JS Organic Practical Course

Carbon-13 and Carbon-DEPT Spectra
Additional 2D and other NMR data
General IR information
Selected reading list
Generic Carbon-13 data is provided for various products produced in the Junior Sophister Organic Chemistry Practical Course

A standard carbon-13 spectrum (proton decoupled) is provided.
Routine Carbon-13 nmr spectra are not run because of time constraints.
Remember that the carbon-13 nuclide only constitutes 1% of all carbon isotopes.
All the samples were prepared in CDCl₃. The CDCl₃ solvent signal is observed as a triplet centred at 77.0 ppm.
The relevant peaks are listed in ppm. The excitation frequency for the 9.4T magnet is 100.62MHz

Additional carbon spectra to determine the number of protons attached to a given signal are provided using the Carbon-13 DEPT 135° and Carbon-13 DEPT 90° experiments. These spectra are displayed in a comparative format.

Carbon DEPT experiments are read as follows:

DEPT 135°
CH₂ resonances are inverted
CH₃ and CH remain normal upward phase

DEPT 90°
CH resonances only are observed
C with no protons attached are NOT seen in DEPT experiments

Carbon-13 spectra are provided for the following products:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Product Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cis-5,5,10,10-Tetrachlorotricyclo[7.1.0.0⁴,6]decane</td>
</tr>
<tr>
<td>2A</td>
<td>Diethyl Benzylphosphonate</td>
</tr>
<tr>
<td>2B</td>
<td>(E,E)-1,4-Diphenyl-1,3-butadiene</td>
</tr>
<tr>
<td>3A</td>
<td>cis-Cyclohex-4-ene-1,2-dicarboxylic acid anhydride</td>
</tr>
<tr>
<td>3B</td>
<td>cis-Cyclohex-4-ane-1,2-dicarboxylic acid anhydride</td>
</tr>
<tr>
<td>4</td>
<td>2,6-Dimethyl-5-hydroxy-heptan-3-one</td>
</tr>
<tr>
<td>5A</td>
<td>1-Phenyl-1,4-butanediol</td>
</tr>
<tr>
<td>5B</td>
<td>γ-Phenyl-γ-butyrolactone</td>
</tr>
<tr>
<td>6</td>
<td>(-)cis-Caran-trans-4-ol</td>
</tr>
</tbody>
</table>

A phosphorous-31 spectrum is provided for DethylBenzylphosphonate (2A)
Phosphorous-31 is an NMR active spin ½ nuclide The excitation frequency for the 9.4T magnet is 162 MHz
On closer inspection of the carbon-13 spectrum - three additional signals are observed. What can these signals be attributed to?
Experiment 1  \textit{Cis-5,5,10,10-Tetrachlorotricyclo[7.1.0.0^{4,6}]decane}
Why are the carbon-13 split into doublets?
Experiment 2a $^{31}$P NMR  Diethyl Benzylphosphonate
Experiment 2b  $^{13}$C NMR  (E,E)-1,4-Diphenyl-1,3-butadiene
Experiment 2b  $^{13}$C NMR  (E,E)-1,4-Diphenyl-1,3-butadiene
Experiment 3a  cis-Cyclohex-4-ene-1,2-dicarboxylic acid anhydride
Experiment 3a  

cis-Cyclohex-4-ene-1,2-dicarboxylic acid anhydride
Experiment 3b  cis-Cyclohex-4-ane-1,2-dicarboxylic acid anhydride
Experiment 3b  cis-Cyclohex-4-ane-1,2-dicarboxylic acid anhydride
Experiment 4  2,6-Dimethyl-5-hydroxy-heptan-3-one
Experiment 4  2,6-Dimethyl-5-hydroxy-heptan-3-one
Experiment 5a  1-Phenyl-1,4-butanediol
Experiment 5a  1-Phenyl-1,4-butanediol
Experiment 5b  γ-Phenyl-γ-butyrolactone
Experiment 5b  \( \gamma \)-Phenyl-\( \gamma \)-butyrolactone
Experiment 6  
(-)cis-Caran-trans-4-ol
Experiment 6  (-)cis-Caran-trans-4-ol
Additional NMR spectral data to aid structural determination

The information in the spectral data is provided to:
- simplify some complexity found in proton spectra
- link proton and carbon data
- allow clearer explanation(s) of the structure

Types of data are supplied:
- 2D homonuclear correlation spectra (HH COSY or TOCSY)
- 2D heteronuclear correlation spectra (CH COSY or HSQC)
- 2D Long range heteronuclear correlation spectra (HMBC)
- 1D Selective TOCSY (homonuclear correlation)
- 1D Selective Nuclear Overhauser spectra (NOE)
Additional NMR Data is supplied for experiments:

