CHEM 8M, NMR Spectroscopy for Structure Determination



ethyl propanoate ... says who?!

NMR =

Nuclear Magnetic

Resonance

INSTRUMENTATION

ATOMIC NUCLEI, ex. ¹H atoms



Time (s) FID δ (ppm)

Spectrum

¹H NMR is used determine or confirm a chemical structure

- Chemical Equivalence: How many different types of protons are in the molecule?
- Chemical shift: What is the chemical environment of those protons?
- Integration: How many H's are represented by each signal?
- Splitting: How many H's are nearby?



FIGURE 22.11 ¹H NMR spectrum of ethyl propanoate at 200 MHz.

One type of "NMR-active" nucleus can be observed in an experiment at a time: ¹H, ¹³C, ¹¹B

- ¹H NMR = "proton NMR" is most common / useful because ¹H isotope > 99% abundance.
 - Small amount of sample (< 10mg)
 - Quick run time (< 5 min).

0

- Chemical shift range: 0 12 ppm
- ¹³C NMR = "carbon NMR" is also widely used.
 - ¹³C isotope < 1% abundance
 - more sample (< 30mg)
 - longer run time (30+ min)
 - Chemical shift range: 0 220 ppm



TABLE 21.1 Deuterated solvents for NMR spectroscopy						
Solvent	Structure	Residual ¹ H signal (ppm)	¹³ C chemical shift (ppm)			
Chloroform-d Acetone-d ₆	$CDCl_3$ $CD_3(C=O)CD_3$	7.26 (singlet) 2.04 (quintet)	77.0 (triplet) 29.8 (septet), 206.5 (singlet)			
Deuterium oxide Dimethyl sulfoxide-d ₆	D_2O $CD_3(S=O)CD_3$	4.6 (broad singlet) 2.49 (quintet)	39.7 (septet)			

CHEMICAL SHIFTS, EQUIVALENCY, & CHEMICAL ENVIRONMENTS

- Nearby atoms / FG's cause the chemical shift to be higher (deshielded) or lower (shielded)
 - Shielding = electron clouds 'protecting' the nucleus from experiencing the magnetic field of the NMR instrument
- Pi bonds, electron-withdrawing groups (EWG's), & electronegative (EN) atoms cause deshielding

Deshielded H's

Strong δ^+ ↑Chemical shift Shielded H's

Weak $\delta^{\scriptscriptstyle +}$

 \downarrow Chemical shift



CH₃OCH₃



Si(CH₃)₄

Relate the terms below to propanoic acid...

- Chemical Equivalence

- Integration

- Chemical Shifts



How to Predict ¹H NMR Spectra



- 1. Chemical Equivalence: How many ¹H NMR absorptions are expected?
 - How many types of non-equivalent protons?
- 2. Integration: What is the ratio of peak areas expected upon integration of the spectrum?
- 3. Approximate the **chemical shift** for each type of proton using the NMR correlation tables.
 - Table 22.2...H-C-("Group") used to assign most appropriate chemical shift range
 - Tables 22.3 and 22.4 are used to calculate an expected chemical shift based on nearby atoms
 - i. Use Table 22.4 for H's connected to a benzene ring; use Table 22.3 for all other H's
- 4. Splitting & (n+1) rule: Number of H's adjacent to each set of H's

H₃CO[~]

0

Proton Splitting aka ¹H-¹H Coupling and the "n+1 Rule"

• Non-equivalent signals (neighboring proton nuclei) effect each other's peak shape.



N = number of hydrogens on adjacent carbons (neighbors)





Frequency (Hz)

¹H spectrum of ethyl propanoate has two 2H Common NMR terminology.

1 two 3H triplets (A&D).



Signal D is a 3H triplet at 1.3 ppm: " δ 1.1 (3H triplet)"

- All D nuclei spin against B field with central chemical shift @ 1.3 ppm
- D has 2 neighbors (signal C, n = 2) that are 50 / 50 with & against B field



FIGURE 22.12 ¹H NMR spectra of *tert*-butyl acetate in the region from 0 to 500 Hz at (a) 60 MHz and (b) 200 MHz. The chemical shift of each signal is the same regardless of the spectrometer frequency.

Preparing for NMR Problem Set

- watch the "How to do the NMR problem set" video (Canvas) and use the template below to follow along with the problem-solving process.

... Predict the number signals, integration, splitting, and chemical shift (range and calculated)

Br Sigr	al Integration	Splitting	Range (ppm)	Shift (ppm)*
Br				

Signal	Integration	Splitting	Chemical Shift Range (ppm)	Calculated Chemical Shift (ppm)*

<u>Structural Elucidation</u> - Propose a structure from chemical formula, IR, & ¹H NMR

Watch the "How to do the NMR problem set" video (Canvas) and use the template below to follow the problemsolving process.

- Calculate degrees of unsaturation (total number of pi bonds and/or rings) from the molecular formula
- use IR to identify possible functional group(s),
- draw structure fragments based on signal information (2H doublet = CH₂CH),
- then put the fragments together in the **final structure**.
- Check your work by calculating chemical shifts of the proposed structure.

C₃H₆O; **IR** 1720 cm⁻¹, 2900 cm⁻¹; ¹H **NMR** – δ 2.0 ppm (3H singlet)

C₅H₁₂O; **IR** 3300 cm⁻¹, 2900 cm⁻¹; ¹H **NMR** – δ 4.0 ppm (1H broad singlet), δ 3.5 ppm (2H triplet), δ 1.6 (1H nonet), δ 1.5 ppm (2H quartet), δ 0.9 (6H doublet)

What's the resonance frequency, Kenneth?

See optional/supplemental video (Canvas) on what a chemical shift really is.

Chemical shift (ppm) = <u>frequency of proton relative to TMS</u> Maximum operating frequency of instrument (MHz)

Ex. *tert*-butyl acetate is dissolved in a solution of CDCl₃ (w/ 0.1 % TMS) and ¹H NMR spectra are run on two different instruments.

(a)



FIGURE 22.12 ¹H NMR spectra of *tert*-butyl acetate in the region from 0 to 500 Hz at (a) 60 MHz and (b) 200 MHz. The chemical shift of each signal is the same regardless of the spectrometer frequency.