Chem Factsheet

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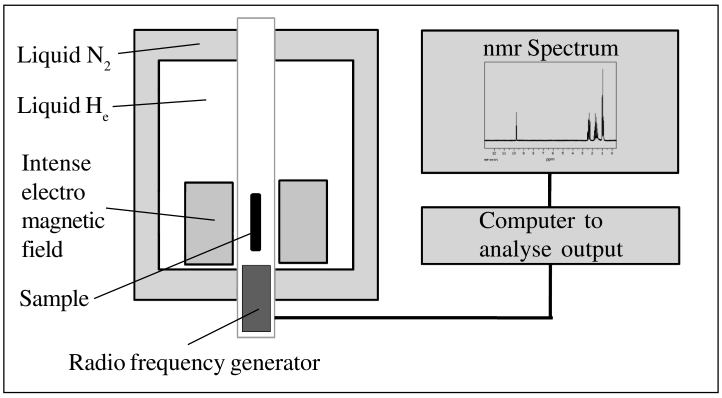
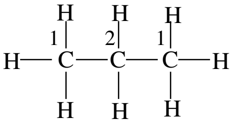
C-13 Nuclear Magnetic Resonance (NMR) Spectroscopy

- C-13 nmr spectroscopy is used to *detect* and *differentiate* C atoms in organic molecules by detecting ^{13}C isotopes.
- Only about 1% of all carbon atoms in molecules are the ^{13}C isotope, the rest being ^{12}C plus a very small proportion of radioactive ^{14}C.
- ^{13}C is statistically distributed throughout *all* the different positions in an organic molecule.
- ^{13}C NMR relies on the magnetic properties of the ^{13}C nuclei. ^{12}C and ^{14}C nuclei do not have such properties.
- When a sample is dissolved in a suitable solvent with a little tetramethylsilane [= TMS = $Si(CH_3)_4$] added to act as a reference, subjected to a suitable intense electro-magnetic field and a range of radio frequencies, the ^{13}C nuclei in the sample absorb *certain frequencies* from the radio waves (see diagram below).



- ^{13}C nuclei in ***different molecular environments*** absorb different amounts of energy via different radio frequencies ("resonance"), allowing them to be differentiated.

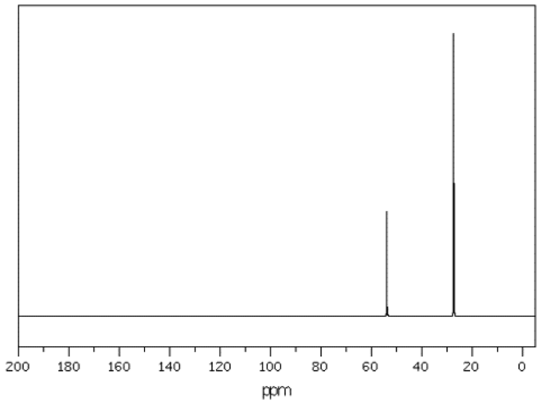


Propane

C atoms having "*different molecular environments*" means they are bonded to *different* atoms / groups. For example, the structure of propane above shows it has two different C molecular environments because those labelled (1) are each bonded to 3 H atoms and a CH_2CH_3 group whereas C atom (2) is bonded to 2H atoms and 2 CH_3 groups.

- The technique assigns a *chemical shift* (*δ*) to each molecular environment by measuring its absorption *relative* to that of the reference (TMS). *δ* is measured in parts per million (ppm).
- Splitting (coupling) of C13 signals by H atoms bonded to a C atom are avoided by "*decoupling*" – in essence, this involves causing the H atoms to flip very rapidly between their two magnetic orientations so that the C atoms experience an averaged, zero effect.
- Computer analysis of the absorption patterns and strengths produces a *^{13}C nmr spectrum* which consists of a plot of the *chemical shift* (*δ*) of each ^{13}C type against absorption strength. The following shows a typical C13 spectrum:

The C13 nmr Spectrum of 2-chloropropane, $CH_3CHClCH_3$



- Interpretation of such spectra yields a lot of information about the structure of the sample's molecule.

What Is A Suitable Solvent?

Like proton nmr, $CDCl_3$ is commonly used as the solvent. This contains a C atom and will therefore cause a ^{13}C nmr absorption. However, it produces only a single absorption because it has only one ^{13}C environment and this always occurs at the same point in the spectrum. The signal can therefore be removed from the spectrum to avoid confusion.

Why Is TMS Used As A Reference?

Like in proton nmr, TMS is commonly used as the reference. By convention this is set as *chemical shift, δ, zero* and other ^{13}C absorptions are then measured relative to it.

Because it contains four C atoms with the same molecular environment, TMS produces a sharp, intense absorption which can be identified accurately. It is also non-toxic and inert which means it will not react with the sample and change its structure. Further, it is volatile allowing it to be easily separated from the sample. Finally, it absorbs at frequencies which do not interfere with those absorbed by any sample.

