

I. ^1H NMR spectroscopy

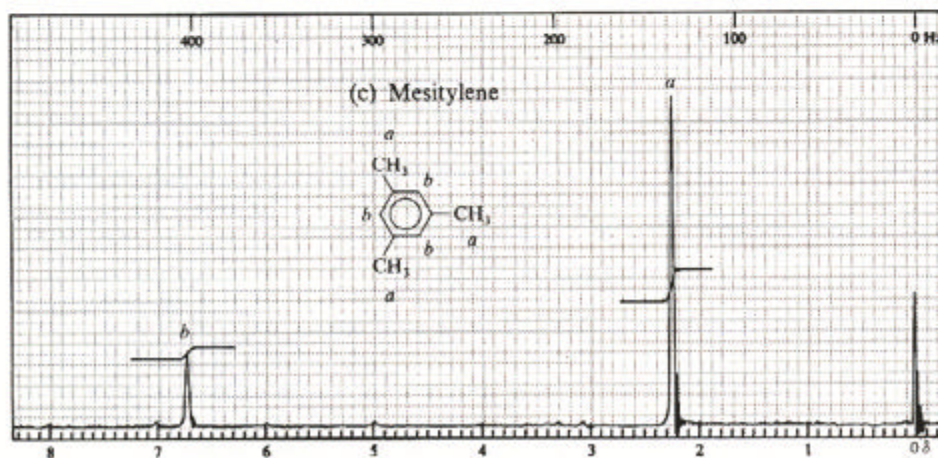
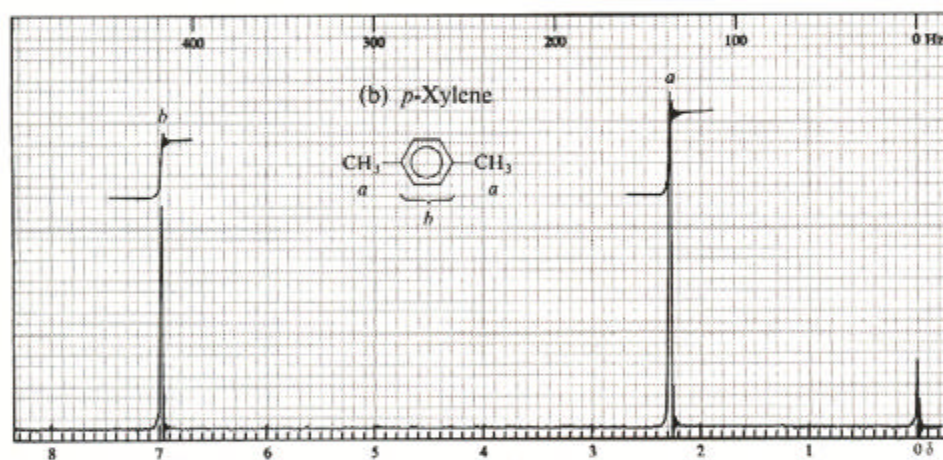
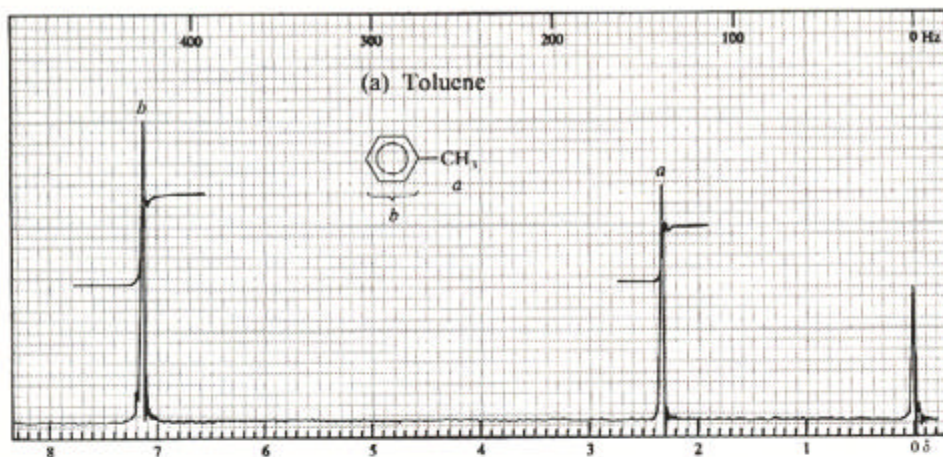
A. Theory

