

Organic Chemistry

Notes Part 17

Electromagnetic radiation (8th edition, Chapter 13.1, 9th edition, same)

The electromagnetic spectrum is shown in Figure 13.1 (both editions) and reproduced below. The wavelength is shown above the spectrum and is nanometers. We will be concerned with three regions which are the following: the ultra-violet region, the infrared region, and the radio frequency range.

Highest energy						Lowest Energy
10^{-2}		10	400	750	$10^{5.5}$	10^8
Gamma Ray	X-ray	Ultra Violet	Visible	Infrared	Microwave	Radio Frequency

Planck's equation is $E = h\nu$ where E is the energy, h is Planck's constant and ν is the frequency. How is the wavelength that is shown in the diagram above related to the frequency? The equation that relates wavelength and frequency is $c = \nu\lambda$ where c is the speed of light, ν is the frequency and λ is the wavelength.

Some facts to keep in mind are the following:

- The shorter the wavelength, the higher the energy.
- The higher the frequency, the shorter the wavelength.
- Energy is absorbed at specific wavelengths by organic molecules if the wavelength is the energy between two states which could be nuclear spin states (NMR), two vibrational states (IR) or two electronic states (UV/VIS).

Nuclear Magnetic Resonance (NMR) (8th edition [13.3 (1H)], [13.14 (13C NMR)], 9th edition, same]

Nuclear magnetic resonance spectroscopy is defined by Carey as "a method for structure determination based on the effect of molecular environment on the energy required to promote a given nucleus from a lower energy spin state to a higher energy state." A more detailed explanation of each part of NMR is given below.

History (Not in your book.)

It was first detected by Felix Bloch and Edward Purcell in 1946 for which they shared the 1952 Nobel Prize in physics.

Nuclear (Part 1 of NMR)

For an atom to be NMR active, it must have either an odd atomic number or an odd atomic mass. Many of the atoms in the periodic table are NMR active. It will then have a spin quantum number that can be seen by the NMR. The underlined molecules below are NMR active.



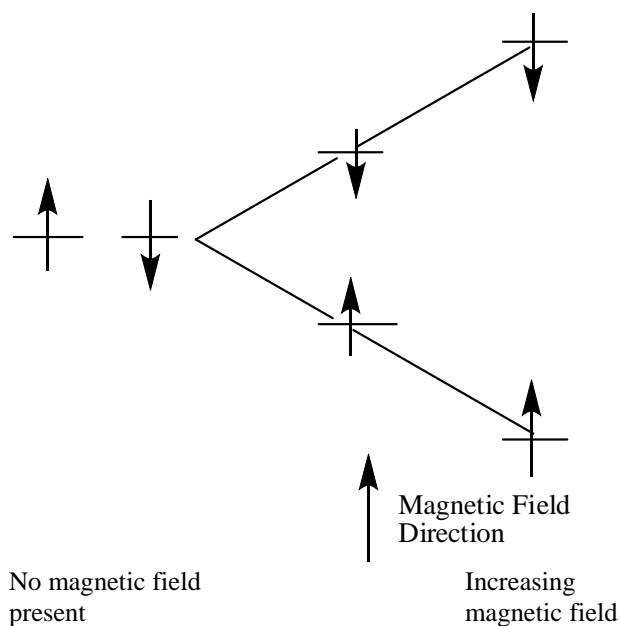
Both of the two hydrogen atoms above are NMR active. H¹ is the predominant isotope of hydrogen and this makes H¹ NMR easier to acquire.

Unlike hydrogen, ¹³C is the minor isotope of carbon and makes carbon NMR much more of a challenge.

Magnetic (Part 2 of NMR)

A magnet is required to align the spins that certain atoms possess. In the absence of a magnetic field, the spins are in a random order. However, once the spins are put in a magnetic field, the spins align either WITH or AGAINST the field. The spins that are aligned with the field are of LOWER energy than those that are aligned against the field. As you increase the magnetic field, the energy difference between the two spin levels increases and this is shown below.

(8th edition, Figures 13.3, 13.4, 9th edition, same)



Magnets can either be PERMANENT magnets or SUPER-CONDUCTING magnets. Super-conducting magnets are required for increasing the magnet field.

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Resonance (Part 3 of NMR)

Resonance is defined (at least in this class) as the absorption of radiation by ORGANIC MOLECULES.

We could talk about how big the magnets are in NMR spectrometers but we talk instead of the frequency required to get the proton to resonate. For example, a 100 MHz NMR has a bigger magnet than a 60 MHz NMR. An 800 MHz NMR has a much bigger magnet than a 100 MHz NMR.

