^{13}C NMR Spectroscopy

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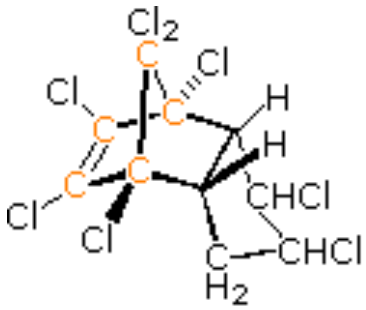
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm

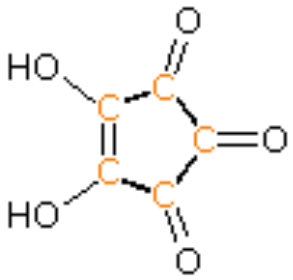
The power and usefulness of 1H NMR spectroscopy as a tool for structural analysis should be evident from the past discussion.

Unfortunately, when significant portions of a molecule lack C-H bonds, no information is forthcoming.

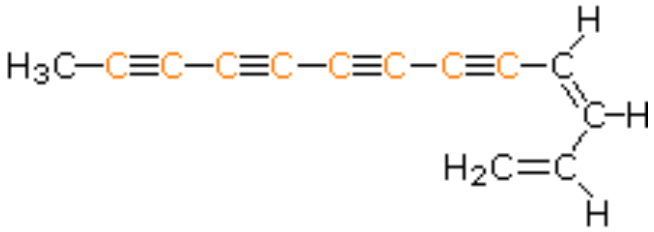
Examples



chlordane



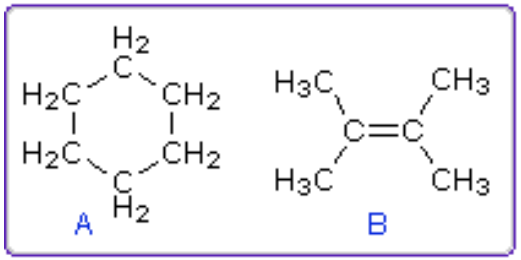
croconic acid

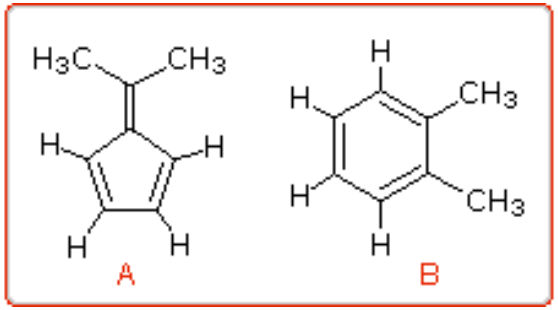


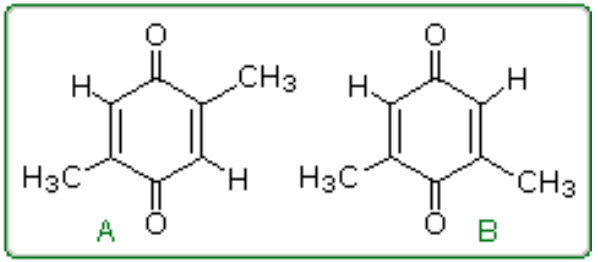
a polyacetylene from *Dahlia*

Even when numerous C-H groups are present, an unambiguous interpretation of a proton NMR spectrum may not be possible.

Pairs of isomers (A & B) which display similar proton NMR spectra







These difficulties would be largely resolved if the carbon atoms of a molecule could be probed by NMR in the same fashion as the hydrogen atoms.

Fortunately, 1.1% of elemental carbon is the ^{13}C isotope, which has a spin I = 1/2, so in principle it should be possible to conduct a carbon NMR experiment.

It is worth noting, that if much higher abundances of ^{13}C were naturally present in all carbon compounds, proton NMR would become much more complicated due to large one-bond coupling of ^{13}C and ^{1}H.

Obstacles needed to be overcome before carbon NMR emerged as a routine tool:

i) As noted, the abundance of 13C in a sample is very low (1.1%), so higher sample concentrations are needed.

