nmr spectroscopy

1

2 nmr spectroscopy

NMR spectroscopy is the most powerful tool for characterizing organic molecules, because it can be used to identify the carbon–hydrogen framework in a compound.

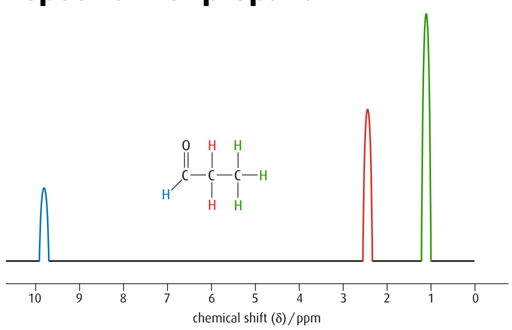
NMR provides some of the most direct evidence for their structures.

3 nmr spectroscopy

Unlike IR & mass spectroscopy, a particular NMR spectrum, usually, gives us a unique molecular structure.

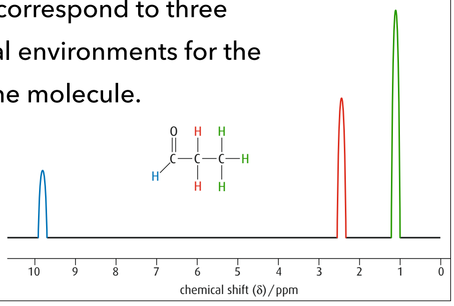
Peaks in the NMR spectrum correspond to groups of protons (hydrogen atoms) in different chemical environments.

4 nmr spectrum of propanal



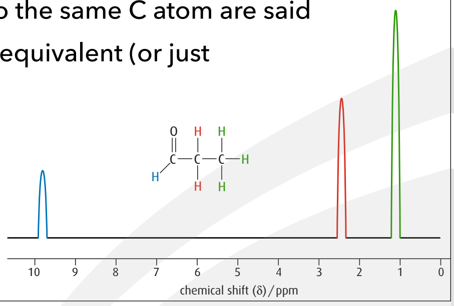
5 nmr spectrum of propanal

The three peaks correspond to three different chemical environments for the protons (1H) in the molecule.



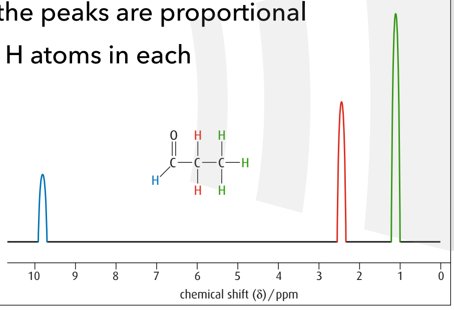
6 nmr spectrum of propanal

H atoms joined to the same C atom are said to be chemically equivalent (or just 'equivalent').



7 nmr spectrum of propanal

The areas under the peaks are proportional to the number of H atoms in each environment.



8 number of peaks

The number of NMR peaks is equal to the number of different types of protons in a compound.

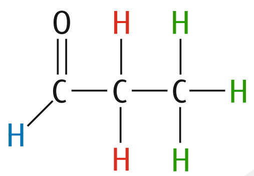
In many compounds, deciding whether two protons are in identical or different environments is intuitive.

9 ¹H environments

Any CH_3 group is different from any CH_2 group, which is different from any CH group in a molecule.

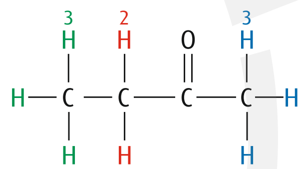
Two CH_3 groups may be identical (as in CH_3OCH_3) or different (as in $CH_3OCH_2CH_3$), depending on what each CH_3 group is bonded to.

10 ¹H environments in propanal



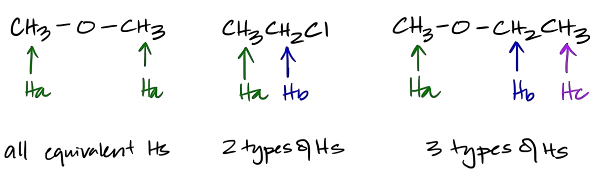
H atoms joined to the same C atom are said to be chemically equivalent (or just 'equivalent').

11 butanal

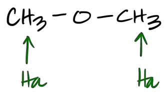


Butanal has three different environments for the protons, and the number of hydrogen in each environment is given on top.

12 ¹H environments

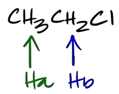


13 example 2



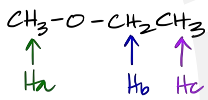
Each CH_3 group is bonded to the same (–OCH_3), making both CH_3 groups equivalent.

14 example 3



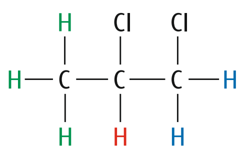
The Hs of the CH_3 are different from the Hs of the CH_2

15 example 4



The Hs of the CH_2 group are different from those in each CH_3 group. The two CH_3 groups are also different from each other; one CH_3 group is bonded to –OCH_2CH_3 and the other is bonded to –CH_2OCH_3.