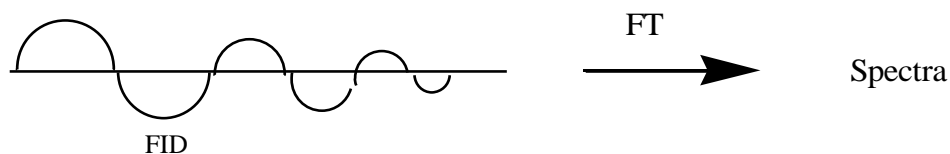
(8th edition, Problem 13.1, 9th edition, same) Most of the NMR spectra in this text were recorded on a spectrometer having a field strength of 4.7 Tesla (200 MHz for ¹H). The first generation of widely used NMR spectrometers were 60-MHz instruments. What was the magnetic field strength of these earlier spectrometers? What is the field strength of the 920-MHz instruments now commercially available?

$$\frac{4.7}{200} = \frac{X}{60}$$

a) $X = 1.41$

FT-NMR (8th edition, Figure 13.5, 9th edition, same)

In an FT-NMR, all of the nuclei are excited at the same time. The spins are tipped 90 ° and the receiver records the spins as they return back to their original position. The data is recorded as the FREE INDUCTION DECAY (also called the FID). A Fourier transform converts the FID into a spectrum. An example of this is shown below.



Spectra to structure or structure to spectra

The two ways to work a spectral problem are:

- 1) converting the STRUCTURE to a spectra – This means we have the structure of a molecule and draw a spectra.
- 2) converting a SPECTRA to a structure- This is the usual way to work problems and you will be given a spectra. You will usually be given a sheet that contains a proton NMR spectrum, a carbon NMR spectrum, an IR spectrum, a Mass Spectrum and a UV spectrum. You will then give the possible structure of a molecule that could give all of the spectra.

Four questions for PROTON NMR will help you solve the problem regardless of which way you are working the problem.

There are THREE questions for carbon NMR. The four questions for ¹H NMR are given below.

(8th edition, Chapter 13.6, 9th edition, same)

- 1) (Structure to spectra) How many different types of protons are present in a molecule?)

There are three different types of protons possible in a molecule. These three types are shown below.

_____ - protons that are the same regardless of whether the solvent is a chiral or achiral solvent.

_____ - protons that are different in chiral solvents but the same in achiral solvents. CDCl₃, _____, is a common solvent for NMR and is _____. *It must be mentioned in the problem whether a chiral or achiral solvent is being used.*

_____ - protons that are different in any solvent whether it is chiral or achiral.

How do we know if protons are homotopic, enantiotopic, or diastereotopic? A couple of methods exist to determine how protons are related. The first item to look for is a _____. A plane of symmetry allows protons to be equal.

An easy way to tell how protons are related is to replace the protons with a group and then name the molecule. If the molecules have the same name, the protons are _____.

If the molecules have the same name except for being different enantiomers, the protons are _____.

Finally, if the molecules have names that differ due to being diastereomers, the protons are _____.

When do you have enantiotopic protons? This case usually happens when you have a CH_2 group (methylene) with two different groups attached to the methylene group. An example is shown below.

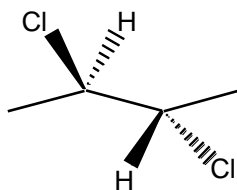
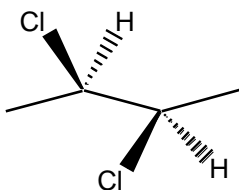
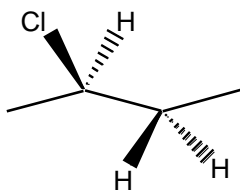


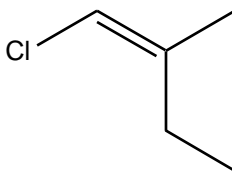
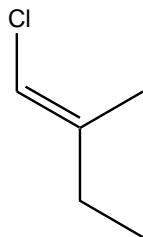
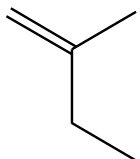
Protons in a chiral solvent: _____



Protons in an achiral solvent: _____

When do you have diastereotopic protons? There are at least two possibilities for diastereotopic protons. One is that there is a chiral center already present in the molecule and a CH_2 is present in the molecule. Another possibility is when a double bond is present. It does not matter whether the solvent is chiral or achiral. Some examples are shown below. Indicate below the drawings how many types of protons are present. Given besides each drawing is a molecule where each hydrogen has been replaced by a group which is chlorine in this example. How are the drawings related?





