Nuclear Spin Interactions
Multiple Spin Systems

- Thus far, we have concentrated on spin-spin coupling with only one other nonequivalent set of H atoms
- More complex splittings arise when a set of H atoms couples to more than one set H atoms
- A tree diagram shows that when H_b is adjacent to nonequivalent H_a on one side and H_c on the other, the resulting coupling gives rise to a doublet of doublets

www.anilmishra.name   14

Nuclear Spin Interactions
Multiple Spin Systems
A Splitting Diagram for a Doublet of Doublets

www.anilmishra.name   15

Nuclear Spin Interactions
Multiple Spin Systems

- if H_c is a set of two equivalent H, then the observed splitting is a doublet of triplets

www.anilmishra.name   16

Nuclear Spin Interactions
Multiple Spin Systems

multiplicity → $(n_a+1)(n_b+1)$

What is the splitting pattern for CH_2?

$^3J_{Hb} = 6$ Hz
$^3J_{Ha} = 7$ Hz

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1
1 7 21 35 35 21 7 1

$^3J_{Hb} = 6$ Hz

Coupling to H_b splits the CH_2 resonance into a doublet separated by 6 Hz

Down-field resonance split into quartet

Coupling to H_a splits each doublet into a quartet separated by 7 Hz

up-field resonance split into quartet

www.anilmishra.name   17

Nuclear Spin Interactions
Multiple Spin Systems

Coupling Constants Provide Connectivity Information
– chemical shifts identify what functional groups are present

NMR Peaks for coupled nuclei share the same coupling constants

CH   CH₂   CH₃

6 Hz 6 Hz   7 Hz 6 Hz 6 Hz 7 Hz   7 Hz 7 Hz

Integral: 1   2   3

www.anilmishra.name   18

Nuclear Spin Interactions
Multiple Spin Systems

- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- Example: H^a of styrene which is split by an adjacent H *trans* to it (J = 17 Hz) and an adjacent H *cis* to it (J = 11 Hz).

www.anilmishra.name   19

Nuclear Spin Interactions
Multiple Spin Systems

Nuclear Spin Interactions
Multiple Spin Systems

- in ethyl propenoate, an unsymmetrical terminal alkene, the three vinylic hydrogens are nonequivalent

Nuclear Spin Interactions
Multiple Spin Systems

- Because the angle between C-H bond determines the extent of coupling, bond rotation is a key parameter
- In molecules with relatively free rotation about C-C sigma bonds, H atoms bonded to the same carbon in CH_3 and CH_2 groups generally are equivalent
- If there is restricted rotation, as in alkenes and cyclic structures, H atoms bonded to the same carbon may not be equivalent
- Nonequivalent H on the same carbon will couple and cause signal splitting
- This type of coupling is called geminal coupling

Nuclear Spin Interactions
Karplus Equation

The magnitude of the J coupling is dictated by the torsion Angle (dihedral Angle) between the two coupling nuclei according to the Karplus equation.

$$J = A + B\cos(\theta) + C \cos^2(\theta)$$
$$A = 1.9, B = -1.4, C = 6.4$$

Karplus Relation

A, B and C Depends on the substituent electronegativity.

Interpreting NMR Spectra

- Alkanes
  - ^{1}H-NMR signals appear in the range of δ 0.8-1.7
  - ^{13}C-NMR signals appear in the considerably wider range of δ 10-60
- Alkenes
  - ^{1}H-NMR signals appear in the range δ 4.6-5.7
  - ^{1}H-NMR coupling constants are generally larger for *trans* vinylic hydrogens (J= 11-18 Hz) compared with *cis* vinylic hydrogens (J= 5-10 Hz)
  - ^{13}C-NMR signals for sp^2 hybridized carbons appear in the range δ 100-160, which is downfield from the signals of sp^3 hybridized carbons

Interpreting NMR Spectra

Interpreting NMR Spectra

- Alcohols
- ¹H-NMR O-H chemical shifts often appears in the range δ 3.0-4.0, but may be as low as δ 0.5.
  - ¹H-NMR chemical shifts of hydrogens on the carbon bearing the -OH group are deshielded by the electron-withdrawing inductive effect of the oxygen and appear in the range δ 3.0-4.0
- Ethers
  - a distinctive feature in the ¹H-MNR spectra of ethers is the chemical shift, δ 3.3-4.0, of hydrogens on carbon attached to the ether oxygen
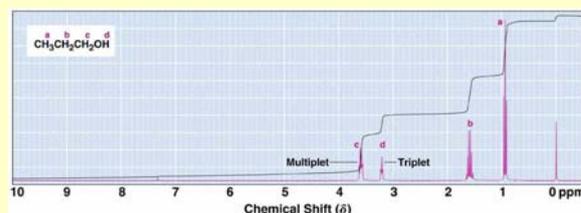
www.anilmishra.name   26

Interpreting NMR Spectra

- ¹H-NMR spectrum of 1-propanol

www.anilmishra.name   27

Interpreting NMR Spectra

- Aldehydes and ketones
  - ¹H-NMR: aldehyde hydrogens appear at δ 9.5-10.1
  - ¹H-NMR: a-hydrogens of aldehydes and ketones appear at δ 2.2-2.6
  - ¹³C-NMR: carbonyl carbons appear at δ 180-215
- Amines
  - ¹H-NMR: amine hydrogens appear at δ 0.5-5.0 depending on conditions

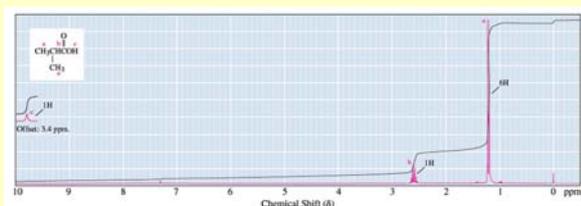www.anilmishra.name   28

Interpreting NMR Spectra

- Carboxylic acids
  - ¹H-NMR: carboxyl hydrogens appear at δ 10-13, lower than most any other hydrogens
  - ¹³C-NMR: carboxyl carbons in acids and esters appear at δ 160-180

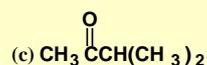www.anilmishra.name   29

Interpreting NMR Spectra
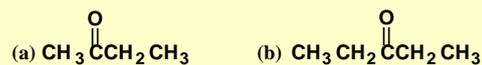

www.anilmishra.name   30

Problems

predict the number of ¹H-NMR signals and the splitting pattern of each

(a) $CH_3CCH_2CH_3$ (with C=O)   (b) $CH_3CH_2CCH_2CH_3$ (with C=O)

(c) $CH_3CCH(CH_3)_2$ (with C=O)

www.anilmishra.name   31

Interpreting NMR Spectra

Molecular formula C_3H_8O

Interpreting NMR Spectra

Molecular formula $C_7H_{12}O_4$

Interpreting NMR Spectra

Molecular formula $C_5H_{10}O$

Interpreting NMR Spectra

Molecular formula C_8H_{10}

Interpreting NMR Spectra

Molecular formula $C_7H_{14}O$

Interpreting NMR Spectra

Molecular formula $C_7H_{14}O$