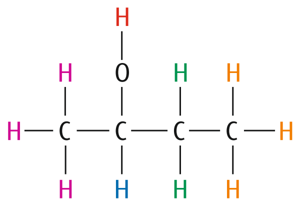
16 skill check 1



# of different ^1H environments ________

Ratio of Hs in each environment ________________

17 skill check 2



# of different ¹H environments ________

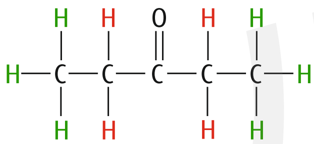
Ratio of Hs in each environment ________________

18 different ¹H environments

To work out the number of environments for ¹H, you must consider whether or not the molecule is symmetrical.

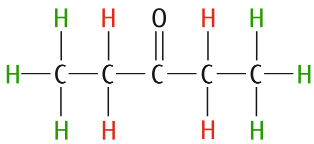
If the molecule is not symmetrical, H atoms on each different atom will be in different chemical environments.

19 ¹H environments in pentan-3-one



There are only two different chemical environments for the protons in pentan-3-one, as the molecule is symmetrical.

20 ¹H environments in pentan-3-one



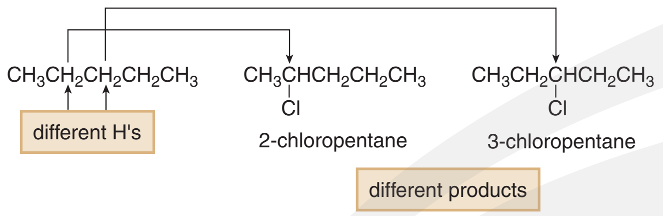
The six Hs shown on the two CH_3 are equivalent – all in the same chemical environment & the four Hs on the two CH_2 are also equivalent to each other.

21 similar ^1H environments

A good way to compare two H atoms, replace each H by Cl, and examine the substitution products that result. If the names are different after substituting the Cl in both cases, they are two different H environments.

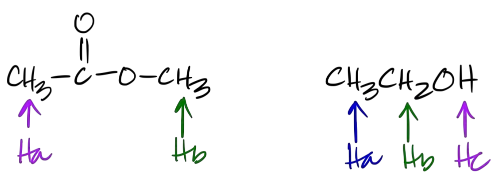
22 pentane

different H environments in $CH_3CH_2CH_2CH_2CH_3$



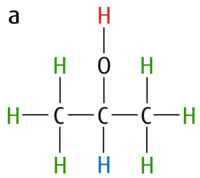
23 examples 7 & 8

24 examples 9 &10



25 propan-2-ol

a



Three different ¹H environments. The six Hs in the two CH_3 groups are equivalent.

The number of Hs in each environment is 6 : 1 : 1.

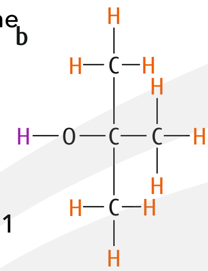
26 2-methylpropan-2-ol

The Hs on CH_3 groups attached to the same C atom will be equivalent.

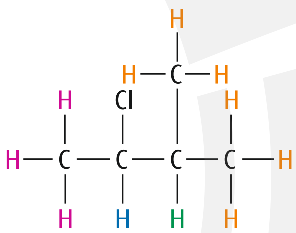
There are only two ¹H environments here.

Ratio of Hs in each environment = 9:1

b



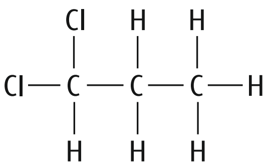
27 skill check 3



# of different ¹H environments ________

Ratio of Hs in each environment ________________

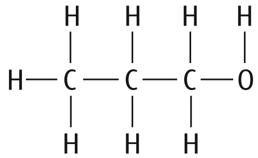
28 skill check 4



# of different ¹H environments ________

Ratio of Hs in each environment ________________

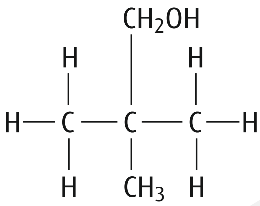
29 skill check 5



# of different ¹H environments ________

Ratio of Hs in each environment ________________

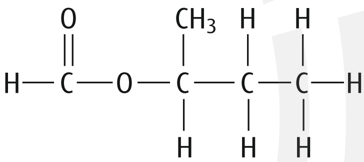
30 skill check 6



# of different ¹H environments ________

Ratio of Hs in each environment ________________

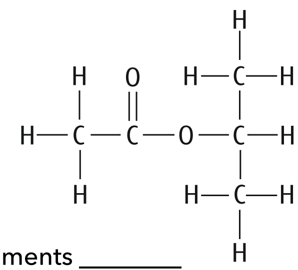
31 skill check 7



# of different ¹H environments ________

Ratio of Hs in each environment ________________

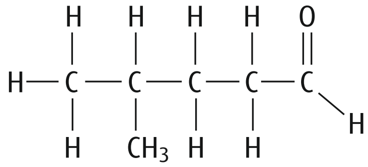
32 skill check 8



# of different ¹H environments ________

Ratio of Hs in each environment ________________

33 **skill check 9**



# of different ^{1}H environments ________

Ratio of Hs in each environment ________________

34 **skill check 11**

Find the no. of different ^{1}H environments & the ratio of Hs in each environment in the following:

CH_3CH_3 $CH_3CH_2CH_2CH_3$

35 **skill check 12**

Find the no. of different ^{1}H environments & the ratio of Hs in each environment in the following:

$CH_3CH_2CH_3$ $CH_3CO_2CH_2CH_3$

36 **skill check 13**

Find the no. of different ^{1}H environments & the ratio of Hs in each environment in the following:

$CH_3CH_2CO_2CH_2CH_3$ CH_3CHO

37 skill check 15

Find the no. of different [1]H environments & the ratio of Hs in each environment in the following:

$(CH_3)_2CHCH(CH_3)_2$

38 position of peaks: chemical shift

In a NMR spectrum each H environment shows up as a peak and the x-axis value are each environment's chemical shift.

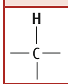
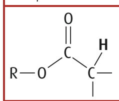
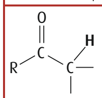
The area/height of each peak is determined by the no. of Hs in each environment.

39 chemical shift

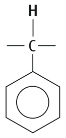
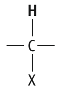
The chemical shift of each peak gives information about the structural environment of the nuclei producing that signal.

Some typical values for the chemical shifts of protons in different environments are given below.

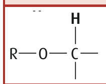
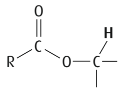
40 chemical shift

Type of proton	Chemical shift / ppm	Comments
	0.9–1.7	H on a carbon chain but not next to any other functional groups
	2.0–2.5	H on a C next to C=O of an ester
	2.1–2.7	H on a C next to C=O of an aldehyde or ketone

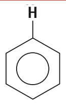
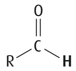
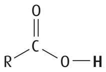
41 chemical shift

Type of proton	Chemical shift / ppm	Comments
	2.3–3.0	H on a C attached to a benzene ring
 X is a halogen	3.2–4.4	H attached to a C that also has a halogen atom attached

42 chemical shift

Type of proton	Chemical shift / ppm	Comments
	3.3–3.7	H attached to a C that has an O attached
	3.7–4.8	H on a C next to C–O of an ester
R—O—H	0.5–5.0	H attached to O in an alcohol

43 chemical shift

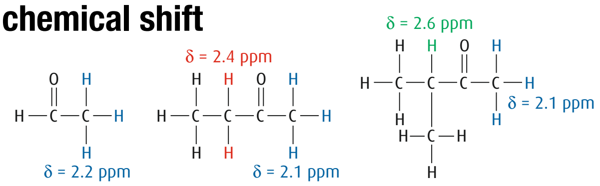
Type of proton	Chemical shift / ppm	Comments
	6.7–8.2	H attached to a benzene ring
	9.4–10.0	H attached to C=O of an aldehyde
	9.0–13.0	H on an O in a carboxylic acid

44 chemical shift

The values are approximate and can vary depending on other groups attached.

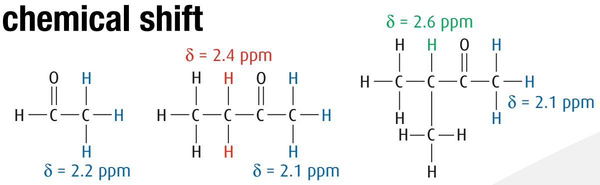
For instance, it makes a difference how many other Hs are attached to the C atom to which the H we are interested in is attached.

45 chemical shift



The ranges in the table include all possibilities, and we just look at the environment of the proton rather than the number of Hs in that environment.

46 chemical shift



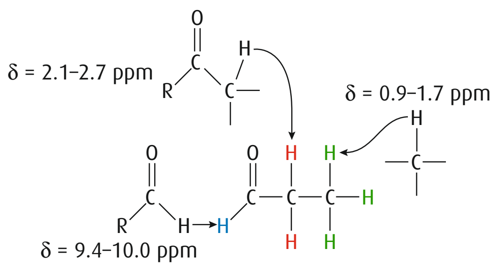
Thus we can assume that the chemical shift of an H on a C next to the C=O of an aldehyde or ketone comes in the range 2.1–2.7, no matter how many other Hs are attached.

47 chemical shifts of propanal

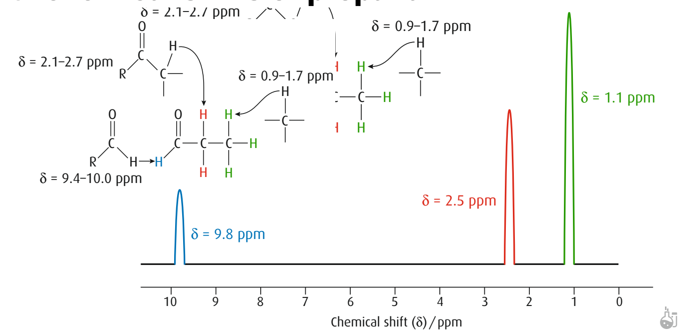
When using the table of chemical shift values, you must try to find the best match to the proton environments in the molecule you are studying.