When do you have homotopic protons? As stated above, look for a plane of symmetry.

How many different types of protons does methane have? _____

How many different types of protons does ethane have? _____

How many types of protons does pentane have? _____.

(8th edition, Problem 13.9, 9th edition, same) How many signals would you expect to find in the ^1H NMR spectrum of each of the following compounds?

a) 1-bromobutane

e) 2,2-Dibromobutane

d) 1,4-Dibromobutane

h) 1,1,1-Tribromobutane

(8th edition, Problem 13.10, 9th edition, same) How many signals would you expect to find in the ¹H NMR spectrum of each of the following compounds?

a) Vinyl bromide

b) 1,1-Dibromoethene

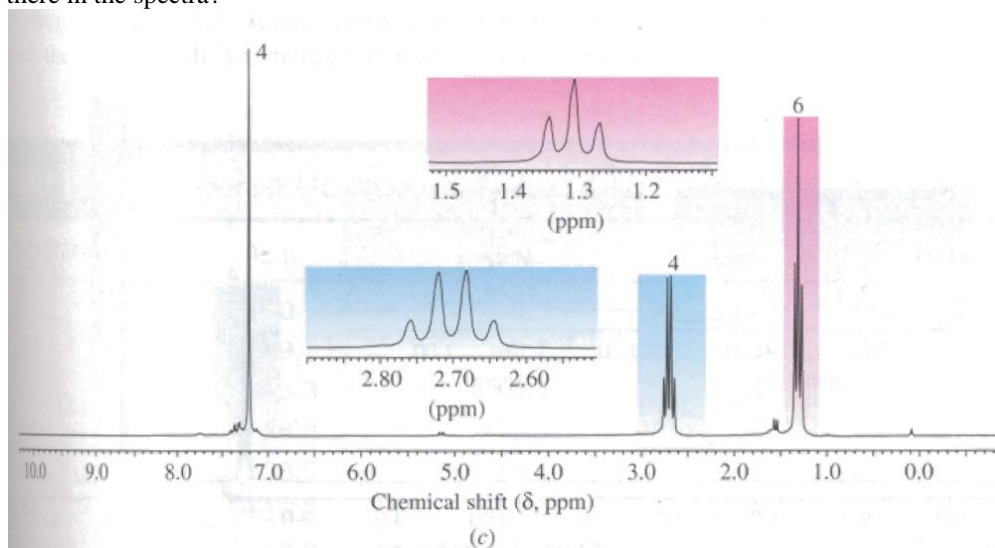
c) cis-1,2-Dibromoethene

d) trans-1,2-Dibromoethene

e) Allyl bromide

1) (Spectra to structure) How many different types of protons are present in a molecule?

Given below is the 200 MHz ¹H spectra in (8th edition, Figure 13.52, pg. 598, 9th edition, Fig. 13.51, pg. 569). How many different peaks are there in the spectra?



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2) Where do things show up? (8th edition, Chapter 13.4, 13.5, 9th edition, same)

Chemical shift is defined by Carey as “a measure of how shielded the nucleus of a particular atom is. Nuclei of different atoms have different chemical shifts, and nuclei of the same atom have chemical shifts that are sensitive to the molecular environment. In proton and carbon-13 NMR, chemical shifts are cited as δ , or parts per million (ppm), from the hydrogens or carbons, respectively, of tetramethylsilane.”

Protons show up in different locations due to the electronic environment. Therefore, we must assign a standard so that all of the spectra that are run have the same scale. The standard that has been chosen is _____ which is

abbreviated as _____ and is shown above. This standard is advantageous for a couple of reasons. The first reason is that the protons are all equal and the molecule has twelve equivalent protons. Very little TMS is needed in your sample to be seen by the NMR machine. Secondly, TMS shows up in a location on the spectra that few organic compounds interfere with the location. Finally, TMS is a low boiling compound and can be easily removed from the solution by the addition of a little _____. The chemical shift is defined by the following equation.

Let us assume you run a proton NMR at CBU on our 60 MHz NMR and have a peak show up at 1 δ . You then take the same sample over to St. Jude and run it on the 800 MHz NMR. Where does the peak show up? _____. The benefit of the higher field magnet is the number of hertz between zero and one δ . On the CBU NMR, the difference is _____ Hz. On the St. Jude NMR, the difference is _____ Hz. The take home lesson is you always want _____!!

A proton NMR is usually plotted from 0 δ to 10 δ . Can peaks show up outside of this range? _____. Given below is the chemical shift scale with the type of hydrogen transposed on it.