What Are Typical Chemical Shift (δ) Values For C-13?

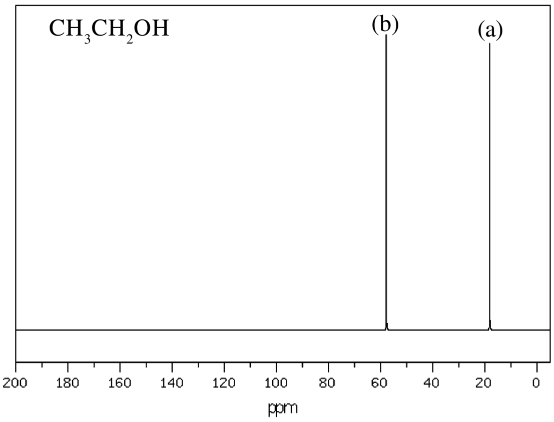
The following table shows the ranges of ^{13}C nmr absorptions observed for particular types of molecular environment.

Type of **C**	Group	δ values / ppm	Type of **C**	Group	δ values / ppm
C-C	Alkyl	5 – 40	R-CN	Nitrile	110 - 125
R-**C**-Cl or Br	Haloalkane	10 – 70	R-**CO**-	Ester, acid	160 - 185
R-CO-**C**	Ketone	20 – 50	R-**CO**-	Aldehyde, ketone	190 - 220
R-**C**-NH_2	Amine	25 – 60	$\mathbf{C_6H_5}$-	Aryl	110 - 160
R-**C**-O	Alcohol, ester, acid	50 – 90	R-**C=C-H**	Alkene	90 - 150

Note : δ values for *proton* nmr tend to be in the range 0 – 12, much narrower than the range observed for ^{13}C.

How Are 13C nmr Spectra Interpreted?

1. Count the number of absorptions ("peaks") – this gives the number of *different* ^{13}C environments in the molecule.
2. The ratio of signal *areas* indicates the ratio of C atoms in the different molecular environments. Do not attach too much significance to this point because the heights do not necessarily reflect the areas!



Example 1: The C-13 spectrum of ethanol shown opposite indicates that ethanol contains C atoms in *two* different molecular environments – (a) and (b) – $^{(a)}\mathbf{CH_3}{}^{(b)}\mathbf{CH_2}OH$. In addition, the 1:1 signals suggest the number of atoms in the two environments are equal.

3. Signals with *higher* δ values are associated with C atoms which are *nearer to electronegative atoms* (e.g. O) in the molecule.

   e.g. the C atoms in environment (b) of ethanol are nearer the O atom of the OH group than those of environment (a) causing $^{(b)}C$ to absorb at about $\delta = 58$ ppm while $^{(a)}C$ absorbs at only about $\delta = 17$ ppm.

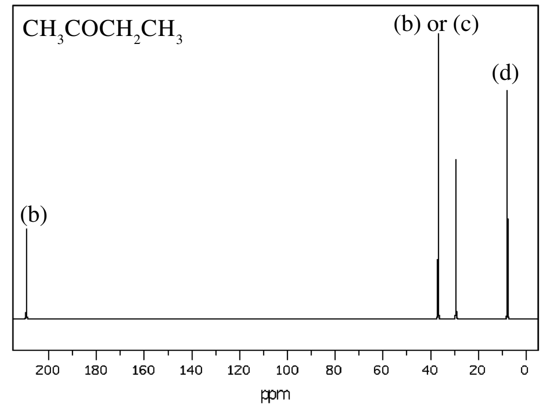
4. Use a table of δ values (see earlier) to assign *specific groups* to each nmr signal. Applying this to the ethanol spectrum gives:

δ value from spectrum	Corresponding δ range from data table	Type of group indicated	C Assigned
17	5 – 40	**C**-C	$^{(a)}C$
58	50 – 90	R-**C**-O	$^{(b)}C$

Note: *more symmetrical* structures produce *simpler nmr spectra* with fewer peaks.

Example 2: Butanone

C13 nmr Spectrum of Butanone



Four different molecular environments –
(a) to (d) – $^{(a)}\mathbf{CH_3}{}^{(b)}\mathbf{CO}{}^{(c)}\mathbf{CH_2}{}^{(d)}\mathbf{CH_3}$.

Note, the 1:1:1:1 ratio is not seen.

The C of the C=O group [(b)] is nearest the O atom and has a much higher δ value (≈ 210 ppm).

The $^{(d)}C$ is furthest from O and has the lowest δ value (≈ 8 ppm).

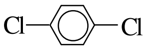
δ value from spectrum	Corresponding δ range from data table	Type of group indicated	C Assigned
8	5 – 40	**C**-C	$^{(d)}$C
25	20 – 50	R-CO-**C**	$^{(a)}$C or $^{(a)}$C
37	20 – 50	R-CO-**C**	$^{(a)}$C or $^{(a)}$C
210	190 - 220	R-**C**O-	$^{(b)}$C

Practice Questions

1. Decide how many C13 nmr signals would be produced by each of the following molecules and use the data table to assign a δ range to each.

