

## 12.10: $^{13}\text{C}$ NMR SPECTROSCOPY

### THE BASICS OF $^{13}\text{C}$ -NMR SPECTROSCOPY

The magnetic moment of a  $^{13}\text{C}$  nucleus is much weaker than that of a proton, meaning that NMR signals from  $^{13}\text{C}$  nuclei are inherently much weaker than proton signals. This, combined with the low natural abundance of  $^{13}\text{C}$ , 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. Unlike  $^1\text{H}$ -NMR signals, the area under a  $^{13}\text{C}$ -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 ( $\text{CH}_2$ ) peaks. Peak integration is generally not useful in  $^{13}\text{C}$ -NMR spectroscopy, except when investigating molecules that have been enriched with  $^{13}\text{C}$  isotope (see section 5.6B).

The resonance frequencies of  $^{13}\text{C}$  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  $^{13}\text{C}$  signals using a completely separate 'window' of radio frequencies. Just like in  $^1\text{H}$ -NMR, the standard used in  $^{13}\text{C}$ -NMR experiments to define the 0 ppm point is tetramethylsilane (TMS), although of course in  $^{13}\text{C}$ -NMR it is the signal from the four equivalent carbons in TMS that serves as the standard. Chemical shifts for  $^{13}\text{C}$  nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for  $^{13}\text{C}$  compared to 12 ppm for protons (see Table 3 for a list of typical  $^{13}\text{C}$ -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  $^1\text{H}$ -NMR spectra. The chemical shift of a  $^{13}\text{C}$  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,  $\text{sp}^2$  hybridization results in a large downfield shift. The  $^{13}\text{C}$ -NMR signals for carbonyl carbons are generally the furthest downfield (170–220 ppm), due to both  $\text{sp}^2$  hybridization and to the double bond to oxygen.

#### Example 12.10.1

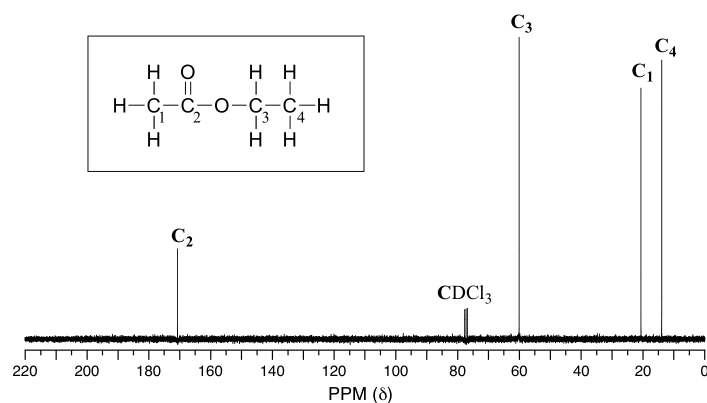
How many sets of non-equivalent carbons are there in each of the molecules shown in exercise 5.1?

#### Example 12.10.2

How many sets of non-equivalent carbons are there in:

- toluene
- 2-pentanone
- para-xylene
- triclosan

Because of the low natural abundance of  $^{13}\text{C}$  nuclei, it is very unlikely to find two  $^{13}\text{C}$  atoms near each other in the same molecule, and thus we do not see *spin-spin coupling between neighboring carbons in a  $^{13}\text{C}$ -NMR spectrum*. There is, however, **heteronuclear coupling** between  $^{13}\text{C}$  carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. For clarity, chemists generally use a technique called **broadband decoupling**, which essentially 'turns off' C-H coupling, resulting in a spectrum in which all carbon signals are singlets. Below is the proton-decoupled  $^{13}\text{C}$ -NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons.



While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, another modern NMR technique called DEPT (Distortionless Enhancement by Polarization Transfer) allows us to determine how many hydrogens are bound to each carbon. For example, a DEPT experiment tells us that the signal at 171 ppm in the ethyl acetate spectrum is a quaternary carbon (no hydrogens bound, in this case a carbonyl carbon), that the 61 ppm signal is from a methylene ( $\text{CH}_2$ ) carbon, and that the 21 ppm and 14 ppm signals are both methyl ( $\text{CH}_3$ ) carbons. The details of the DEPT experiment are beyond the scope of this text, but DEPT information will often be provided along with  $^{13}\text{C}$  spectral data in examples and problems.

## CONTRIBUTORS AND ATTRIBUTIONS

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