

13.10: CHARACTERISTICS OF ^{13}C NMR SPECTROSCOPY

OBJECTIVES

After completing this section, you should be able to

- Determine the number of distinct C atoms in a molecule.
- Use the chemical shifts table to determine functional groups present in a molecule.
- Assign a chemical shift to each carbon in a given molecule.

THE BASICS OF ^{13}C -NMR SPECTROSCOPY

Unlike ^1H -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. Peak integration is generally not useful in ^{13}C -NMR spectroscopy, except when investigating molecules that have been enriched with ^{13}C isotope.

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. This means you will only see the ^{13}C nuclei in a ^{13}C NMR experiment like in the ^1H NMR experiments we just looked at, we only saw hydrogens. Just like in ^1H -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 ^1H -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.

✓ EXAMPLE 13.10.1

- How many sets of non-equivalent carbons are there in each of the molecules shown in exercise 5.1?
- How many sets of non-equivalent carbons are there in:
 - o toluene
 - o 2-pentanone
 - o para-xylene
 - o triclosan

(all structures are shown earlier in this chapter)

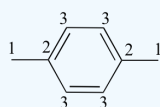
Solution

a

- 8 signals (each carbon is different)
- 11 signals (the two enantiotopic CH_2CH_3 groups are NMR-equivalent)
- 6 signals (each carbon is different)
- 16 signals (the fluorobenzene group only contributes 4 signals due to symmetry)