Thus, in the spectrum of propanal, the H attached directly to the C=O group would be expected to have a chemical shift in the range 9.4–10.0 ppm; indeed, the peak for this proton occurs at a chemical shift of 9.8ppm.

48 chemical shifts of propanal



49 chemical shifts of propanal



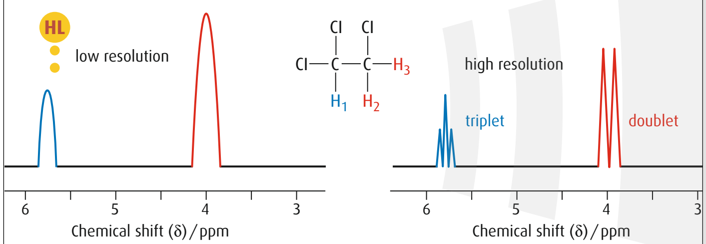
50 high-resolution nmr spectra

The low- and high-resolution NMR spectra of 1,1,2-trichloroethane are shown in the next slide.

$CHCl_2CH_2Cl$

There are two peaks in the low-resolution spectrum, as there are two different chemical environments for H.

51 1,1,2-trichloroethane $CHCl_2CH_2Cl$

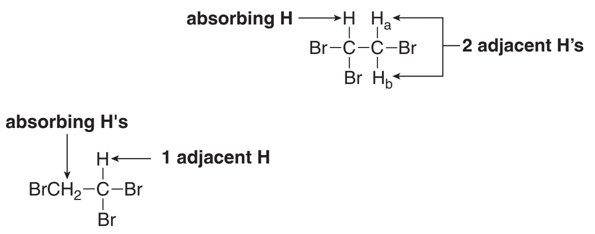


52 high-resolution nmr spectra

However, in the high-resolution spectrum, each of these peaks is split.

In general, if there are 'n' protons (Hs) on the adjacent carbon atom, the signal for a particular proton will be split into (n+1) peaks.

53 examples of adjacent Hs



54 rules for splitting

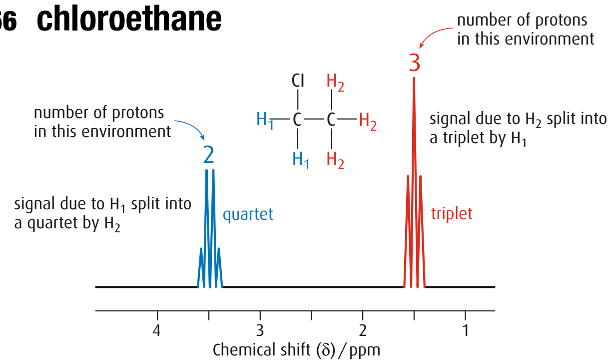
Protons on the same atom (e.g. CH_3, CH_2) do not interact with each other. They are chemically equivalent.

Splitting generally only occurs with protons on adjacent carbon atoms.

55 chloroethane CH_3CH_2Cl

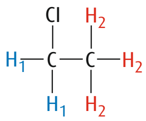
There are two sets of peaks in this spectrum of chloroethane, as there are two different chemical environments for H. The total area under the peaks at δ = 1.5 ppm is greater than that under the peaks at δ = 3.5 ppm, as there are more protons in this environment.

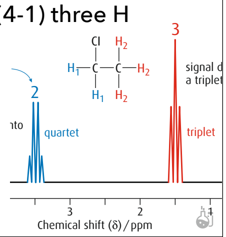
56 chloroethane



57 chloroethane

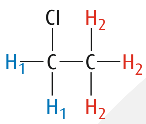
The signal at δ = 3.5ppm is split into a quartet. A quartet consists of four peaks, so we can deduce from the presence of a quartet that there are (4-1) three H atoms on the adjacent C atom.

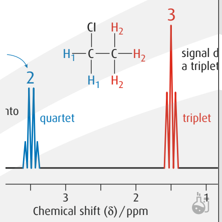




58 chloroethane

The signal at δ = 1.5ppm is split into a triplet, so there must be (3-1) two H atoms on the adjacent carbon.



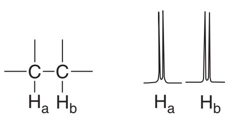


59 splitting peaks & names

Number of peaks	Name
1	singlet
2	doublet
3	triplet
4	quartet

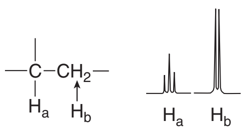
60 common splitting patterns

[1]



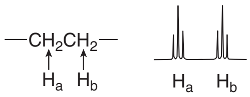
- H_a: one adjacent H_b proton
- H_b: one adjacent H_a proton

[2]

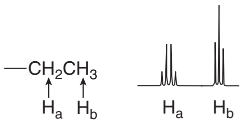


- H_a: two adjacent H_b protons
- H_b: one adjacent H_a proton

61 common splitting patterns

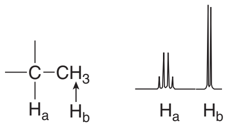
[3] 

- H_a: two adjacent H_b protons
- H_b: two adjacent H_a protons

[4] 

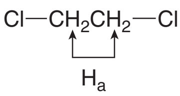
- H_a: three adjacent H_b protons
- H_b: two adjacent H_a protons

62 common splitting patterns

[5] 

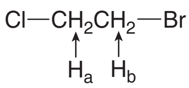
- H_a: three adjacent H_b protons
- H_b: one adjacent H_a proton

63 splitting example 1



All protons (Hs) are equivalent (H_a), so there is no splitting and the NMR peak is one singlet.

