

Chapter 14: 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:

- 14.1 Introduction to NMR Spectroscopy
- 14.2 Fourier Transform NMR
- 14.3 Shielding*
- 14.4 The Number of Signals in the ^1H NMR Spectrum*
- 14.5 The Chemical Shift*
- 14.6 The Relative Position of ^1H NMR Signals*
- 14.7 Characteristic Values of Chemical Shifts*
- 14.8 Integration of NMR Signals*
- 14.9 Diamagnetic Anisotropy
- 14.10 Splitting of the Signals*
- 14.11 More Examples of ^1H NMR Spectra*
- 14.12 Coupling Constants*
- 14.13 Splitting Diagrams*
- 14.14 Time Dependence of NMR Spectroscopy
- 14.15 Protons Bonded to Oxygen and Nitrogen*
- 14.16 Use of Deuterium in ^1H NMR Spectroscopy[#]
- 14.17 Resolution of ^1H NMR Spectra
- 14.18 ^{13}C NMR Spectroscopy*
- 14.19 DEPT ^{13}C NMR Spectra[#]
- 14.20 Two-dimensional NMR Spectroscopy[#]

* Sections that will be focused

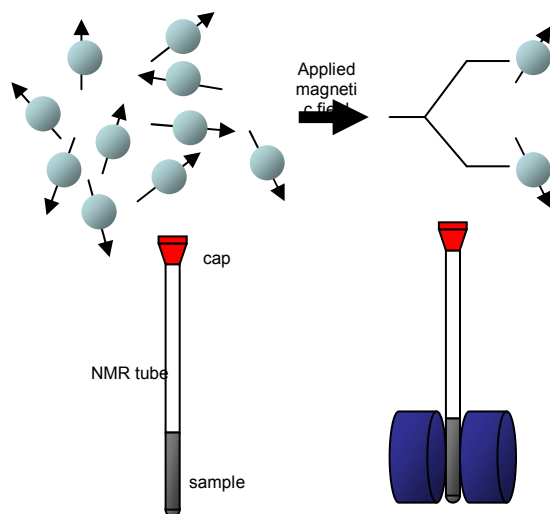
[#] Sections that will be skipped

Recommended additional problems

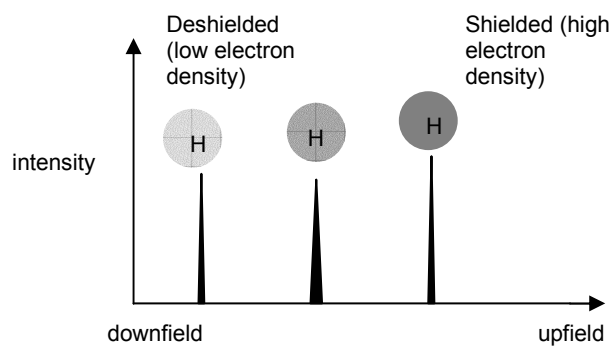
41 – 61, 63 – 71

Class Note

14.1 Introduction to NMR Spectroscopy and 14.2 Fourier Transform NMR

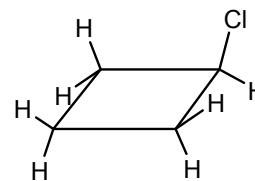
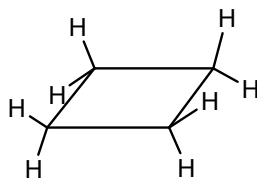
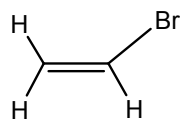
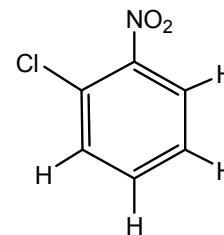
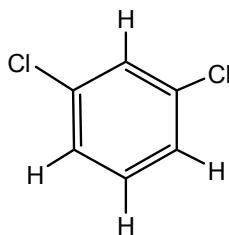
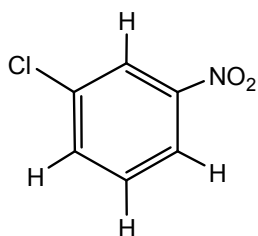
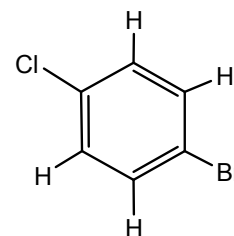
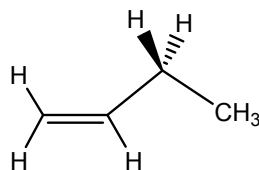
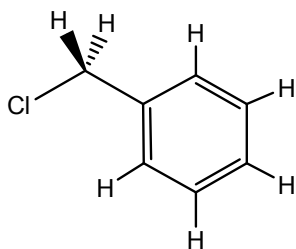
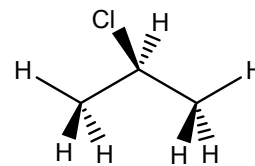
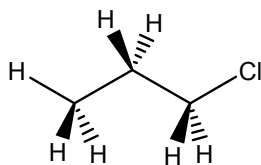
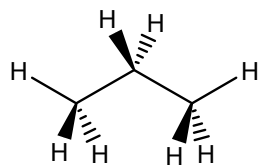