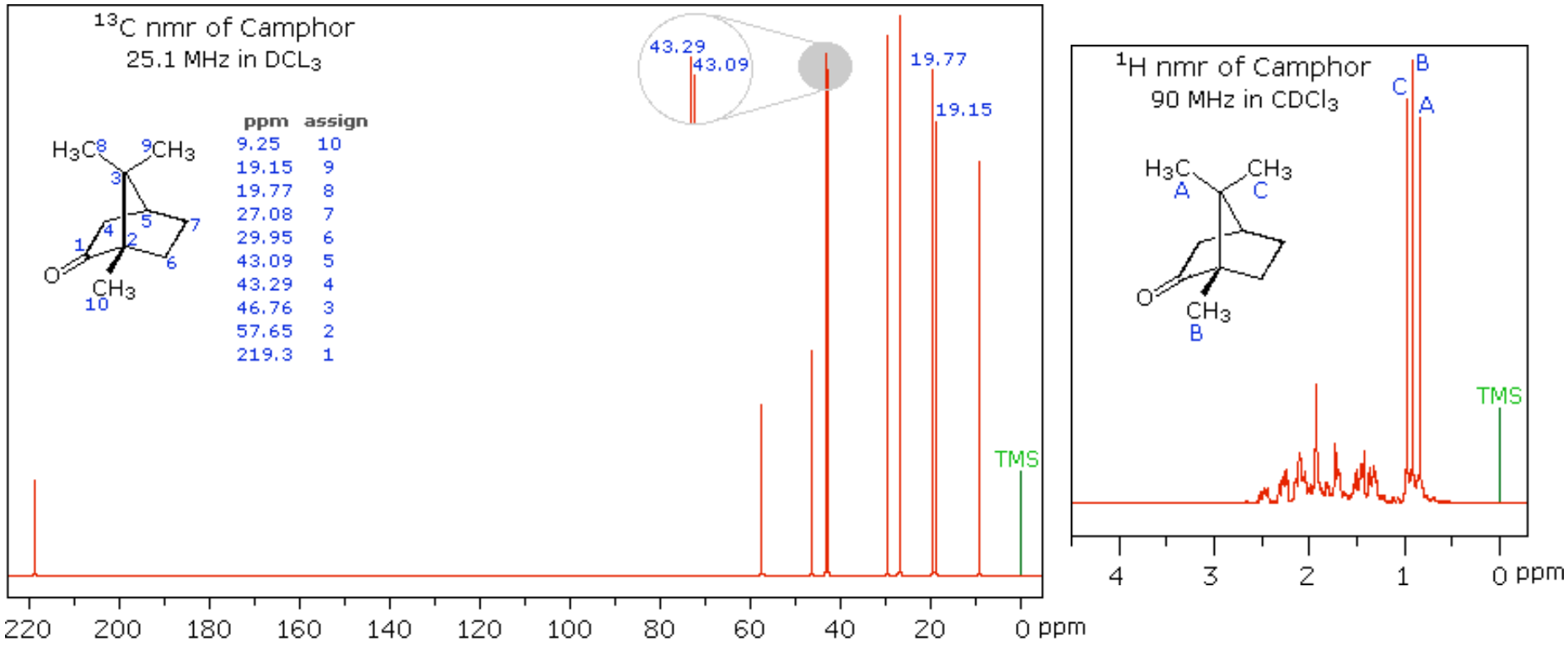
ii) The 13C nucleus is over fifty times less sensitive than a proton in the nmr experiment, adding to the previous difficulty.

iii) Hydrogen atoms bonded to a 13C atom split its NMR signal by 130 to 270 Hz, further complicating the NMR spectrum.

Solution:

Use of high-field pulse technology coupled with broad-band heteronuclear decoupling of all protons.

