frequency at *B* = 7.2 T (in MHz) |
|---|---|---|---|---|---|
| $^{1}$H | ½ | 99.985 | 1.000 | 0.999 | 300.00 |
| $^{2}$H | 1 | 0.015 | 0.010 | $1.5 \times 10^{-6}$ | 46.05 |
| $^{13}$C | ½ | 1.10 | 0.00018 | $2.0 \times 10^{-6}$ | 75.43 |

## Upfield/downfield

For historical reasons we call a signal at high ppm values being "downfield", and one at low ppm values "upfield".

| High ppm | | Low ppm |
|---|---|---|
| **Downfield** | ← → | **Upfield** |
| Deshielded | | Shielded |

More simply still, signals may also be described as being "to the left" or "to the right".

## Number of $^{13}$C NMR signals

Every non-equivalent carbon will give rise to a $^{13}$C NMR signal. Unless you deal with compounds with an unusual structure, the chemical shift, $\delta_C$, of a $^{13}$C NMR signal will fall into the range of 0 – 220 ppm. It is customary to tabulate ALL experimental $^{13}$C NMR signals (but NOT of solvents). You do NOT quote ranges.

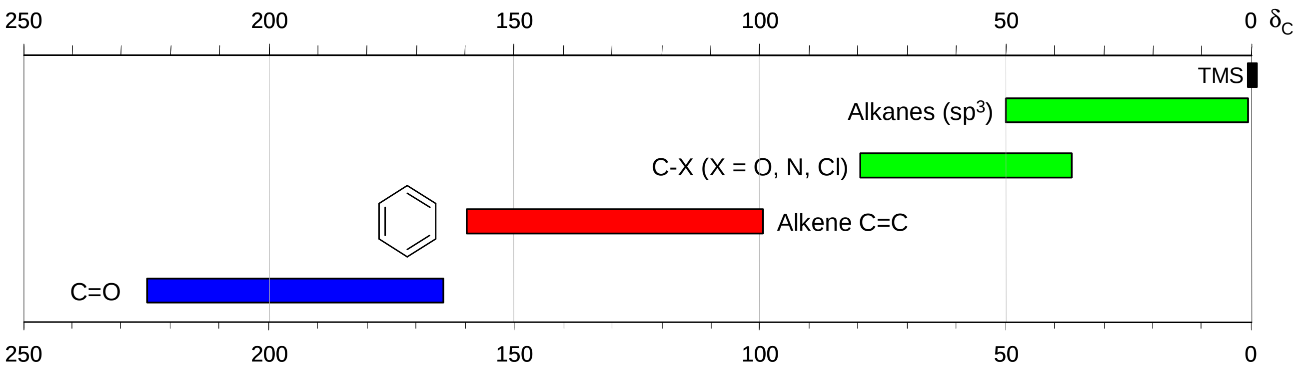
Until you run some 2D NMR spectra of your compound, you won't be able to unambigously assign every carbon to a particular signal, particularly when shifts get close (<10 ppm). This is not essential. What is important is that **the tabulated number of signals equals the number you would expect theoretically, by looking at the structure and counting the number of non-equivalent carbon atoms.** DEPT spectra provide an additional carbon inventory. This is the first thing you do as a trained chemist when you check someone else's NMR data (*i.e.* count the numbers of $CH_3$s, $CH_2$s etc.). If the numbers do not match, then the sample may be impure, or some signals might overlap, or are missing or, worse still, the proposed structure of the compound is wrong.

# $^{13}C$ NMR Spectroscopy

## Typical chemical shifts

$^{13}C$ NMR chemical shifts fall roughly into two regions, above and below 100 ppm: $sp^2$ carbons to the left, $sp^3$ to the right.

- Aliphatic ($sp^3$-hybridised) carbons give rise to a signal in the 0 – 50 ppm region; substitution with an electronegative atom (O, N, Cl, F) can shift the signal downfield to about 80 ppm.
- Alkene/aromatic ($sp^2$-hybridised) carbons usually show up in the 100 – 160 ppm region, whereas alkyne resonances are found slightly lower ($\delta_C$ 80 – 100).
- Carbonyl carbons come furthest downfield, between 165 and 220 ppm.