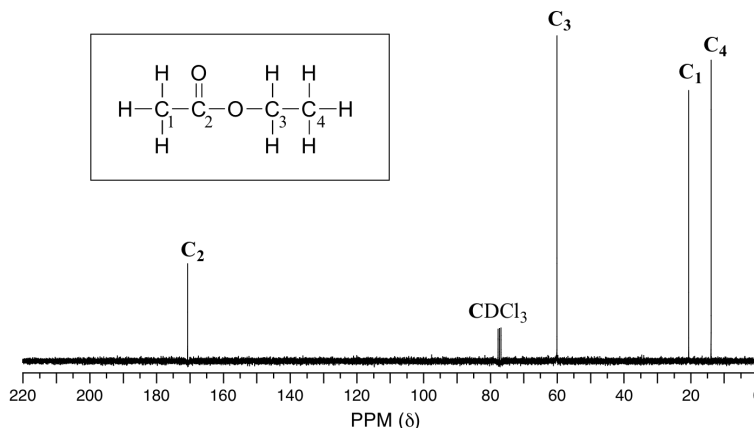
b

- 5 signals
- 5 signals
- 3 signals

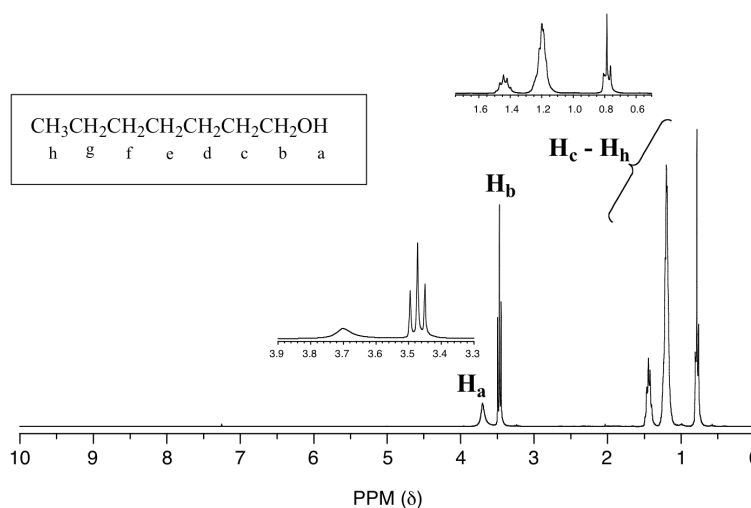


- 6 signals

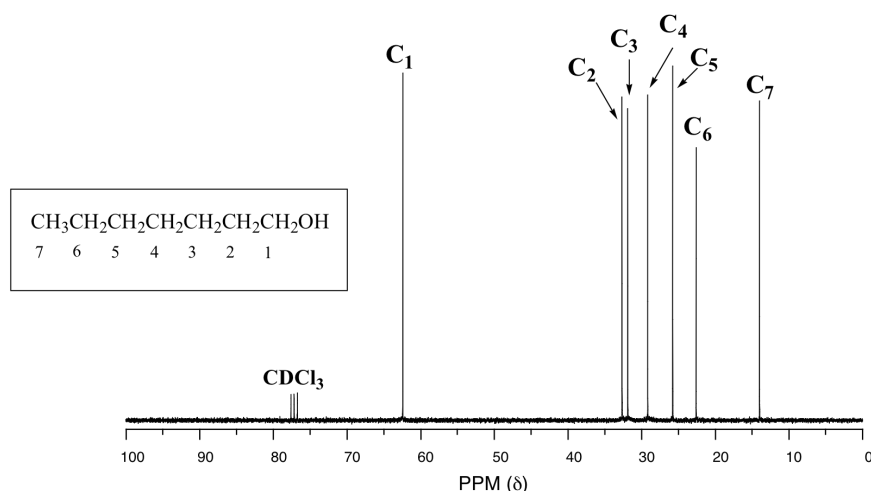
Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two ^{13}C atoms near each other in the same molecule, and thus we do not see *spin-spin coupling between neighboring carbons in a ^{13}C -NMR spectrum*. There is, however, **heteronuclear coupling** between ^{13}C carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. 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}C -NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons.



One of the greatest advantages of ^{13}C -NMR compared to ^1H -NMR is the breadth of the spectrum - recall that carbons resonate from 0-220 ppm relative to the TMS standard, as opposed to only 0-12 ppm for protons. Because of this, ^{13}C signals rarely overlap, and we can almost always distinguish separate peaks for each carbon, even in a relatively large compound containing carbons in very similar environments. In the proton spectrum of 1-heptanol, for example, only the signals for the alcohol proton (H_a) and the two protons on the adjacent carbon (H_b) are easily analyzed. The other proton signals overlap, making analysis difficult.



In the ^{13}C spectrum of the same molecule, however, we can easily distinguish each carbon signal, and we know from this data that our sample has seven non-equivalent carbons. (Notice also that, as we would expect, the chemical shifts of the carbons get progressively smaller as they get farther away from the deshielding oxygen.)



This property of ¹³C-NMR makes it very helpful in the elucidation of larger, more complex structures.

¹³C NMR CHEMICAL SHIFTS

The Carbon NMR is used for determining functional groups using characteristic shift values. ¹³C chemical shifts are greatly affected by electronegative effects. If a H atom in an alkane is replaced by substituent X, electronegative atoms (O, N, halogen), ¹³C signals for nearby carbons shift downfield (left; increase in ppm) with the effect diminishing with distance from the electron withdrawing group. Figure 13.11.1 shows typical ¹³C chemical shift regions of the major chemical class.