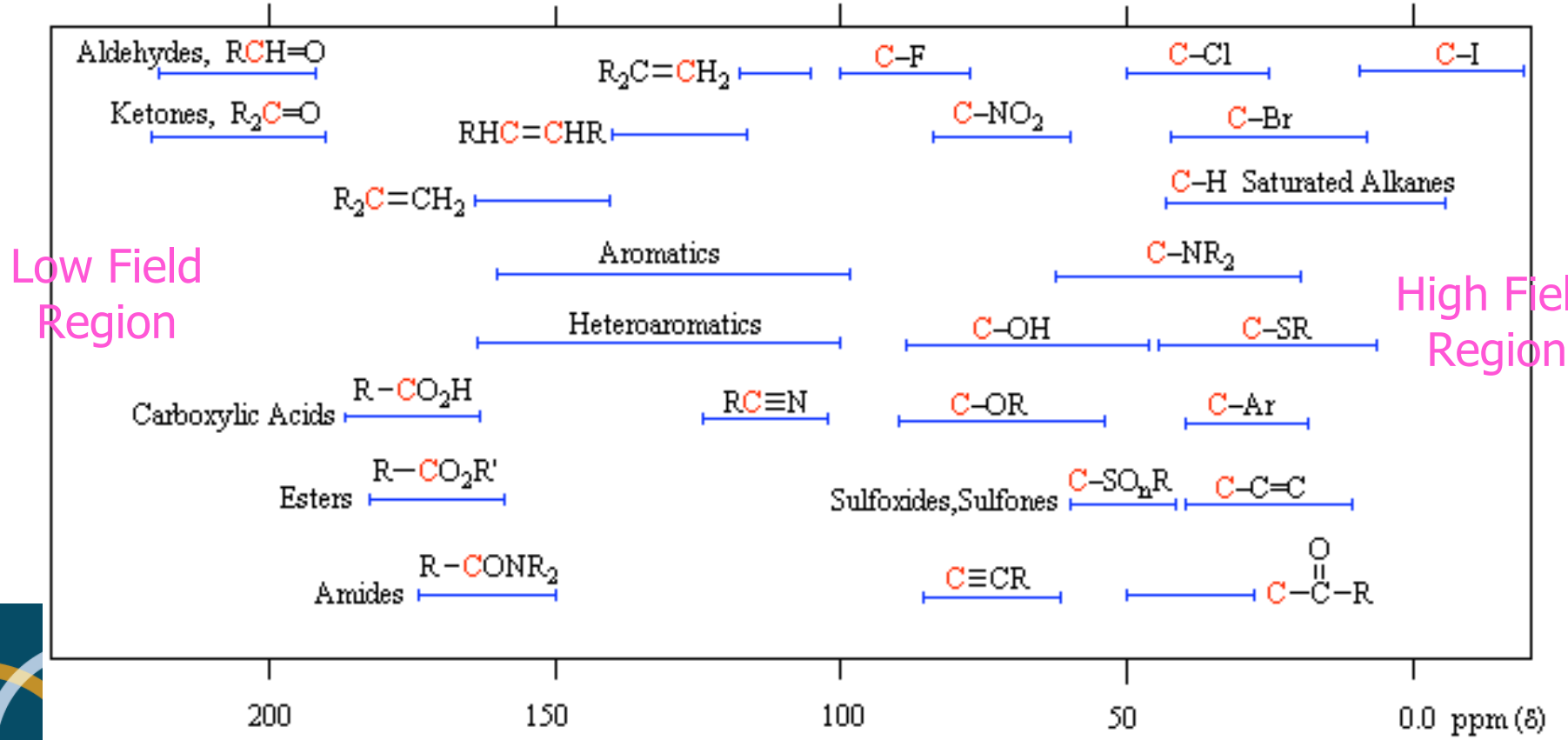
The Spectrum of Camphor



The dispersion of 13C chemical shifts is nearly twenty times greater than that for protons.

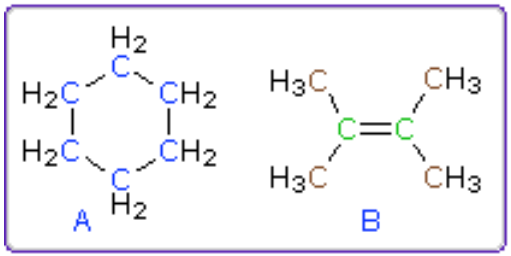
Unlike proton NMR spectroscopy, **the relative strength of carbon NMR signals are not normally proportional to the number of atoms generating each one**.