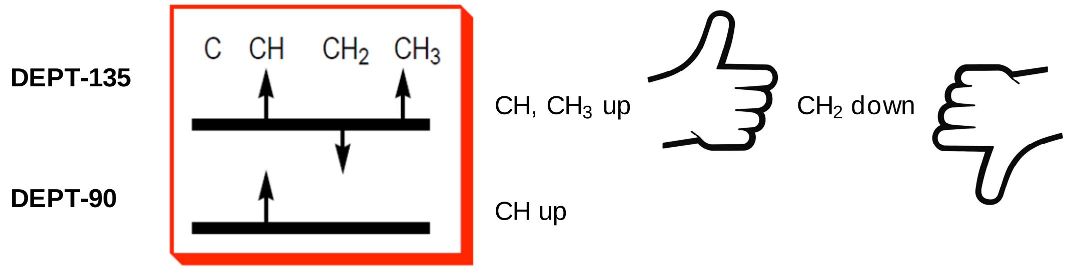



## DEPT

DEPT (short for Distortionless Enhancement by Polarisation Transfer) spectra are commonly used to distinguish between $CH_3$, $CH_2$ and CH signals. Quaternary carbon (C) signals without any hydrogens attached do not show up in a DEPT spectrum and are identified by comparison with the broadband-decoupled $^{13}C$ NMR spectrum. Plots usually consist of two types of DEPT spectra, DEPT-135 and DEPT-90.

DEPT-135 has CH and $CH_3$ signals up, whereas $CH_2$ signals are down.

DEPT-90 shows "only" CH signals and is thus used to differentiate between CH and $CH_3$.




Because the DEPT experiment depends on the size of $^{1}J_{CH}$ which can vary a lot, peak suppression in DEPT-90 is not always perfect and may still give rise to residual $CH_3$ and $CH_2$ signals. In such cases you need to use some chemical intuition.

## Factors affecting chemical shifts

Electropositive elements (Si, Li) next to a carbon will shift its signal upfield, and electronegative elements (O, F, N, Cl) will shift the signal downfield, because they donate and withdraw electrons, respectively.

| | $CH_3F$ | $CH_3OH$ | $CH_3NH_2$ | $CH_3Cl$ | $(CH_3)_4Si$ | $CH_4$ | $CH_3Li$ |
|---|---|---|---|---|---|---|---|
| $\delta_C$ | **75.2** | **50.2** | **26.9** | **24.9** | **0** | **-2.3** | **-14.0** |

Beware that this is a rather simplistic view and inferences have to be applied with caution. In case of doubt, look up typical chemical shifts for similar compounds in a good NMR book or search for suitable model compounds in an NMR database. Unless you deal with compounds of an unusual structure, $^{13}$C NMR chemical shifts can be predicted quite reliably using a program such as ChemBioDraw (unlike $^{1}$H NMR chemical shifts which can vary noticeably with solvent, concentration and temperature).

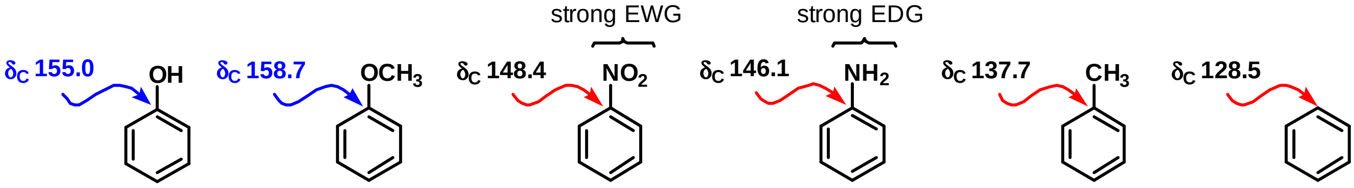
The inductive effect is additive.

| | $CHCl_3$ | $CH_2Cl_2$ | $CH_3Cl$ | $CH_4$ |
|---|---|---|---|---|
| $\delta_C$ | 77.0 | 53.5 | 24.9 | -2.3 |