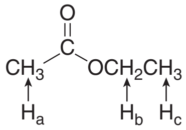
64 splitting example 2



There are two peaks. Ha & Hb are nonequivalent protons bonded to adjacent C atoms, so they split each other's peak.

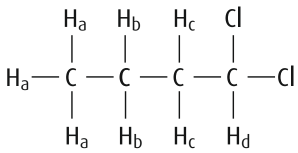
The H_a signal is split into a triplet by the two H_b protons. The H_b signal is split into a triplet by the two H_a protons.

65 splitting example 3

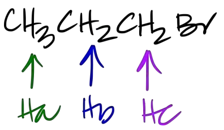


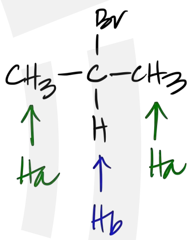
There are three peaks. H_a has no adjacent nonequivalent pro- tons, so its signal is a singlet. The H_b signal is split into a quartet by the three H_c protons. The H_c signal is split into a triplet by the two H_b protons.

66 splitting example 4



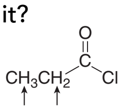
67 splitting examples 5 & 6

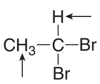


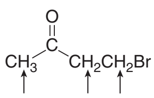


68 skill check

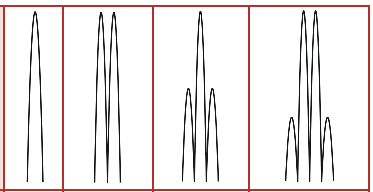
Into how many peaks will each indicated proton be split?

a. 

b. 

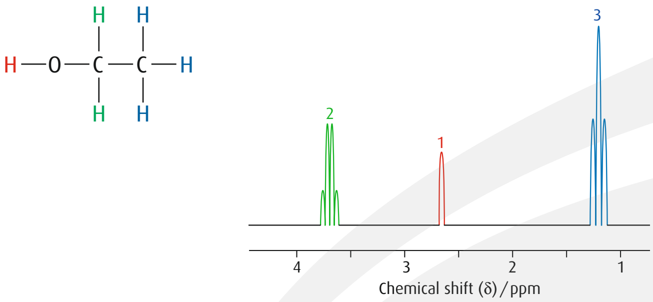
c. 

69 splitting rules

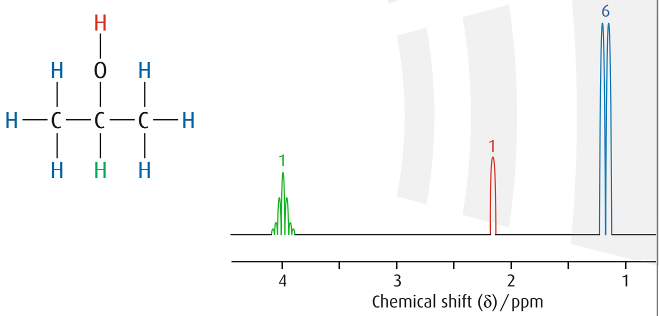


	singlet	1 : 1 doublet	1 : 2 : 1 triplet	1 : 3 : 3 : 1 quartet
Multiplicity	1	2	3	4
No. of equivalent protons on adjacent C atoms	0	1	2	3

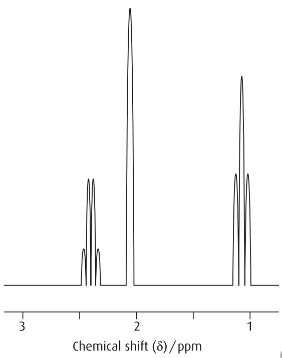
70 nmr spectrum of ethanol



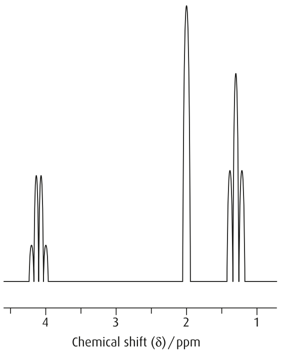
71 nmr spectrum of propan-2-ol



72 skill check - C_4H_8O



73 skill check - $C_4H_8O_2$

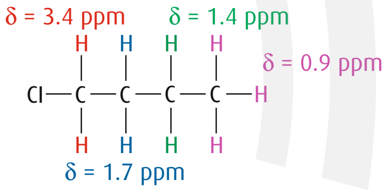


74 chemical shifts & electronegative atoms

The presence of very electronegative atoms in a molecule can cause chemical shifts to move to higher values.

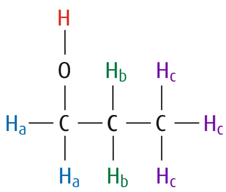
The closer the protons are to the very electronegative atom, the greater the effect.

