6.2: C-13 NMR Spectroscopy- Signal Averaging and FT-NMR

> **◑ Learning Objectives**
>
> - Learn how ^{1}H NMR and ^{13}C NMR are similar and different.
> - Understand the basics of how ^{13}C NMR works.

Why are we talking about ^{13}C NMR when the ^{12}C isotope of carbon - which accounts for up about 99% of the carbons in organic molecules? The ^{12}C isotope does not have a nuclear magnetic moment, and thus is NMR-inactive (cannot be seen by the NMR). Fortunately for organic chemists, however, the ^{13}C isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic moment just like protons, which is why we will be discussing ^{13}C NMR spectroscopy and not ^{12}C NMR spectroscopy. Most of what the theory we have learned about ^{1}H-NMR spectroscopy also applies to ^{13}C-NMR, although there are several important differences.

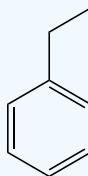## The basics of ^{13}C NMR spectroscopy

The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton. This means that NMR signals from ^{13}C nuclei are inherently much weaker than proton signals. Combining the weaker magnetic moment with the low natural abundance of ^{13}C, means that it is much more difficult to observe carbon signals: more sample is required, and often the data from hundreds of scans must be averaged in order to bring the signal-to-noise ratio down to acceptable levels.
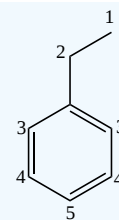
Chemical Shift

The resonance frequencies of ^{13}C nuclei are lower than those of protons in the same applied field - in a 7.05 Tesla instrument, protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This is fortunate, as it allows us to look at ^{13}C signals using a completely separate 'window' of radio frequencies. Just like in ^{1}H-NMR, the standard used in ^{13}C NMR experiments to define the 0 ppm point is tetramethylsilane (TMS), although of course in ^{13}C NMR it is the signal from the four equivalent *carbons* in TMS that serves as the standard. Chemical shifts for ^{13}C nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for ^{13}C compared to 12 ppm for protons (see Table 3 for a list of typical ^{13}C NMR chemical shifts). This is also fortunate, because it means that the signal from each carbon in a compound can almost always be seen as a distinct peak, without the overlapping that often plagues ^{1}H NMR spectra. The chemical shift of a ^{13}C nucleus is influenced by essentially the same factors that influence a proton's chemical shift: bonds to electronegative atoms and diamagnetic anisotropy effects tend to shift signals downfield (higher resonance frequency). In addition, sp^2 hybridization results in a large downfield shift. The ^{13}C NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both sp^2 hybridization and to the double bond to oxygen. Symmetry will also play a role in how many signals are observed on a ^{13}C NMR spectrum. If there is no symmetry, then each carbon should show up as a signal in the spectrum. If symmetry is present in the molecule, then there will be less than the total number of carbons in the molecule. Only non-equivalent carbons will appear as a signal in ^{13}C NMR.

> **✔ Example 6.2.1**
>
> How many sets of non-equivalent carbons are there in ethyl benzene?
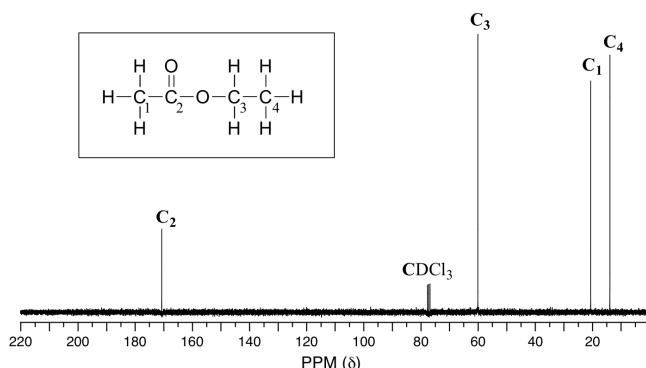>
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>
> **Solution**

There are 5 different carbons in ethyl benzene. There is symmetry in ethyl benzene in the aromatic ring. On the labeled molecule, there are two carbon 3's and two carbon 4's due to the symmetry of the molecule.

Integration

Unlike ^{1}H NMR signals, the area under a ^{13}C NMR signal cannot be used to determine the number of carbons to which it corresponds. This is because the signals for some types of carbons are inherently weaker than for other types – peaks corresponding to carbonyl carbons, for example, are much smaller than those for methyl or methylene (CH$_2$) peaks. There are some quantitative ^{13}C NMR experiments that when enriched with ^{13}C can be integrated, but typically it is not done.
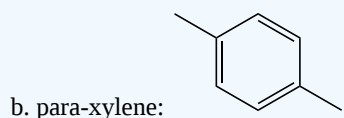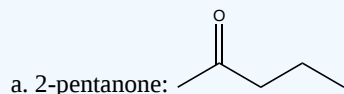
Spin-spin Splitting

Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two ^{13}C atoms near each other in the same molecule, which means that spin-spin coupling is not observed between neighboring carbons in a ^{13}C NMR spectrum. However, there is heteronuclear coupling between ^{13}C carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. Proton-coupled ^{13}C spectra show complex overlapping multiplets, which makes for a very difficult interpretation. For clarity, chemists generally use a technique called broadband decoupling , which essentially 'turns off' C-H coupling, resulting in a spectrum where all carbon signals are singlets. Below is the proton-decoupled ^{13}C NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons with no spin-spin splitting.
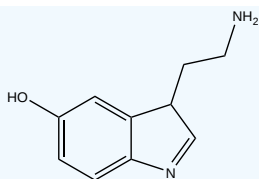

While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, there are other ^{13}C NMR experiments that can give more information, such as Distortionless Enhancement by Polarization Transfer (DEPT) allows us to determine how many hydrogens are bound to each carbon.

> **? Exercise 6.2.1**
>
> How many sets of non-equivalent carbons are there in:
>
> a. 2-pentanone:
>
> b. para-xylene:

c. serotonin:

Answer

    a. 5 non-equivalent carbons

    b. 3 non-eqivalent carbons

    c. 10 non-equivalent carbons

Contributors and Attributions

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