

Chapter 13: NMR Spectroscopy

Learning Objectives:

1. Know how nuclear spins are affected by a magnetic field, and be able to explain what happens when radiofrequency radiation is absorbed.
2. Be able to predict the number of proton and carbon NMR signals expected from a compound given its structure.
3. Be able to predict the splitting pattern in the proton NMR spectrum of a compound given its structure.
4. With the aid of a chart of chemical shifts from ^1H and ^{13}C NMR, be able to assign peaks in an NMR spectrum to specific protons in a compound.
5. Be able to interpret integration of NMR spectra.
6. Be able to use NMR spectra to determine the structures of compounds, given other information such as a molecular formula.
7. Be able to calculate coupling constants from ^1H NMR spectra, and utilize the coupling constants for determining compound structure.*
8. Be able to determine the compound structure based on information generated from mass spectrometry, IR, NMR, and elemental analysis.*

* Supplemental material, not included in the textbook

Sections:

- 13.1 An Introduction to NMR Spectroscopy
- 13.2 Fourier Transform NMR
- 13.3 Shielding Causes Different Hydrogens to Show Signals at Different Frequencies*
- 13.4 The Number of Signals in an ^1H NMR Spectrum*
- 13.5 The Chemical Shift Tells How Far the Signal Is from the Reference Signal*
- 13.6 The Relative Position of ^1H NMR Signals*
- 13.7 Characteristic Values of Chemical Shifts*
- 13.8 Diamagnetic Anisotropy
- 13.9 Integration of NMR Signals Reveals the Relative Number of Protons Causing the Signal*
- 13.10 Splitting of the Signals Is Described by the N+1 Rule*
- 13.11 More Examples of ^1H NMR Spectra*
- 13.12 Coupling Constants Identify Coupled Protons*
- 13.13 Splitting Diagrams Explain the Multiplicity of a Signal*
- 13.14 Diastereotopic Hydrogens Are Not Chemically Equivalent
- 13.15 The Time Dependence of NMR Spectroscopy
- 13.16 Protons Bonded to Oxygen and Nitrogen*
- 13.17 The Use of Deuterium in ^1H NMR Spectroscopy[#]
- 13.18 Resolution of ^1H NMR Spectra
- 13.19 ^{13}C NMR Spectroscopy*
- 13.20 DEPT ^{13}C NMR Spectra[#]
- 13.21 Two-dimensional NMR Spectroscopy[#]
- 13.22 NMR Used in Medicines Is Called Magnetic Resonance Imaging