75 chemical shifts & electronegative atoms



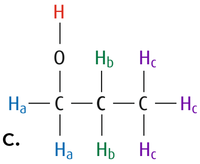
76 complications

When a molecule is asymmetrical and there are non-equivalent protons on both sides of a particular group, the spectrum becomes complex.



77 propan-1-ol

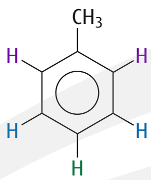
For instance, in the spectrum of propan-1-ol, Hb are split by Ha and Hc.



The signal for Hb could either be described as a quartet of triplets or a triplet of quartets. This signal is very complicated, and an easy way of describing the peak is as a complex multiplet.

78 methylbenzene

For a molecule such as methylbenzene, the protons on the ring are not all equivalent, but because they are in very similar environments, they are likely to show up as just one peak in the NMR spectrum.



79 The use of 'heavy water', D_2O

Protons directly attached to oxygen or nitrogen atoms (O–H or N–H) can appear almost anywhere in an NMR spectrum.

They can, however, be identified by deuterium exchange.

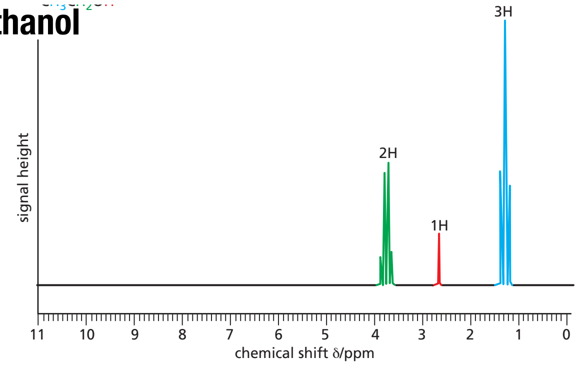
80 The use of 'heavy water', D_2O

If the compound containing them is dissolved in D_2O ('heavy water', D=^{2}H), the protons are exchanged with deuterium atoms in the water.

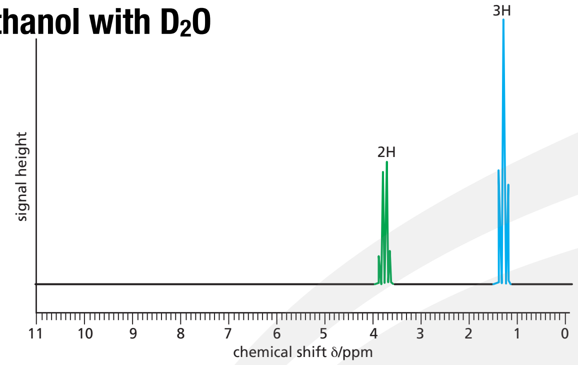
$$CH_3CH_2{-}OH + D_2O \rightleftharpoons CH_3CH_2{-}OD + HDO$$

The peaks due to the –OH or –NH_2 protons disappear.

81 ethanol



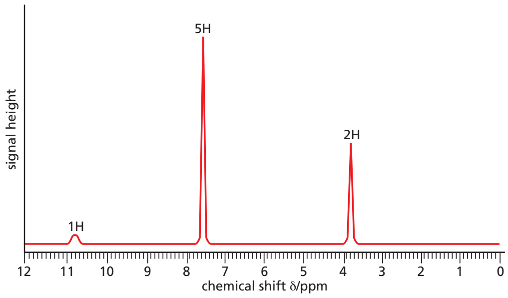
82 ethanol with D_2O



83 skill check 21

The following shows the NMR spectrum of a compound molecular formula $C_8H_8O_2$. The peak at δ = 10.8 disappears on adding D_2O. Work out its structure.

84 skill check 21



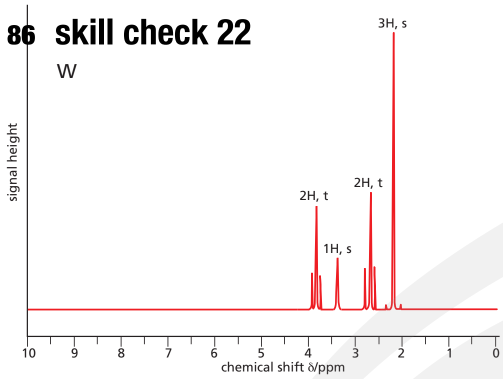
85 skill check 22

Apart from ethyl ethanoate there are at least 15 other isomers of $C_4H_8O_2$. The ^1H NMR spectra of two of them, W and X, are shown below.

Explain the splitting patterns seen in these spectra, and use the spectra to suggest the structures of W and X.