1. The protons and neutrons in atomic nuclei spin, as does the nucleus itself
2. The circulation of nuclear charge can generate a nuclear magnetic moment, μ , along the spin axis
3. The angular momentum of a spinning charged particle (e.g., nucleus) can be described in terms of spin number I , which is the sum of the angular momenta of the spinning nucleons
 - a. If $(p = n)$ then $I = 0$, cannot be detected by NMR
 - b. If $(p + n = \text{even})$ then $I = 0, 1, 2, 3, \dots$, can be detected by NMR
 - c. If $(p + n = \text{odd})$ then $I = 1/2, 3/2, 5/2, \dots$, can be detected by NMR
 - d. When $I = 1/2$ NMR experiments are the easiest
 - e. $I = 1/2$ for ^1H , ^{13}C , ^{19}F , ^{31}P , etc. (30 of 118 odd isotopes)
4. The spin number I describes the number of orientations the spinning particle may assume when exposed to an external magnetic field ($\# = 2I + 1$), i.e., the number of different energy states
5. The exposure of spinning hydrogen nuclei to a powerful magnetic field will result in the protons aligned with the field, precessing about the axis of the applied field in one of two possible spin states
6. RF radiation is applied at a right angle to the magnetic field
7. At the resonance frequency lower energy spins are flipped to the higher energy spin state
8. A detector "observes" the absorption of energy by the sample
9. Since each set of equivalent hydrogens is in a slightly different environment, the amount of RF energy required to make them flip is also different

B. Interpretation: the number of signals

1. In a given molecule, all equivalent protons absorb at the same field strength, and all non-equivalent protons absorb at different field strengths
2. In other words, the number of signals is equal to the number of kinds of protons in a molecule
3. Judging equivalence of two (or more) protons
 - a. Draw the structure of the molecule
 - b. Replace a proton with a "Z"
 - c. If replacement of either of the protons by Z yields the same product or enantiomeric products, then the atoms are equivalent
 - d. To be equivalent protons must also be stereochemically equivalent
 - i. Equivalent enantiotropic protons: the protons on the same carbon as Cl in chloroethane
 - ii. Non-equivalent diastereotropic protons: the protons on the number 1 carbon in 2-bromopropene

C. Interpretation: signal position

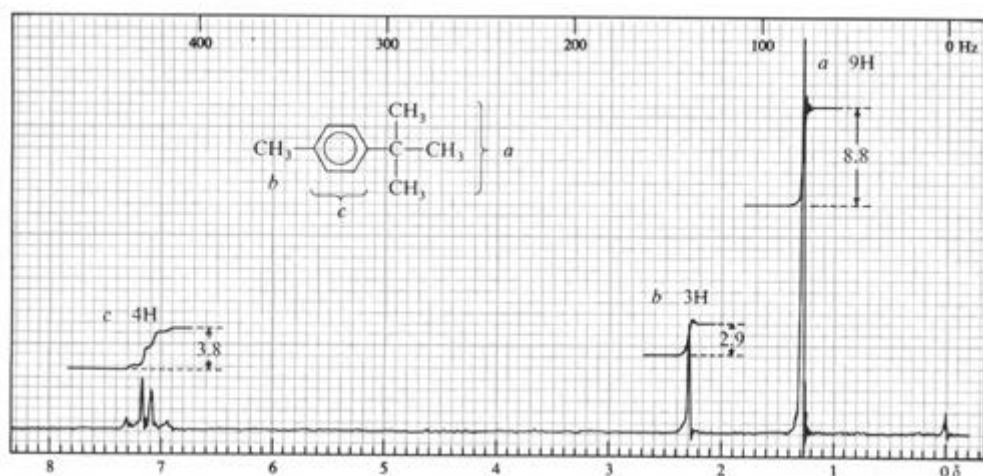


1. Signal position is used to identify the kind of proton: aliphatic, aromatic, allylic, benzylic, primary, secondary, tertiary, adjacent to heteroatoms, etc.
2. When a molecule is placed in a magnetic field its electrons are caused to circulate and generate a secondary induced magnetic field
3. Circulation of electrons around a proton generates a field in opposition to the applied field, which shields the proton
4. Circulation of electrons around adjacent nuclei (especially pi electrons) can either reinforce or take away from the shielding of the proton