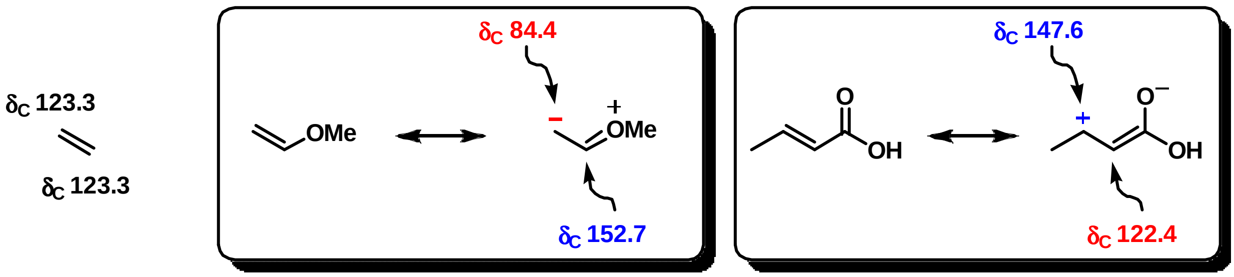
Carbon is just a little more electronegative than hydrogen, with the result that increasing the number of alkyl substituents will also shift a carbon resonance downfield.

| | $(CH_3)_4$**C** | $(CH_3)_3$**CH** | $(CH_3)_2$**CH$_2$** | $CH_3$**CH$_3$** | **CH$_4$** |
|---|---|---|---|---|---|
| $\delta_C$ | 27.7 | 25.0 | 15.9 | 8.4 | -2.3 |

**CAUTION:** The inductive effect argument no longer works for benzenes and alkenes; as the examples below illustrate, the effect of a very strong electron-withdrawing group ($NO_2$) and a very strong electron-donating group ($NH_2$) on the $^{13}$C NMR chemical shift of the *ipso*-carbon can be almost indistinguishable. Only the chemical shift of the *ipso*-carbon (C-O) of a phenol, phenyl ether or vinyl ether can be identified by its unusually high $^{13}$C NMR chemical shift of about 160 ppm. However, $^{13}$C NMR chemical shifts of mono- and disubstituted benzenes may be quite accurately calculated (*e.g.* with ChemBioDraw).

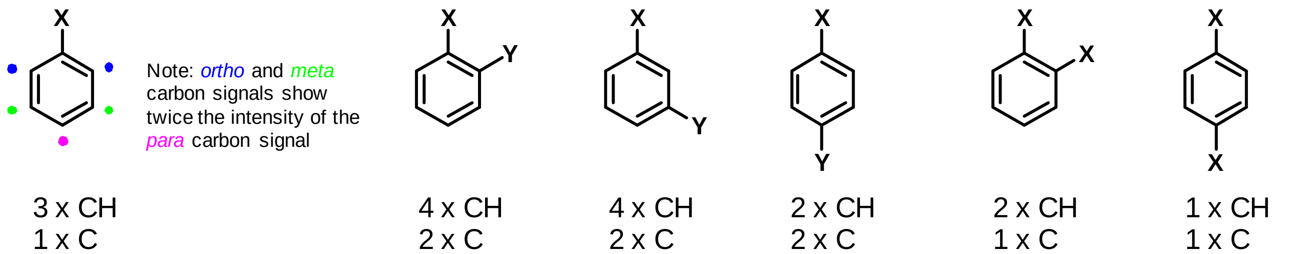



The chemical shifts of a double bond carrying a polar group can be rationalised by looking at the resonance structures. A carbon with a δ+ charge will have a $^{13}$C NMR signal at higher ppm values, whereas the signal of a carbon with a δ– charge will turn up at lower ppm values.




## Aromatic compounds

It is possible to draw conclusions about the substitution pattern of a benzene from the number of its aromatic $^{13}$C NMR signals. Symmetry will always reduce the number of signals, whereas lack of symmetry can result in up to 6 aromatic $^{13}$C NMR signals for a substituted benzene. For example:



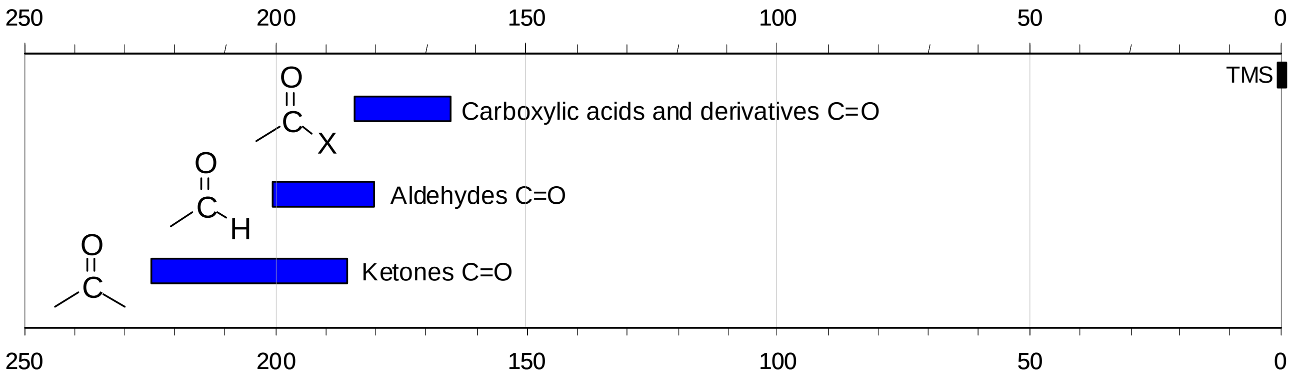

Quaternary carbon signals almost always show a lower intensity than carbons with a hydrogen attached.

## Carbonyl compounds

$^{13}C$ NMR spectra allow you to easily distinguish between ketones, aldehydes and carboxylic acids (or carboxylic acid derivatives). Some general rules:

- Carboxylic acids and carboxylic acid derivatives (esters, amides, anhydrides, acid chlorides) will show up in the narrow region between 165 and 180 ppm.
- Aldehydes and ketones will have chemical shifts $\delta_C$ > 180. The chemical shift $\delta_C$ of some ketone carbonyl carbons may even exceed 200 ppm.
- Aldehydes R-C**H**O will also give rise to a DEPT signal and can thus be easily distinguished from ketones.

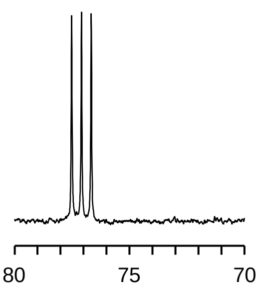
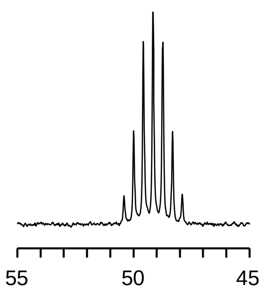
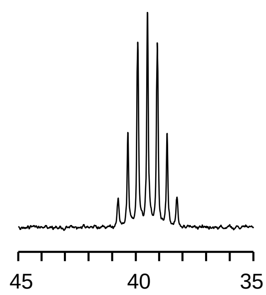
**$^{13}C$ NMR chemical shifts of carbonyl compounds**




## NMR solvents

Most common deuterated solvents except $D_2O$ give rise to signals in the $^{13}C$ NMR spectrum. You should familiarise yourself with the chemical shifts and multiplicities of the more common NMR solvents so that you don't mistake them for signals belonging to your sample.

**Table 1.** **$^{13}C$ NMR chemical shifts and multiplicities of common deuterated NMR solvents**

| | $CDCl_3$ (Deuterochloroform) | $CD_3OD$ (Deuterated methanol) | $(CD_3)_2SO$ or $d_6$-DMSO (Deuterated DMSO) |
|---|---|---|---|
| Residual solvent | 77.00  | 49.05  | 39.43  |

Note that $CDCl_3$ with one deuterium will have 2 × 1 + 1 = 3 lines due to spin-spin coupling with deuterium, whereas a $CD_3$ carbon signal will split up into a septet (2 × 3 + 1 = 7).

Real-life NMR spectra will often also include signals due to impurities such as residual extraction or recrystallisation solvents. For a highly useful summary of NMR data of typical impurities, download the following paper: H. E. Gottlieb, V. Kotlyar, A. Nudelman, "NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities", *J. Org. Chem*. **1997**, *62*, 7512 – 7515. A link can be found on Vision.

For more on NMR spectroscopy, see online video tutorial on Vision. **Online videos**