* Sections that will be focused

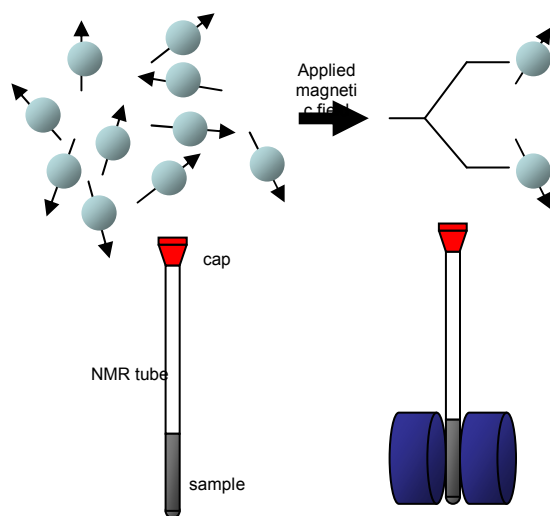
Sections that will be skipped

Recommended additional problems

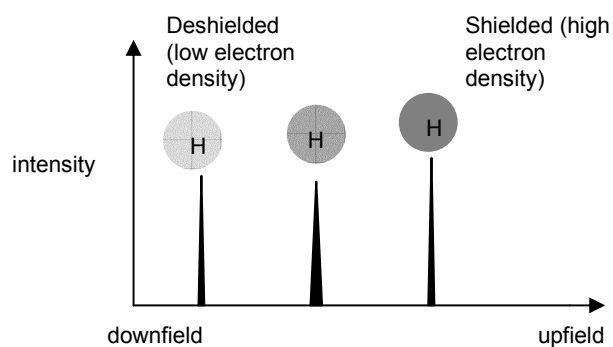
43 – 63, 65 – 72

Class Note

13.1 An Introduction to NMR Spectroscopy and 13.2 Fourier Transform NMR

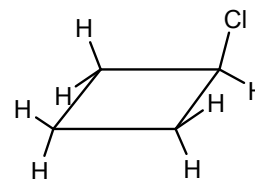
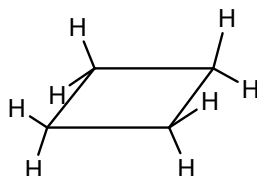
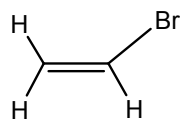
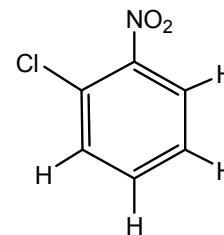
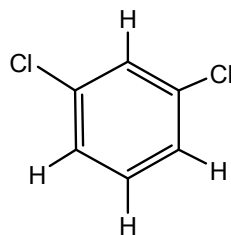
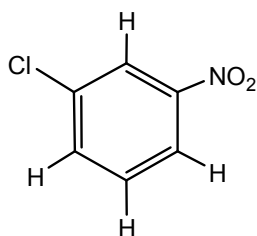
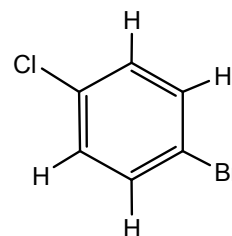
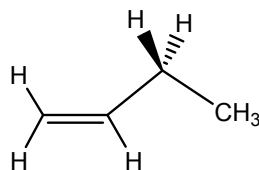
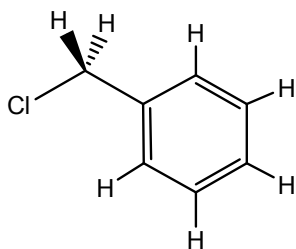
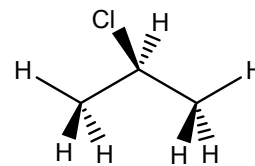
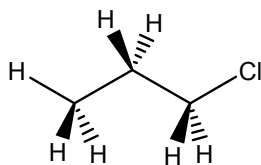
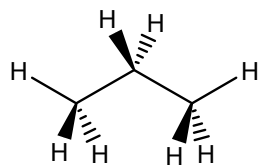


13.3 Shielding Causes Different Hydrogens to Show Signals at Different Frequencies*



13.4 The Number of Signals in an ^1H NMR Spectrum*

***Judge the chemical equivalent of H by the symmetry of molecule**



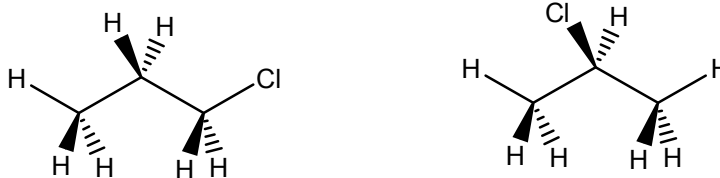
- 13.5 The Chemical Shift Tells How Far the Signals Is from the Reference Signal*,
13.6 The Relative Position of ^1H NMR Signals* and 13.8 Diamagnetic Anisotropy

Internal reference compound: CHCl_3 (from CDCl_3) and $(\text{CH}_3)_4\text{Si}$ (TMS)

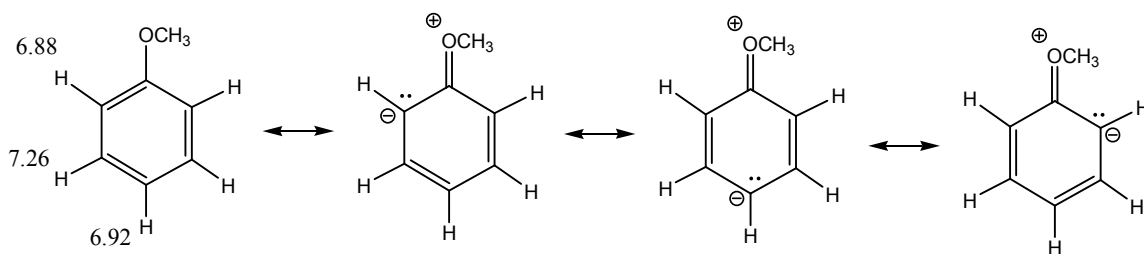
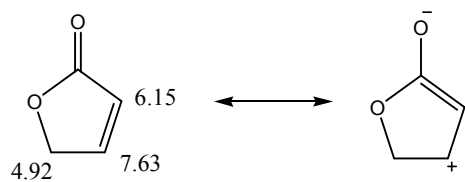
***Signal of TMS = 0 ppm ($\text{CHCl}_3 = 7.27$ ppm)**