5. Compared with a "naked" (unshielded) proton, a shielded proton requires a higher applied field strength (upfield shift), and a deshielded proton requires a lower applied field strength (downfield shift)
6. Shifting is expressed in ppm relative to a standard (usually TMS) with a value of 0.0 ppm
7. Table of **proton NMR shifts**
8. The inductive effect plays some role in shielding
 - a. Electron-withdrawing lowers the electron density around the proton and causes deshielding

D. Interpretation: signal intensity

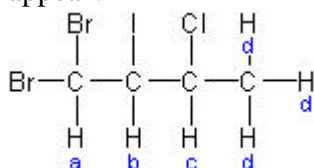
1. The area beneath a peak is directly proportional to the number of hydrogen ions responsible for the signal
2. Most NMR spectrometers electronically integrate the areas beneath spectrum peaks, although step heights are also proportional to equivalent proton numbers
3. Usually need to convert to whole number ratios
4. p-tert-butyl toluene: the ratio of a:b:c is 8.8:2.9:3.8



E. Interpretation: signal splitting (multiplicity)

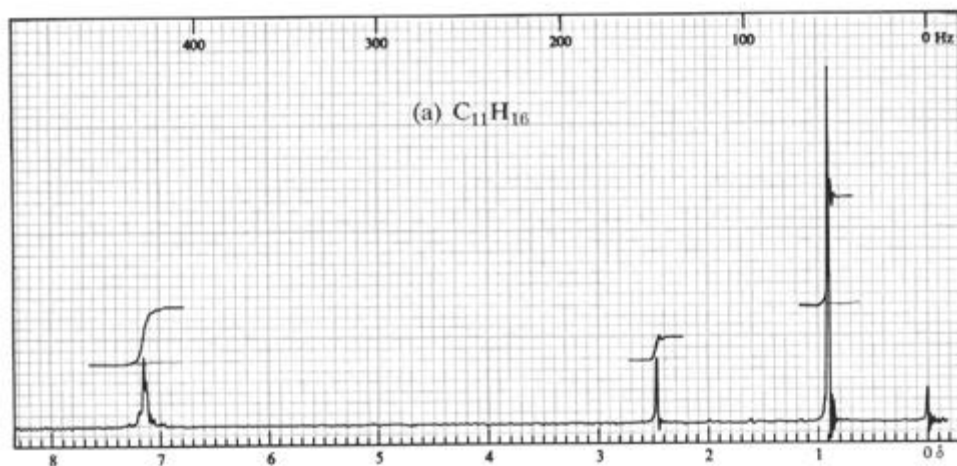
1. Multiplicity: the number of peaks into which a signal is split
2. Splitting of NMR signals is caused by spin-spin coupling (homonuclear coupling, between nuclei of the same isotope), which reflects the environment of the protons with respect to adjacent protons
3. In other words, the magnetic field a proton experiences is also influenced by the spin of adjacent protons, which can result in a slight increase or decrease in the field strength experienced by the protons
4. The experienced field strength increases if adjacent protons are aligned with the applied field
5. The experienced field strength decreases if adjacent protons are aligned against the applied field
6. For n equivalent protons there are 2ⁿ possible spin combinations which results in (n+1) different spin states
7. Example: -CH-CH₂- and the effects of adjacent protons
 - a. For secondary protons, the magnetic field experienced is
 - i. Increased if the 3° proton is aligned with the applied field
 - ii. Decreased if the 3° proton is aligned against the applied field
 - iii. Since the 3° proton can only assume one of two possible spin states (up or down), the 2° signal is split into 2 peaks
 - b. For the tertiary proton, the magnetic field experienced is
 - i. Increased if the 2° protons are aligned with the applied field

- ii. Decreased if the 2° protons are aligned against the applied field
 - iii. Since the 2° proton can only assume four possible spin states (u,u; u,d; d,u; d,d), the 3° signal is split into 4 peaks
 - c. The effect of a trio of equivalent protons on an adjacent proton is 1:3:3:1
 - d. The effect of a quartet of equivalent protons on an adjacent proton is 1:4:6:4:1
8. Usually coupling only takes place between nuclei separated by three or fewer bonds
 9. The protons must be nonequivalent
 10. Protons can couple with any atom that has a magnetic moment (I not equal to zero; beyond the scope of this class)
 11. Which of the following hydrogens will show coupling? How will the peaks appear?