14.3 Shielding



14.4 The Number of Signals in the ^1H NMR Spectrum

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



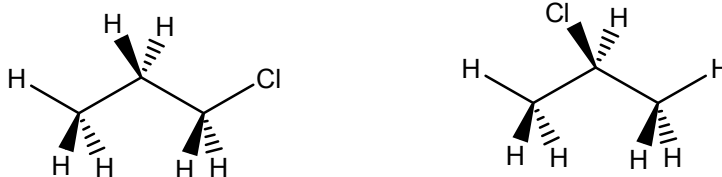
14.5 The Chemical Shift, 14.6 The Relative Position of ^1H NMR Signals, and 14.9 Diamagnetic Anisotropy

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

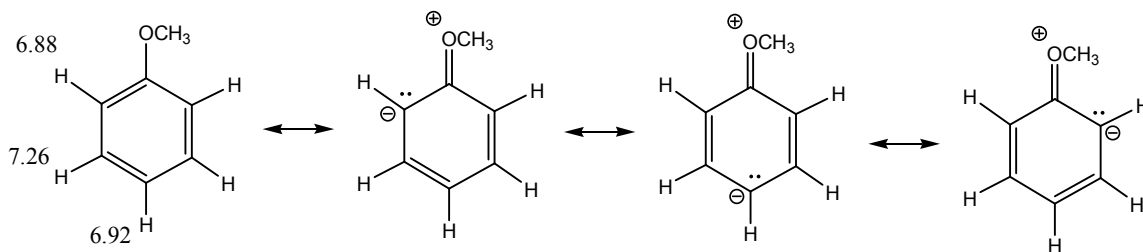
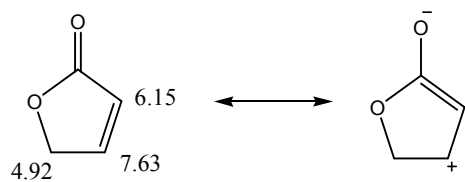
***Signal of TMS = 0 ppm ($\text{CHCl}_3 = 7.27$ ppm)**

***Chemical shift (δ)**

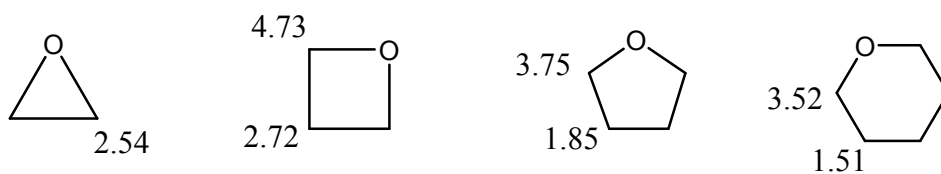
A. Effect from electronegativity (inductive effect)