***Chemical shift (δ)**

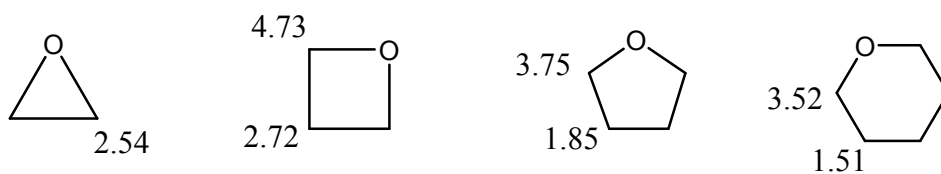
A. Effect from electronegativity (inductive effect)



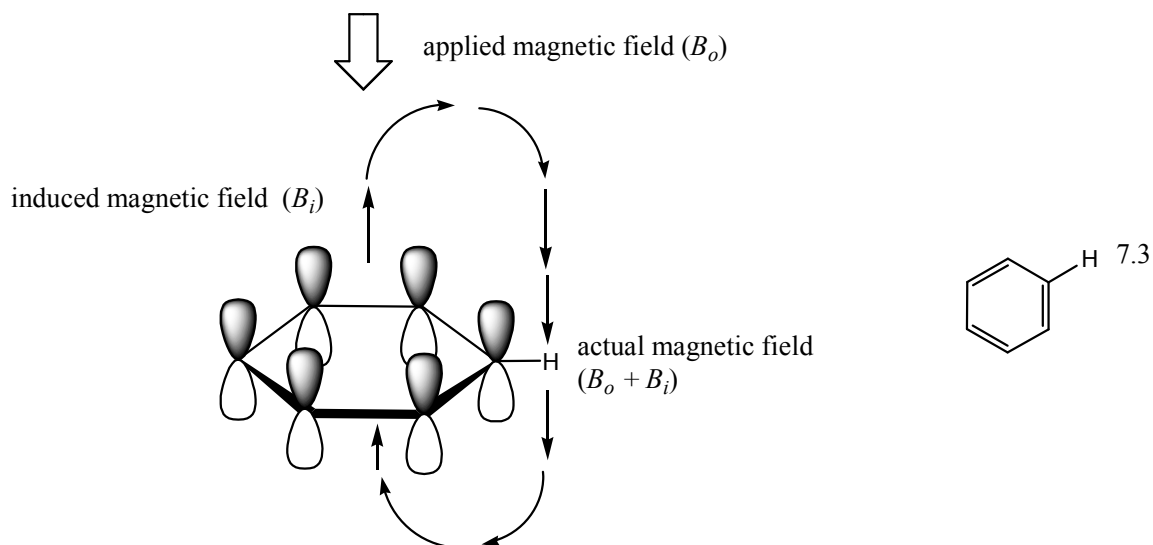
B. Effect from resonance



C. Effect from structure



D. Diamagnetic Anisotropy (anisotropic effect)



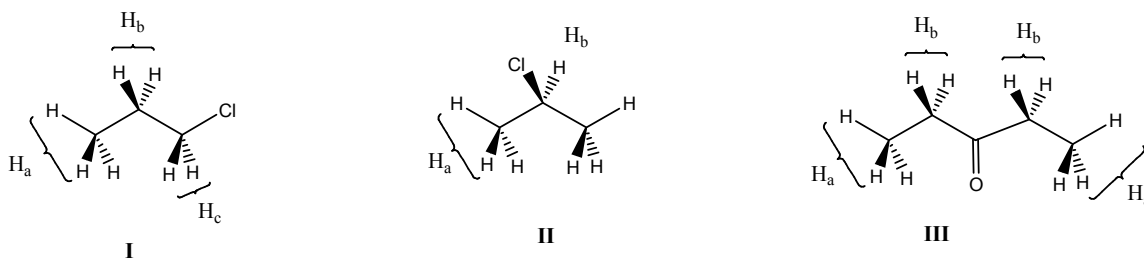
13.7 Characteristic Values of Chemical Shifts*