-1 cis-5,5,10,10-Tetrachlorotricyclo[7.1.0.04,6]decane
-2b (E,E)-1,4-diphenyl-1,3-butadiene
-3a cis-Cyclohex-4-ene-1,2-dicarboxylic Acid Anhydride
-3b cis-Cyclohexane-1,2-dicarboxylic Acid Anhydride
-4 (2,6-Dimethyl-3-heptan-5-one)
-5a (1-Phenylbutane-1,4-diol)
-5b (γ-Phenyl-γ-butyrolactone)
-6 (cis-Caran-trans-4-ol)
Summary of other NMR experiments
Connections through bonds and space

• Correlation Spectra (COSY) – through bond connections
  HH COSY - connections of proton spins through bonds
  1D selective TOCSY (HH COSY like)
  CH COSY (HSQC) - direct link of carbon to proton(s)
  Long range CH COSY (HMBC)

• Connections through space
  Nuclear Overhauser (NOE) experiments
    1D : 1D selective NOE
    2D : NOESY, ROESY
How to read a COSY

- **HH COSY**
  diagonal is the 1D spectrum
  off diagonal signal(s) display the connections of the spins
  true signal *must* have mirror image across the diagonal

- **CH COSY**
  signals are the direct correlation between the C and H

- **Long range CH COSY**
  often can correlate several protons to a carbon
  (or *vice versa* - whichever is most appropriate)
  e.g. links carbon signals with NO protons directly attached
Direct correlation of the hydrogen to carbon resonances

what is the second compound?
2B  CH COSY  (E,E)-1,4-Diphenyl-1,3-butadiene

$^{13}$C - HSQC NMR experiment

Direct correlation of the hydrogen to carbon resonances
Diagonal contains the 1D spectrum

Connections between hydrogens are symmetrical about the diagonal

Generally, the higher the contour the stronger the connection
3A cis-Cyclohex-4-ene-1,2-dicarboxylic Acid Anhydride

CH COSY (edited HSQC)

Direct correlation of the hydrogen to carbon resonances
cis-Cyclohex-4-ene-1,2-dicarboxylic Acid Anhydride
Long Range CH COSY (HMBC)

Multiple correlations of hydrogen to carbon resonances or vice versa
3B  *cis*-Cyclohexane-1,2-dicarboxylic Acid Anhydride

CH  COSY (edited HSQC)

Direct correlation of the *hydrogen to carbon* resonances

Note: the CH$_2$ signals in the edited HSQC are inverted like the DEPT 135° (*i.e.* colour showing the peak is different)
3B  *cis*-Cyclohexane-1,2-dicarboxylic Acid Anhydride
Long Range CH COSY (HMBC)

Multiple correlations of *hydrogens* to *carbon* resonances
4 HH COSY 2,6-Dimethyl-5-hydroxyheptan-3-one

Diagonal contains the 1D spectrum   Connections between hydrogens are symmetrical about the diagonal
1D selective TOCSY (HH correlation) 2,6-Dimethyl-5-hydroxyheptan-3-one

1D selective TOCSY
- method of exploring separate spin systems, only linked HH correlations are observed
- the information is the same as found in the HH COSY but at higher resolution
4 CH COSY (edited HSQC) 2,6-Dimethyl-5-hydroxyheptan-3-one

Methyl region
How to define and understand obscured information in the proton spectrum

Expansion of the 2.40-2.75 ppm region

Spin-Spin Coupling information from the CH$_2$ (Hz) calculate from proton spectrum
4 Long Range CH COSY (HMBC) 2,6-Dimethyl-5-hydroxyheptan-3-one

Notice CH correlations to:
- longer range
  *i.e.* two or more bonds for a CH correlation
- a carbonyl resonance
  *i.e.* a quaternary peak
- a hydroxyl peak

Keto Carbon 216 ppm
4 Long Range CH COSY (HMBC) 2,6-Dimethyl-5-hydroxyheptan-3-one

Expansions of certain regions

keto carbonyl correlations to protons
5A CH COSY of 1-Phenyl-1,4-butanediol

HSQC

$^{13}\text{C}$

$^{1}\text{H}$

$p$

$o,m$ $^{1}\text{H}$ signals overlap

1-Phenyl-1,4-butanediol
5A  HH COSY of 1-Phenyl-1,4-butanediol

![Chemical structure of 1-Phenyl-1,4-butanediol]
5B  CH COSY  \( \gamma \)-Phenyl-\( \gamma \)-butyrolactone

HSQC

spot the overlap
6 cis-caran-trans-4-ol

The proton NMR is complex - only some features can be ascertained from the spectrum.

Carbon-13 and Carbon DEPT 135° and 90° spectra provide clearer information on the structure - match the data to the formula.

The CH COSY (edited HSQC) provides the solution to the proton resonance positions.