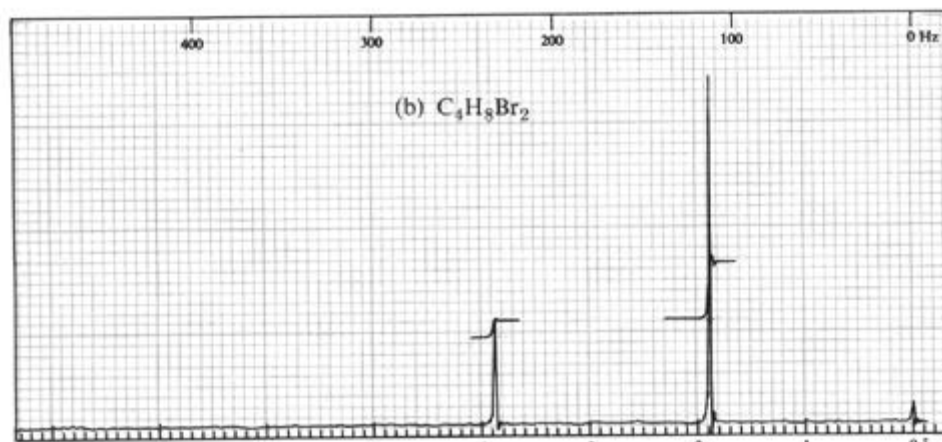


- a. a-b, b-c, c-d will show coupling
- b. Ha and Hd will appear as a doublets
- c. Hb will appear as a triplet (1:2:1) if the coupling constants are equal
- d. Hc will appear as a quintet (1:4:6:4:1) if the coupling constants are equal