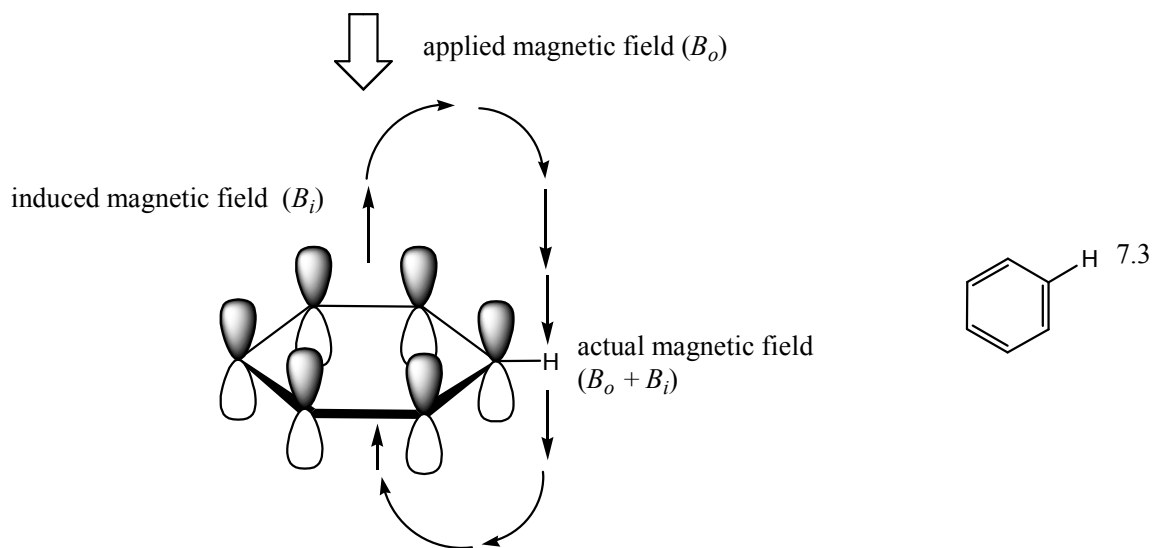
B. Effect from resonance



C. Effect from structure



D. Diamagnetic Anisotropy (anisotropic effect)



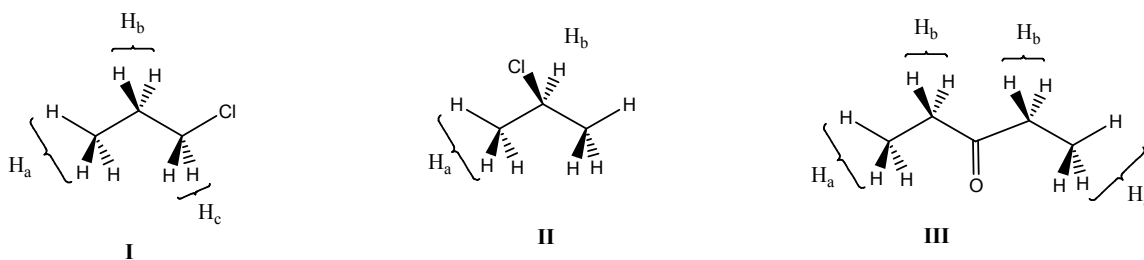
14.7 Characteristic Values of Chemical Shifts