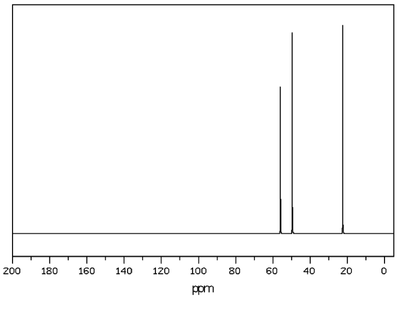
Molecule	No. Signals	δ Ranges
1. $(CH_3)_3CCOOH$		
2. CH_3CH_2Br		
3. 1,4-dimethylbenzene		
4. $Si(CH_3)_4$		
5. CH_3CH_2CHO		

2. Decide how many C13 nmr signals would be produced by each of the molecules in the following table and, where appropriate, label the C with the highest δ value with an asterisk (*).

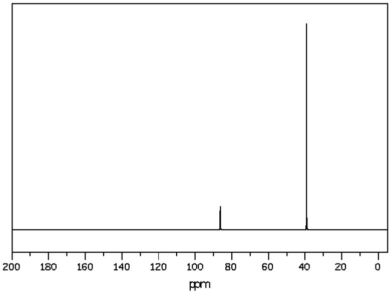
CH_3CH_3	CH_3CH_2COOH	CH_3COCH_3	$CH_3CH_2CH_2CH_3$
$CH_3CH_2CH_2OH$	$CH_3CH(OH)CH_3$	CH_2BrCH_2Br	$CH_3CH=CH_2$
CH_3CHBr_2	$(CH_3)_2C=C(CH_3)_2$		$C_2H_5CO.OC_2H_5$

3. The C13 nmr spectra of 3 isomers of dichloropropane are shown. They include 2,2-, 1,2- and 1,3-dichloropropane. Decide which is which, explaining you deductions.

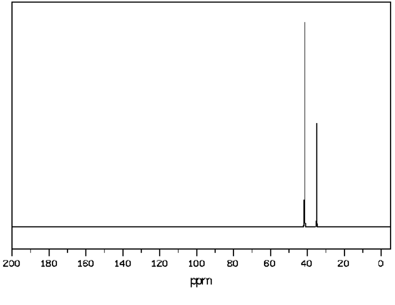
A



B



C



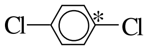
Name the fourth possible isomer and predict the number of C13 signals it would produce.

Answers

1.

Molecule	No. Signals	δ Ranges
1. $(\mathbf{C}H_3)_3\mathbf{CC}OOH$	3	5 - 40, 20 – 50 and 160 - 185
2. $\mathbf{C}H_3CH_2Br$	2	5 - 40 and 10 - 70
3. 1,4-dimethylbenzene	3	5 – 40 and 110 - 160
4. $Si(\mathbf{C}H_3)_4$	1	0
5. $\mathbf{C}H_3\mathbf{C}H_2\mathbf{C}HO$	3	5 – 40, 20 – 50 and 190 - 220

2.

$\mathbf{C}H_3CH_3$	$\mathbf{C}H_3\mathbf{C}H_2\overset{*}{\mathbf{C}}OOH$	$\mathbf{C}H_3\overset{*}{\mathbf{C}}OCH_3$	$\mathbf{C}H_3\mathbf{C}H_2CH_2CH_3$
1	3	2	2
$\mathbf{C}H_3\mathbf{C}H_2\overset{*}{\mathbf{C}}H_2OH$	$\mathbf{C}H_3\overset{*}{\mathbf{C}}H(OH)CH_3$	$\mathbf{C}H_2BrCH_2Br$	$\mathbf{C}H_3\mathbf{C}H{=}\mathbf{C}H_2$
3	2	1	3
$\mathbf{C}H_3\overset{*}{\mathbf{C}}HBr_2$	$(\mathbf{C}H_3)_2\mathbf{C}{=}\overset{*}{C}(CH_3)_2$		$\mathbf{C}_2H_5\overset{*}{\mathbf{C}}O.O\mathbf{C}_2H_5$
2	2	2	5

3. Isomers named are $CH_3CCl_2CH_3$, $CH_2ClCHClCH_3$ and $CH_2ClCH_2CH_2Cl$. These would have 2, 3 and 2 C13 nmr peaks respectively.

   Hence, spectrum A must belong to $CH_2ClCHClCH_3$.

   Spectrum B is likely to be that of $CH_3CCl_2CH_3$ because the much higher δ value is caused by C bonded to **two** electronegative Cl atoms.

   Hence, spectrum C must be that of $CH_2ClCH_2CH_2Cl$.

   The fourth isomer is 1,1-dichloropropane, $CHCl_2CH_2CH_3$. This would have 3 signals, one with a significantly high δ value caused by CCl_2.

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