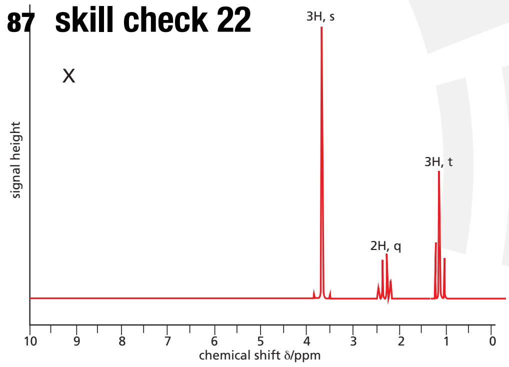
86 skill check 22

W



87 skill check 22

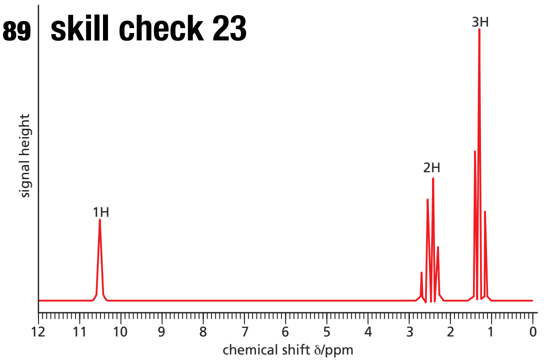
X



88 skill check 23

The following shows the NMR spectrum of compound Y, whose molecular formula is $C_3H_6O_2$. Suggest a possible structure for Y, with reasons.

89 **skill check 23**

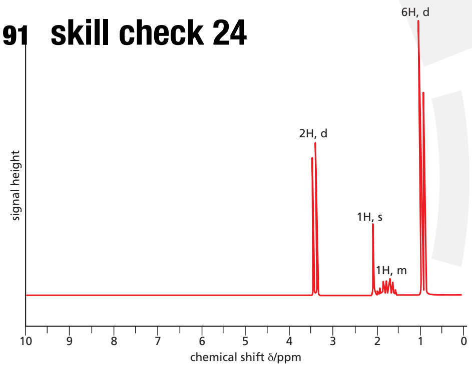


90 **skill check 24**

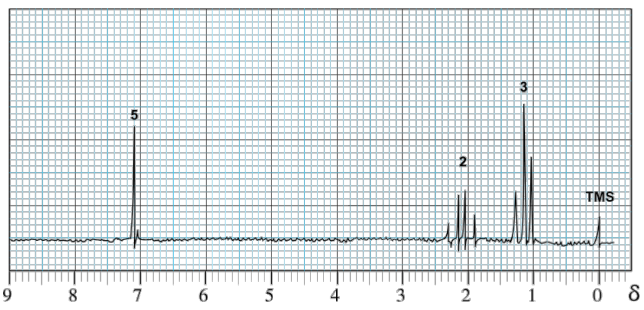
The following shows the ^{1}H NMR spectrum of an alcohol Z.

Suggest the structure of Z, explain the splitting pattern, and predict which peak would disappear when D_2O is added.

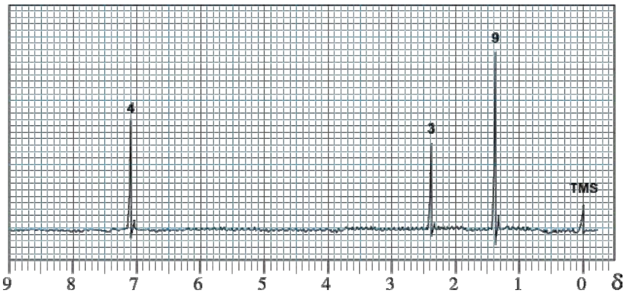
91 **skill check 24**



92 **skill check 25 - C_8H_{10}**



93 skill check 26 - $C_{11}H_{16}$



94 ^{13}C nmr

^{12}C, is the most abundant isotope of carbon. It does not have spin because it has an even number of protons and an even number of neutrons. C-13 can be detected using low-energy radio waves and it is possible to generate ^{13}C-NMR spectra, but C-13 accounts for only about 1.1% of all naturally occurring carbon.

95 ^{13}C nmr

A ^{13}C NMR spectrum is simpler than a 1H spectrum. This is not only because there are usually fewer carbon atoms in a molecule than there are hydrogen atoms, but also because the absorbances in a ^{13}C spectrum usually appear as singlets.

96 ^{13}C nmr

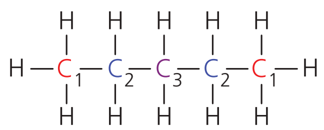
Although this greatly simplifies the spectrum, it has the disadvantage that the intensities of the peaks are not dependent on the number of carbon atoms, and so it is not possible to determine the number of carbon atoms associated with a particular absorbance.

97 ^{13}C nmr

Each peak represents a different carbon environment and each environment will have a different chemical shift.

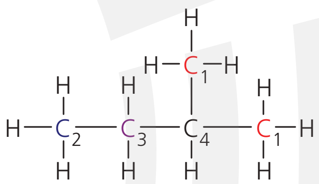
It is essential that you are able to recognise different environments within carbon compounds.

98 pentane



pentane has three different C environments.

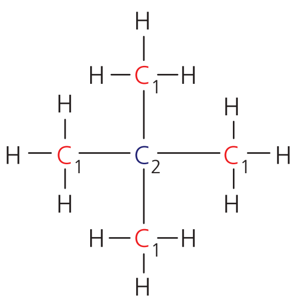
99 2-methylbutane



2-methylbutane has four different C environments.