Table 13.1

13.9 Integration of NMR Signals Reveals the Relative Number of Protons Causing the Signal*

* Diagnostic for ^1H NMR but less accurate for ^{13}C NMR

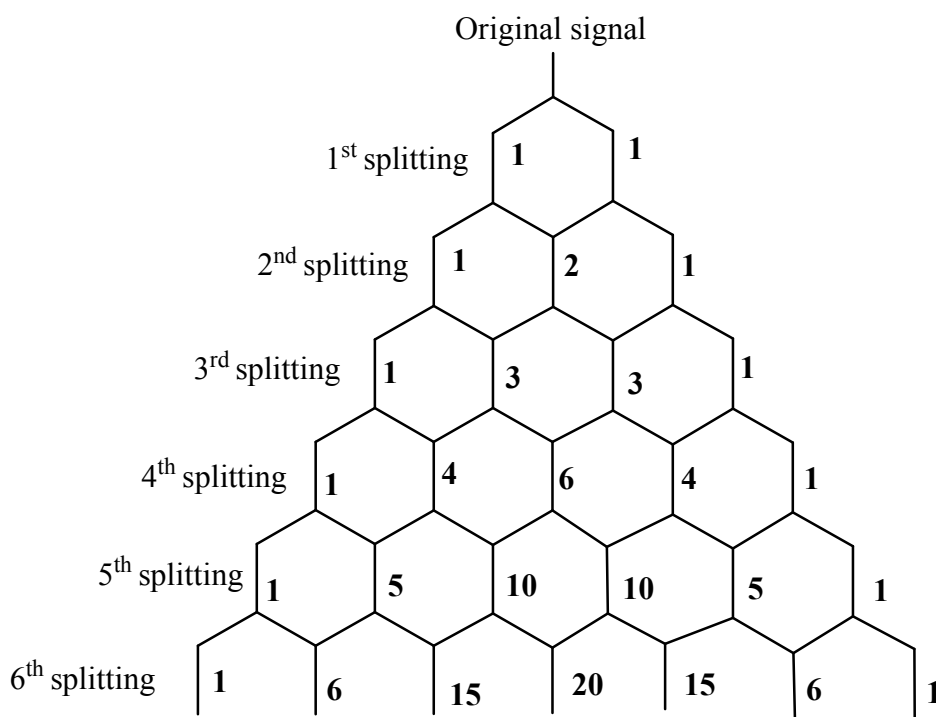
* Ratio rather than exact number



13.10 Splitting of the Signals Is Described by the N+1 Rule*

A. Multiplicity of Signal and Relative Intensities

Ratio	Multiplicity
1 : 1	doublet
1 : 2 : 1	triplet
1 : 3 : 3 : 1	quartet
1 : 4 : 6 : 4 : 1	quintet
1 : 5 : 10 : 10 : 5 : 1	sextet
1 : 6 : 15 : 20 : 15 : 6 : 1	septet

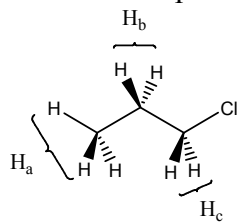


Two important criteria:

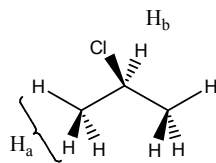
* For $I = 1/2$

* For chemically equivalent nuclei

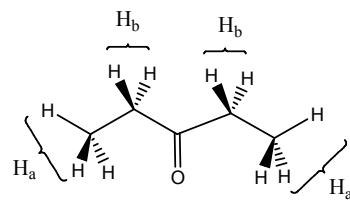
B. Examples



I



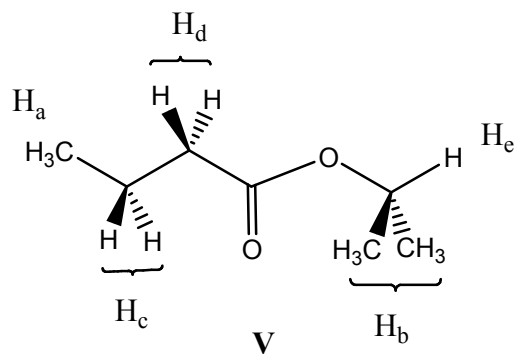
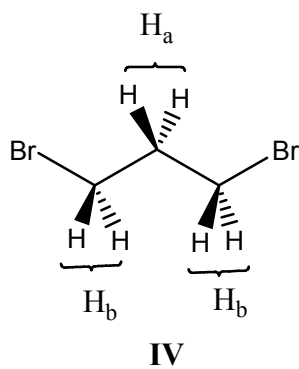
II