13C Chemical Shift Ranges*



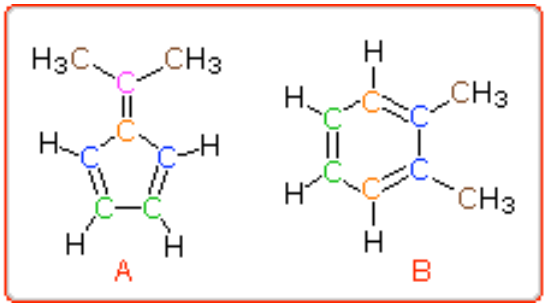
* For samples in CDCl3 solution. The δ scale is relative to TMS at δ=0.

The isomeric pairs previously cited as giving very similar proton NMR spectra are now seen to be distinguished by carbon NMR.



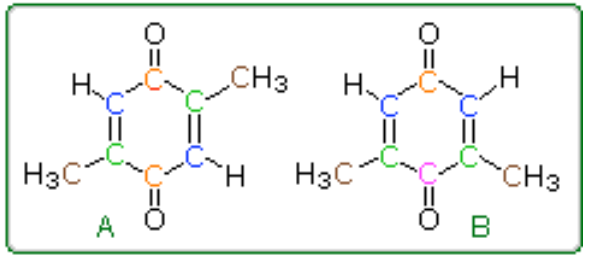
1 signal
27.1 ppm

2 signals
20.4, 123.5



5 signals

4 signals

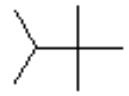


4 signals

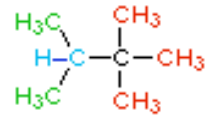
5 signals

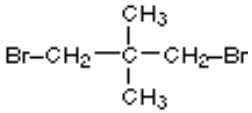
Structurally Equivalent Atoms & Groups

For each of the compounds **A** through **F** indicate the number of structurally-distinct groups of carbon atoms, and also the number of distinct groups of equivalent hydrogens. Enter a number from 1 to 9 in each answer box.

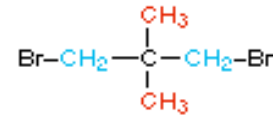
A 

A Number of distinct carbon atoms: ... Number of distinct hydrogen groups:



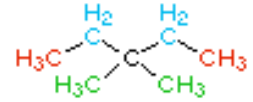
B 

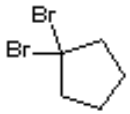
B Number of distinct carbon atoms: ... Number of distinct hydrogen groups:



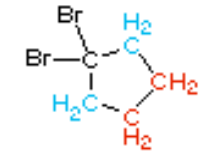
C 

C Number of distinct carbon atoms: ... Number of distinct hydrogen groups:



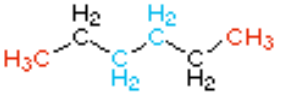
D 

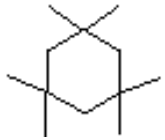
D Number of distinct carbon atoms: ... Number of distinct hydrogen groups:



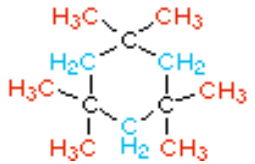
E 

E Number of distinct carbon atoms: ... Number of distinct hydrogen groups:

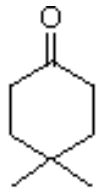


F 

F Number of distinct carbon atoms: ... Number of distinct hydrogen groups:



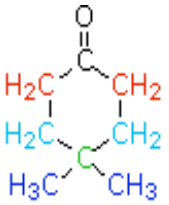
A



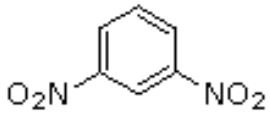
A

Number of distinct carbon atoms: ...
Number of distinct hydrogen groups:

A



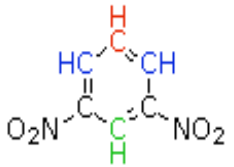
B



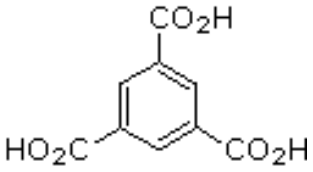
B

Number of distinct carbon atoms: ...
Number of distinct hydrogen groups:

B



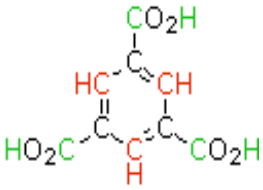
C



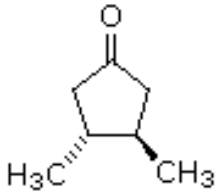
C

Number of distinct carbon atoms: ...
Number of distinct hydrogen groups:

C



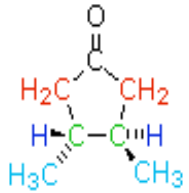
D



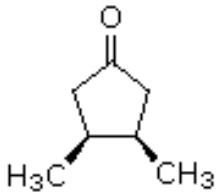
D

Number of distinct carbon atoms: ...
Number of distinct hydrogen groups:

D



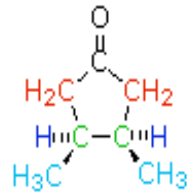
E



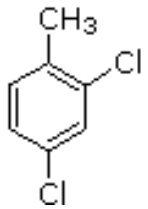
E

Number of distinct carbon atoms: ...
Number of distinct hydrogen groups:

E



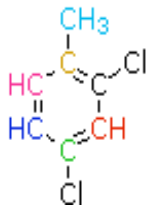
F



F

Number of distinct carbon atoms: ...
Number of distinct hydrogen groups:

F



1. You have three unlabeled vials each containing a trichlorobenzene isomer. In order to correctly identify each compound and properly label its container you have taken their 13C nmr spectra. Match the spectrum characteristics given below with a compound from the following group:

1,2,3-trichlorobenzene
1,2,4-trichlorobenzene
1,3,5-trichlorobenzene

^{13}C NMR:

(i) Two peaks between δ125 and 140 ppm

- ○ 1,2,3-trichlorobenzene
- ○ 1,2,4-trichlorobenzene
- ● 1,3,5-trichlorobenzene

(ii) Six peaks between δ125 and 140 ppm

- ○ 1,2,3-trichlorobenzene
- ● 1,2,4-trichlorobenzene
- ○ 1,3,5-trichlorobenzene

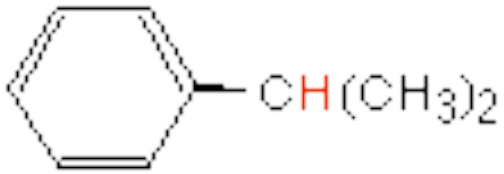
(iii) Four peaks between δ125 and 140 ppm

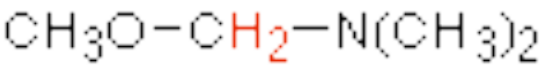
- ● 1,2,3-trichlorobenzene
- ○ 1,2,4-trichlorobenzene
- ○ 1,3,5-trichlorobenzene

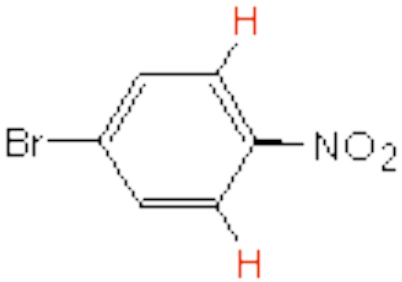
Spin-Spin Splitting in ^{1}H NMR

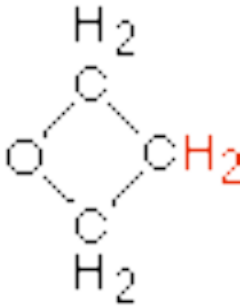
What splitting pattern in the 1H nmr spectrum would you expect for the hydrogen atom(s) colored red in the compounds shown below?

Your choices are: **s** singlet **d** doublet **t** triplet **q** quartet **m** multiplet.