Table 14.1

14.8 Integration of NMR Signals

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

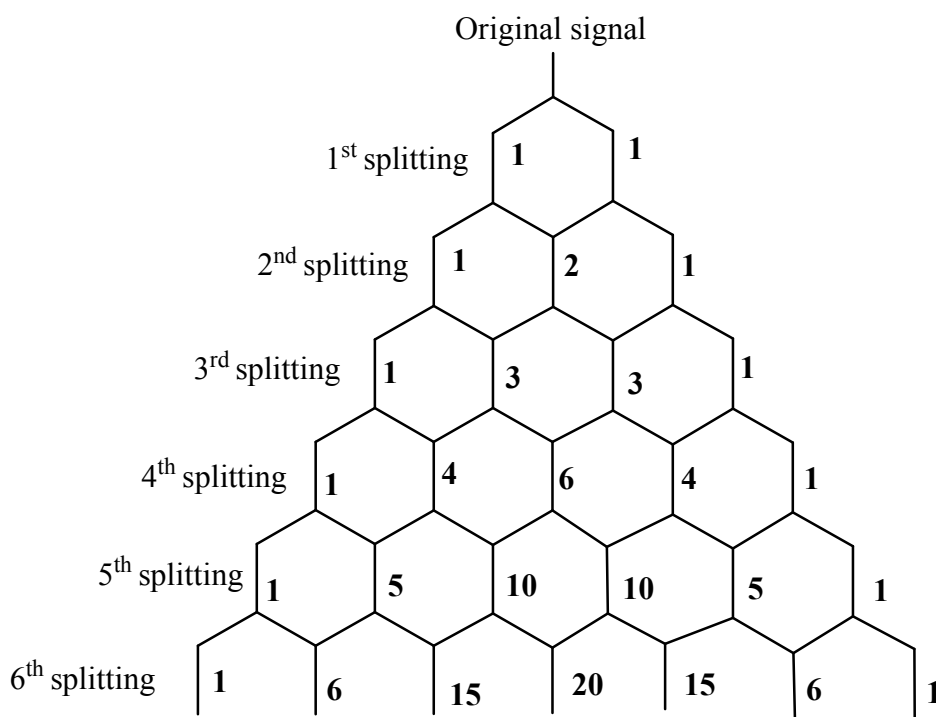
* Ratio rather than exact number



14.10 Splitting of the Signals

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

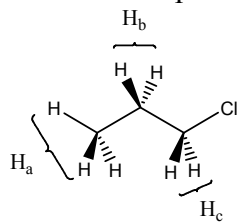


Two important criteria:

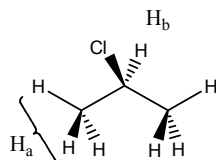
* For $I = 1/2$

* For chemically equivalent nuclei

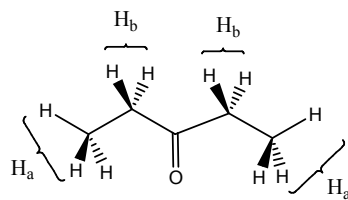
B. Examples



I



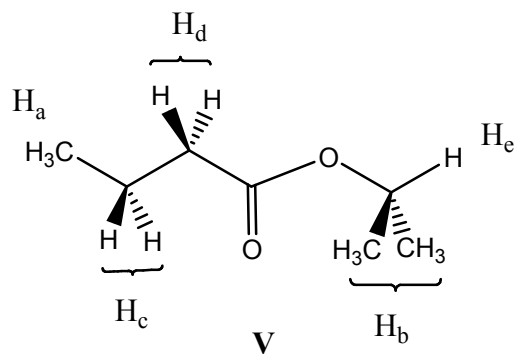
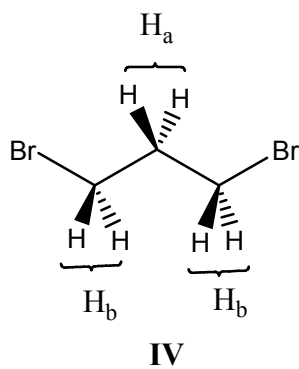
II