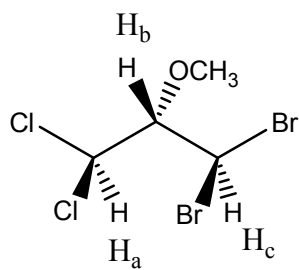
III

13.11 More Examples of ^1H NMR Spectra*

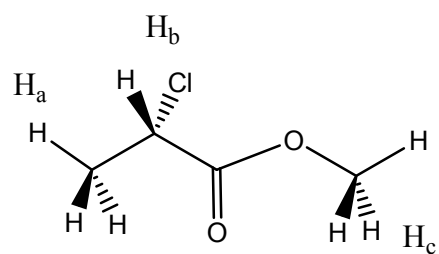
A. More examples



B. Difference between quartet (q) and doublet of doublet (dd)



VI

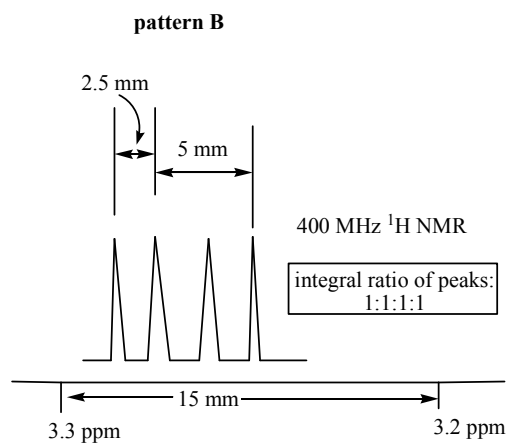
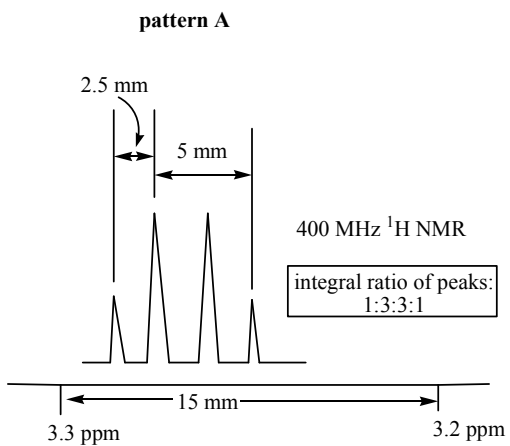


VII

13.12 Coupling Constants Identify Coupled Protons* and 13.13 Splitting Diagrams
Explain the Multiplicity of a Signal*

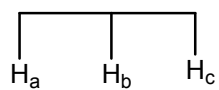
A. Table 14.3 and handout

B. Calculation of coupling constant (J value)



C. Splitting diagrams and J values

(1)



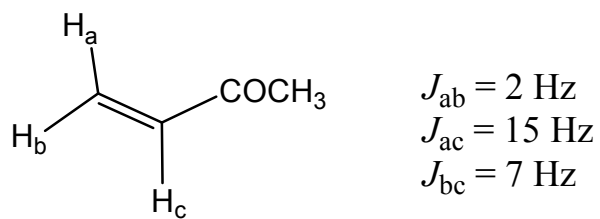
(1) $J_{ab} = J_{ac}$

(2) $J_{ab} > J_{ac}$

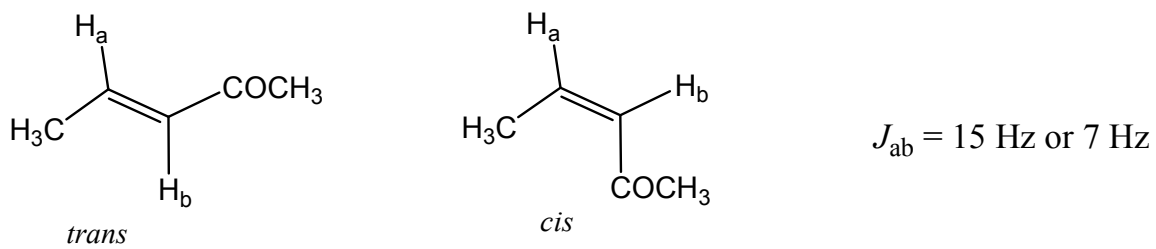
(2) long range coupling (4 bonds)