F. A few examples

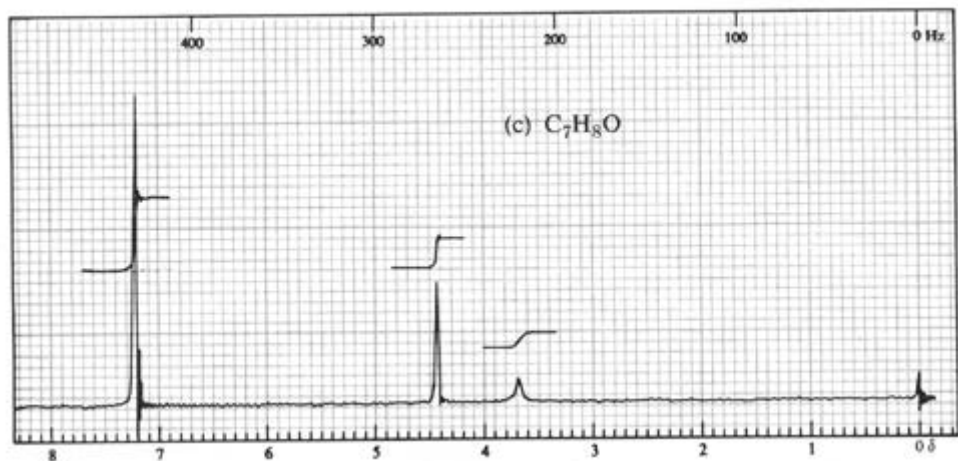


1. neopentyl benzene



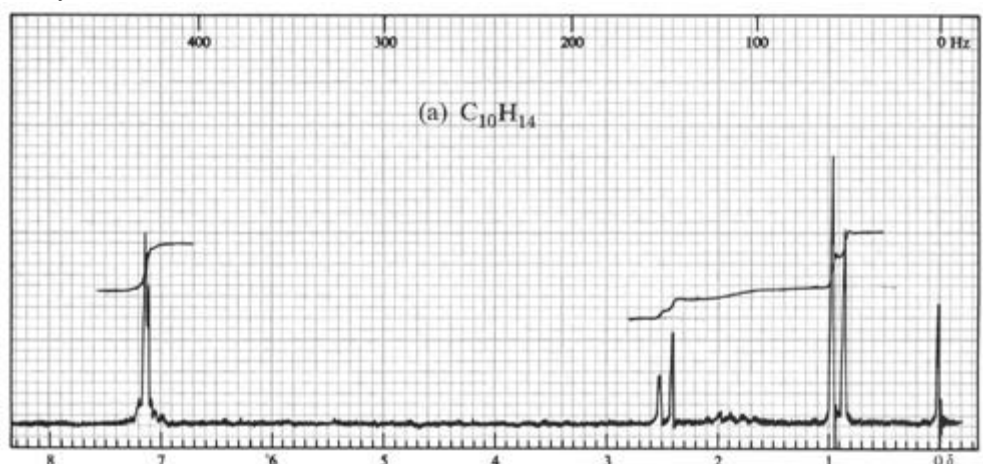
- 2.

isobutylene bromide



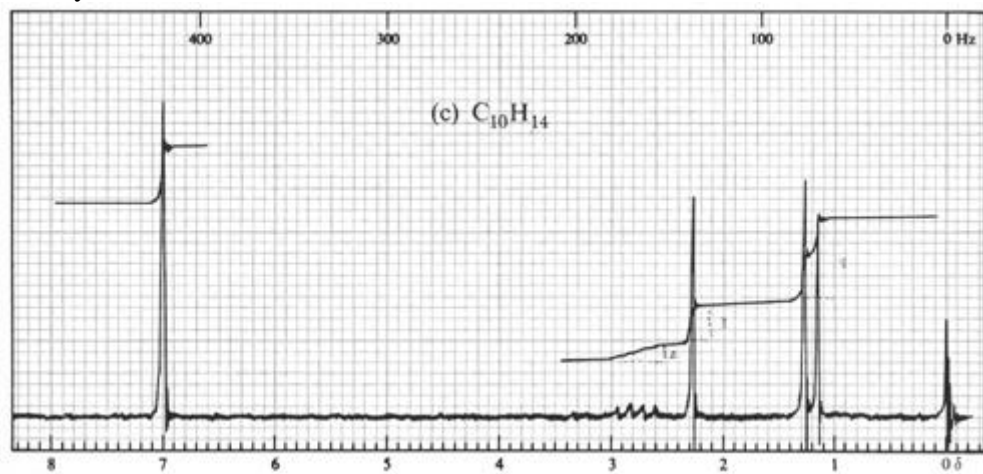
3.

benzyl alcohol



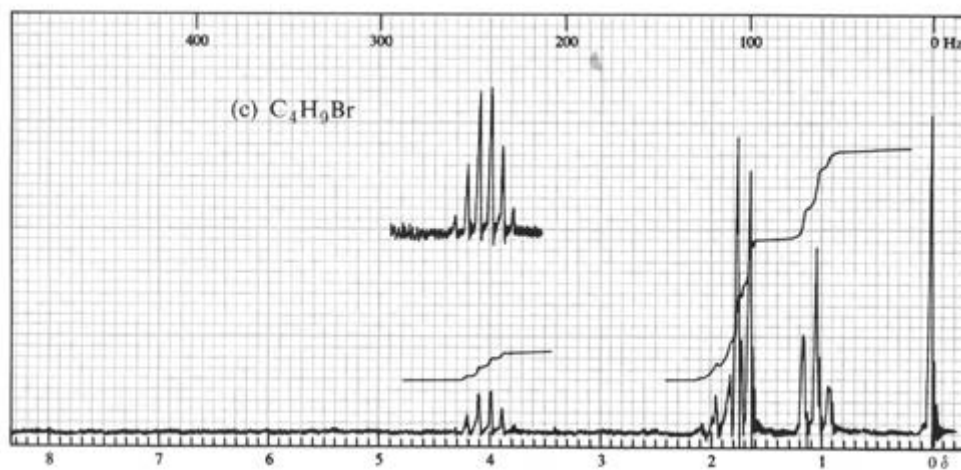
4.

isobutylbenzene



5.

p-isopropyl toluene



6. 1-methyl propyl bromide

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