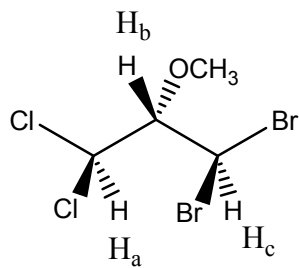
III

14.11 More Examples of ^1H NMR Spectra

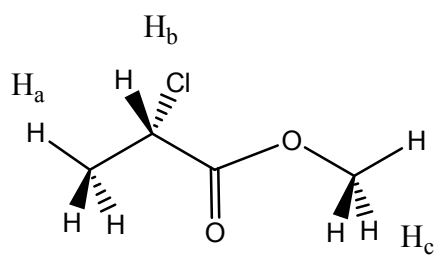
A. More examples



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



VI

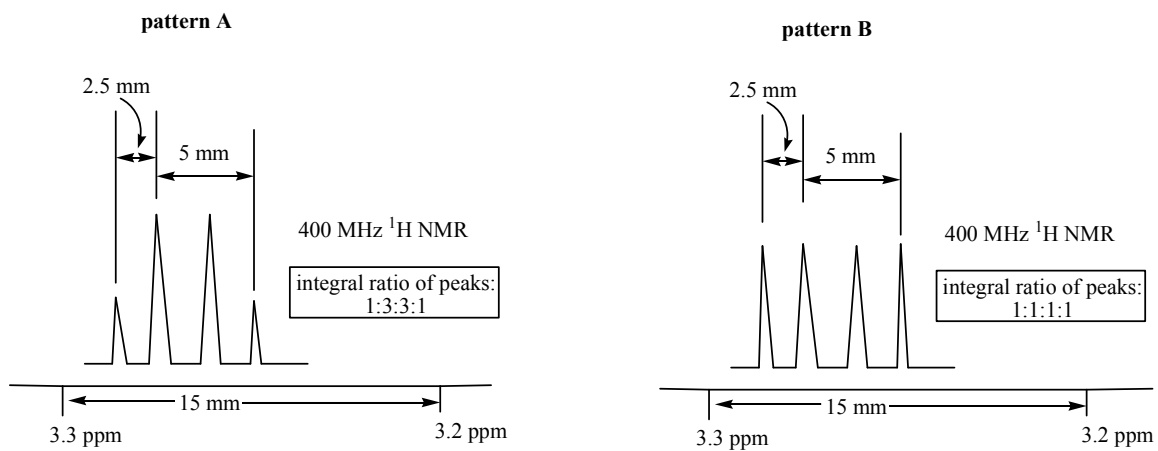


VII

14.12 Coupling Constants and 14.13 Splitting Diagrams

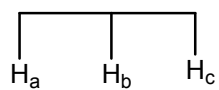
A. Table 14.3 and handout

B. Calculation of coupling constant (J value)



C. Splitting diagrams and J values

(1)



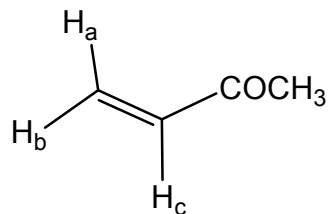
(1) $J_{ab} = J_{ac}$

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

(2) long range coupling (4 bonds)

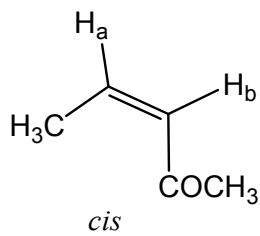
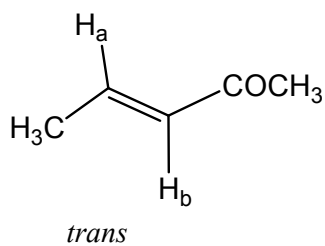
D. Structure determination and J values

(1) Example 1



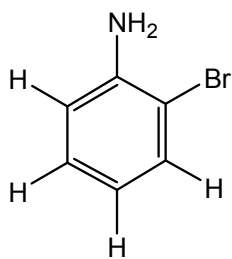
$$\begin{aligned} J_{ab} &= 2 \text{ Hz} \\ J_{ac} &= 15 \text{ Hz} \\ J_{bc} &= 7 \text{ Hz} \end{aligned}$$

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

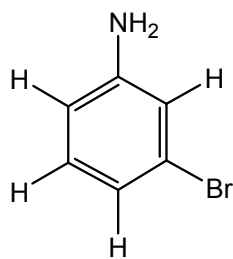


$$J_{ab} = 15 \text{ Hz or } 7 \text{ Hz}$$

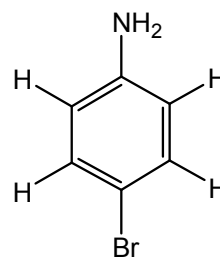
(3) Example 3: determination of the regioisomers of di-substituted benzene derivatives



1,2-di-substituted
(ortho)



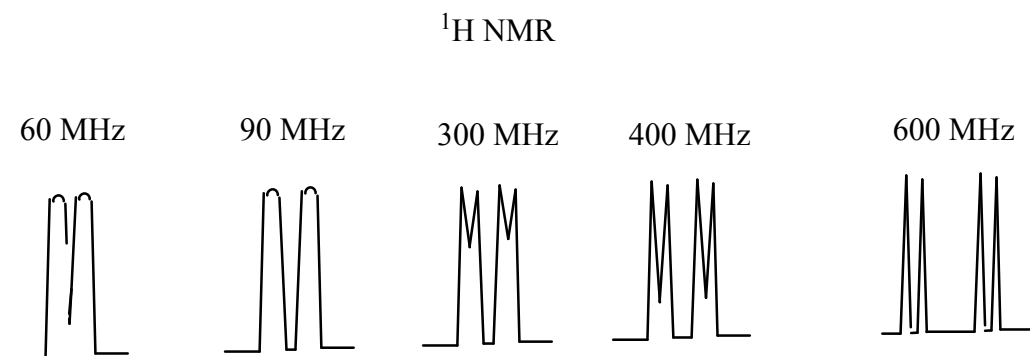
1,3-di-substituted
(meta)



1,4-di-substituted
(para)

14.15 Protons Bonded to Oxygen and Nitrogen and 14.16 Use of Deuterium in ^1H NMR Spectroscopy

14.17 Resolution of ^1H NMR Spectra



14.18 ^{13}C NMR Spectroscopy

A. Table 14.4

Chemical shift and height (intensity)

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