Assign most of the cyclohexyl ring structure from the HH COSY.

from the Long range CH COSY (HMBC) - the ring assignment can be solved.

from the NOE data a key conformational feature can be confirmed.
6. CH COSY (edited HSQC) cis-caran-trans-4-ol
6 HH COSY cis-caran-trans-4-ol

high contour levels - confirms the methylene proton positions
More complex NMR experiments to determine the configuration of the *cis*-Caran-*trans*-ol

**Long range CH COSY**
used to find correlations to proton(s) other than those directly attached to a carbon
used to establish links to hydroxy groups and ‘quaternary’ carbon peaks

**Nuclear Overhauser Effect (NOE)**
This will establish interactions of the spins through **SPACE**
1D Selective NOE experiment – irradiate a specific proton and observe any changes

expect to differentiate between the two *methyl peaks* on the *cyclopropyl* ring
one should be lying in the same plane as the two *cis* protons on the ring

**1D selective TOCSY - HH Correlation from a selected peak**
by varying the spin lock time it is possible to find directly linked spins near and far depending on the experimental conditions
6  Long Range CH COSY (HMBC) *cis*-Caran-trans-4-ol
6 Long Range CH COSY (HMBC) cis-Caran-trans-4-ol

Cyclopropyl CH peaks
Long Range CH COSY (HMBC) cis-Caran-trans-4-ol

Methyl peaks
6  1D selective NOE NMR cis-Caran-trans-4-ol

Normal spectrum

peak irradiated at 0.93ppm

peak irradiated at 1.0ppm

Through space information

positive NOE

No NOE
6 1D selective TOCSY (HH correlation) cis-Caran-trans-4-ol

1D TOCSY with short spin lock time - only certain adjacent spins observed
long spin lock time - all linked HH correlations observed
This is the same result as in HH COSY but at higher resolution
Basic IR analysis

- **Aromatic**
  - C-H st: 3080-3030 cm\(^{-1}\)
  - C=C- st: 1600-1400 cm\(^{-1}\)
  - C-H \(\delta\) oop: 900-600 cm\(^{-1}\)

- **Alkanes**
  - C-H st: 2840-3000 cm\(^{-1}\)
  - CH\(_2\)- \(\delta\): \(~1460\) cm\(^{-1}\)

- **Alkenes**
  - C-H (C=C) st: 3100-3000 cm\(^{-1}\)
  - C=C- st: 1690-1635 cm\(^{-1}\)
  - H-C (=C) \(\delta\) oop: 1000-675 cm\(^{-1}\)
Alcohols

- **-OH st** 3650-3200 cm\(^{-1}\)
  - H bonded: 3550 - 3450 cm\(^{-1}\) (broad)
  - Free OH: 3650 - 3590 cm\(^{-1}\) (sharp)

- **-C-O-(H)** 1260 - 970 cm\(^{-1}\) (strong)
  - 1° -CH\(_2\)OH: 1075 - 1000 cm\(^{-1}\)
  - 2° -CH-OH: 1125 - 1100 cm\(^{-1}\)
  - 3° -C-OH: 1210 - 1100 cm\(^{-1}\)
Ketones

- \(-\text{C}=\text{O~st}\) 1775-1650\text{cm}^{-1}

Lactones

- \(-\text{C}=\text{O~st}\) 1745 - 1650\text{cm}^{-1}
- \(-\text{C}-\text{O}\) 1330 - 1050\text{cm}^{-1}

TWO bands, one strong

\(\gamma\) - lactones  ~1180\text{cm}^{-1}
**Acids**

- -COO-H \(\text{st} \ 3550-2500\text{cm}^{-1}\) broad
- -C=O \(1800-1650\text{cm}^{-1}\) - aliphatic \(1715\text{cm}^{-1}\)
- -CO-OH oop \(\sim 920\text{cm}^{-1}\)

**Acid Anhydrides**

- -C=O \(\text{st} \ 1870 - 1725\text{cm}^{-1}\) two bands
  - Cyclic 6 membered rings \(\sim 1800\text{cm}^{-1}\) and stronger \(\sim 1760\text{cm}^{-1}\)
- -CO-C \(\text{st} \ \sim 920\text{cm}^{-1}\)
Halogens

Chlorine
• **Aliphatic-Cl** $< 830\text{cm}^{-1}$ -often $500-600\text{cm}^{-1}$

Bromine
• **Aliphatic-Br** $< 700\text{cm}^{-1}$
Some suggestions for Further Reading on NMR

There are more than 250 books available in the TCD Library

- Useful introductions on NMR spectroscopy can be found in most general Organic text books
  There are many other useful texts including a basic NMR text in the Oxford Chemistry Primer series (# 32) by Peter Hore

- Texts with emphasis on structural elucidation (a couple of examples here - there are many!):

- Basic and mainly non-mathematical introductions to pulsed NMR techniques:
Suggested Further Reading

- Practical Experimental texts (*i.e.* how to run real NMR experiments):
  - Braun, S., Berger, S., ‘200 and more basic NMR experiments’, Wiley-VCH, 2004

- More advanced (increasingly mathematical, *i.e.*, quantum mechanics and all that!):
  - Freeman, R., ‘Spin Choreography, basic steps in high resolution NMR’, Spektrum, 1996
  - Van der Ven, F., ‘Multidimensional NMR in liquids’, VCH, 1995