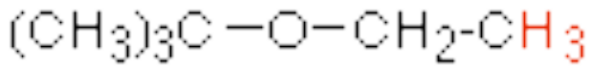
A 

D 

B 

E 

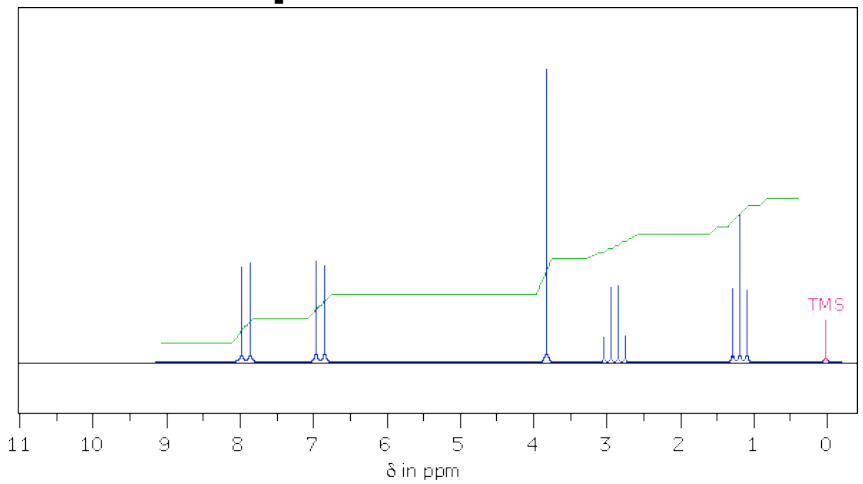
C 

F 

Answers: A) m B) d C) q D) s E) m F) t

Interpreting an NMR Spectrum

The following ^{1}H-NMR spectrum of a $C_{10}H_{12}O_2$ compound was obtained on a 90 MHz spectrometer.



1. Ignoring the TMS, how many discrete groups of proton signals are present in this spectrum? ...
2. What is the multiplicity (s, d, t, q) of the highest field signal from this sample? ...
3. The sample has a singlet at δ = 3.8 ppm. In units of Hz how far is this signal from the TMS signal?
4. What structural feature is suggested by the singlet at δ = 3.8 ppm? ...

   A CH_3–C=O B $-CH_2-$ C –O–H D –O–CH_3 E C–CH_3 F C=C–H

5. From Js, which of the other signals is coupled to the quartet at δ = 2.9 ppm?

   A δ = 1.2 ppm B δ = 3.8 ppm C δ = 6.9 ppm D δ = 7.9 ppm

6. Using the integrator trace and the formula of the sample, assign a whole number ratio to the sample signals as follows:

   7.9 ppm signal ; 6.9 ppm signal ; 3.8 ppm signal ; 2.9 ppm signal ; 1.2 ppm signal

Using Spectroscopy to Determine a Structural Formula

Each of the following 'unknown' problems provides sufficient spectroscopic data to enable you to draw a structural formula.

A compound composed of carbon, hydrogen & oxygen has a molecular ion at m/z=112 amu in its mass spectrum. The base peak is at m/z=28 amu. The infrared spectrum shows strong absorption in the 2850 to 2980 cm-1 region, and very strong absorption at 1717 cm-1. The 1H nmr shows a single sharp signal at δ = 2.7 ppm, and the 13C nmr has two signals (δ = 37 & 208 ppm).

A compound composed of carbon, hydrogen & oxygen has a molecular ion at m/z=90 amu in its mass spectrum. The base peak is at m/z=45 amu. The infrared spectrum shows strong absorption in the 2840 to 2980 cm-1 region, and very strong absorption from 1105 to 1125 cm-1. The 1H nmr shows two sharp signals at δ = 3.40 & 3.55 ppm (intensity ratio 3:2 respectively), and the 13C nmr also has two signals (δ =59 & 72 ppm).

A compound used as a moth repellant has three molecular ion peaks at m/z=146 (100%), 148 (65%) & 150 (10%) amu in its mass spectrum. A pair of smaller peaks are seen at m/z=111 (34%) & 113 (11%). The infrared spectrum shows sharp absorption just above 3000 cm-1 region, and also at 1480 cm-1. The 1H nmr shows a single sharp signal at δ = 7.2 ppm, and the 13C nmr has two signals (δ =133 & 130 ppm).

Thank you for your time and attention!