D. Structure determination and J values

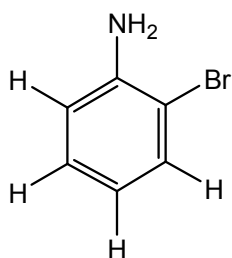
(1) Example 1



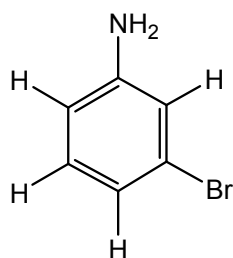
(2) Example 2: determination of *cis* and *trans* isomers



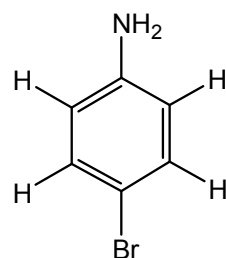
(3) Example 3: determination of the regioisomers of di-substituted benzene derivatives



1,2-di-substituted
(ortho)

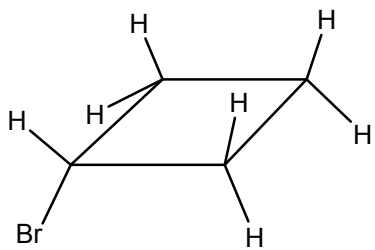


1,3-di-substituted
(meta)



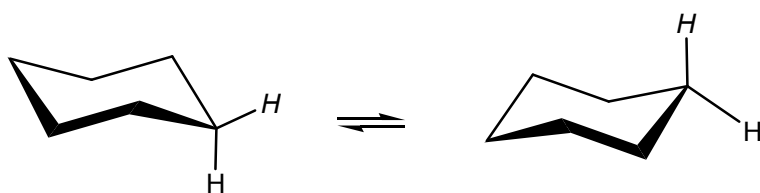
1,4-di-substituted
(para)

13.14 Diastereotopic Hydrogens Are Not Chemically Equivalent



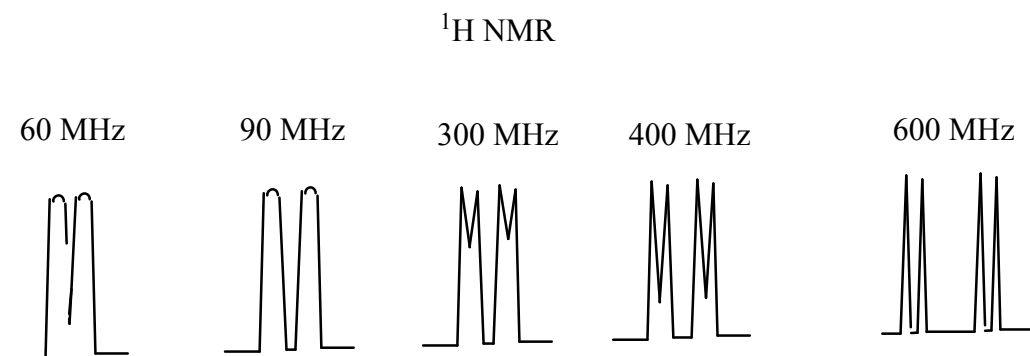
13.15 The Time Dependence of NMR Spectroscopy

Figure 13.29



13.16 Protons Bonded to Oxygen and Nitrogen* and 13.17 The Use of Deuterium in ^1H NMR Spectroscopy[#]

13.18 Resolution of ^1H NMR Spectra



13.19 ^{13}C NMR Spectroscopy*

A. Table 13.4

Chemical shift and height (intensity)

B. Proton-coupled and proton-decoupled ^{13}C spectra

13.22 NMR Used in Medicines Is Called Magnetic Resonance Imaging