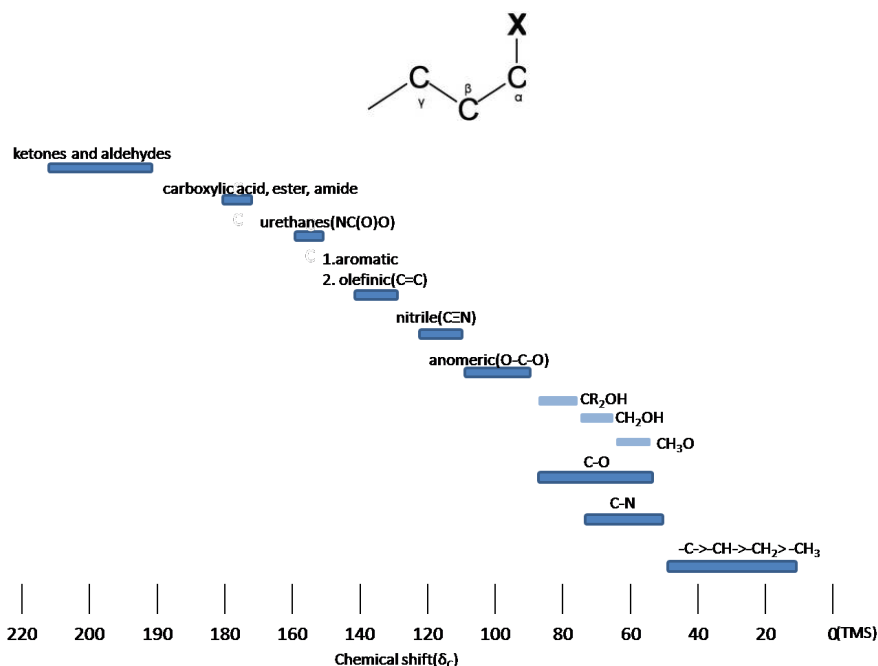


Figure 13.10.1: ¹³C Chemical shift range for organic compound

SPIN-SPIN SPLITTING

Comparing the ¹H NMR, there is a big difference thing in the ¹³C NMR. The ¹³C-¹³C spin-spin splitting rarely exist between adjacent carbons because ¹³C is naturally lower abundant (1.1%)

- ¹³C-¹H Spin coupling:** ¹³C-¹H Spin coupling provides useful information about the number of protons attached a carbon atom. In case of one bond coupling (¹J_{CH}), -CH, -CH₂, and CH₃ have respectively doublet, triplet, quartets for the ¹³C resonances in the spectrum. However, ¹³C-¹H Spin coupling has an disadvantage for ¹³C spectrum interpretation. ¹³C-¹H Spin coupling is hard to analyze and reveal structure due to a forest of overlapping peaks that result from 100% abundance of ¹H.
- Decoupling:** Decoupling is the process of removing ¹³C-¹H coupling interaction to simplify a spectrum and identify which pair of nuclei is involved in the J coupling. The decoupling ¹³C spectra shows only one peak(singlet) for each unique carbon in

the molecule (Fig 13.11.2). Decoupling is performed by irradiating at the frequency of one proton with continuous low-power RF.

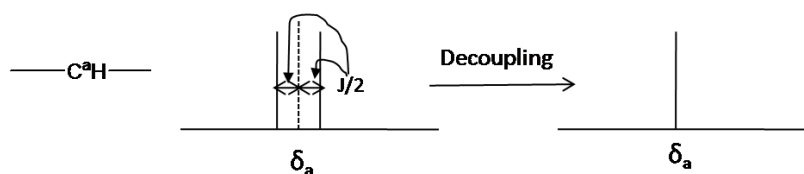


Figure 13.10.2 Decoupling in the ^{13}C NMR

SUMMARY

^{13}C NMR (Carbon-13 Nuclear Magnetic Resonance) Spectroscopy is a powerful analytical technique used to study the structure and connectivity of organic molecules. Unlike proton NMR, which detects hydrogen nuclei, ^{13}C NMR specifically targets the carbon nuclei within a molecule. In ^{13}C NMR spectroscopy, carbon atoms resonate at characteristic frequencies based on their local chemical environment, which is influenced by neighboring atoms and functional groups. These resonances appear as peaks in the NMR spectrum, providing valuable information about the types of carbon atoms present and their surroundings. By analyzing the chemical shifts, intensities, and coupling patterns of these peaks, chemists can deduce crucial structural details such as the number and types of carbon atoms, their connectivity, and the presence of certain functional groups. This information is essential for determining the molecular structure and understanding chemical properties and reactivities.

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