100 2,2-dimethylpropane

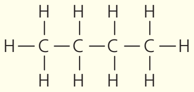
2,2-dimethylpropane has two different C environments



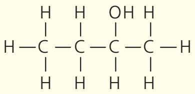
101 skill check

Identify the number of carbon environments in each of the following compounds.

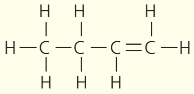
a)



b)

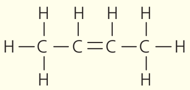


c)

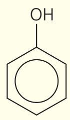


102 skill check

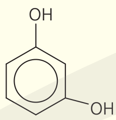
d)



e)

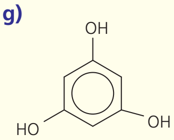


f)

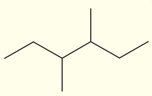


103 skill check

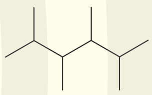
g)



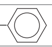
h)



i)



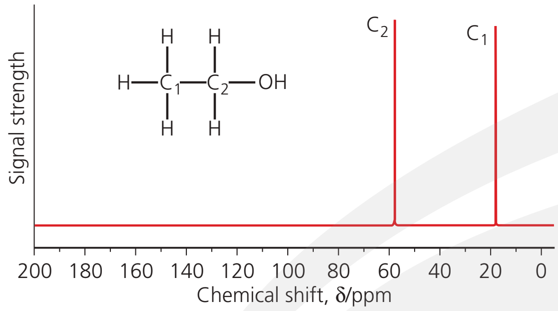
104 ^{13}C nmr table

Hybridisation of carbon atom	Environment of carbon atom	Example structures	Chemical / ppm shift range (δ)
sp^3	alkyl	CH_3—, CH_2—, —CH—	0–50
sp^3	next to alkene/arene	—CH_2—C=C, —CH_2— 	10–40
sp^3	next to carbonyl/carboxyl	—CH_2—COR, —CH_2—CO_2R	25–50
sp^3	next to nitrogen	—CH_2—NH_2, —CH_2—NR_2, —CH_2—NHCO	30–65
sp^3	next to chlorine (—CH_2—Br and —CH_2—I are in the same range as alkyl)	—CH_2—Cl	30–60
sp^3	next to oxygen	—CH_2—OH, —CH_2—O—CO—	50–70

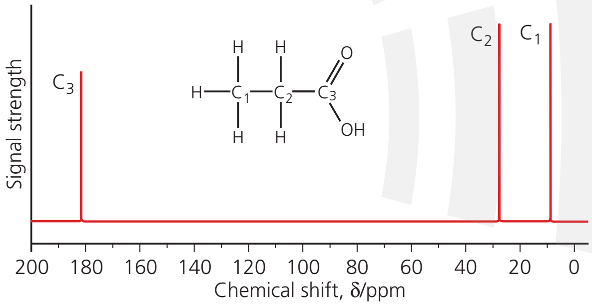
105 ^{13}C nmr chemical shifts table

Hybridisation of carbon atom	Environment of carbon atom	Example structures	Chemical shift range (δ) / ppm
sp^2	alkene or arene	—C=C—, benzene ring	110–160
sp^2	carboxyl	R—CO_2H, R—CO_2R	160–185
sp^2	carbonyl	R—CHO, R—CO—R	190–220
sp	alkyne	R—C≡C—	65–85
sp	nitrile	R—C≡N	100–125

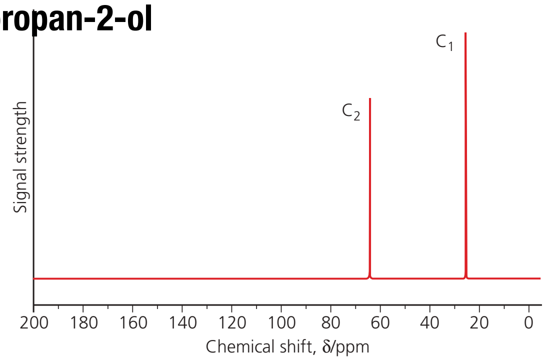
106 ethanol



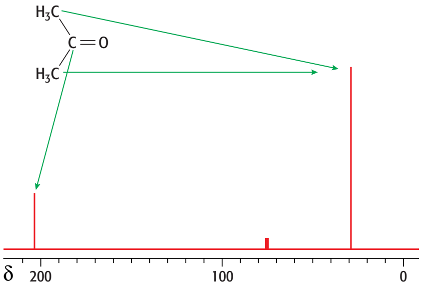
107 propanoic acid



108 propan-2-ol



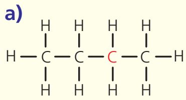
109 propanone



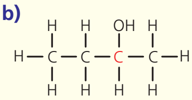
110 skill check

State the range of the chemical shift, δ, in ppm, for each C highlighted in the following structures.

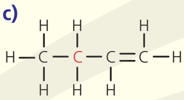
a)



b)

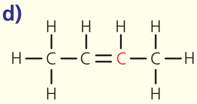


c)

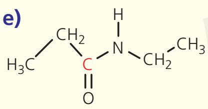


111 skill check

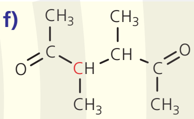
d)



e)

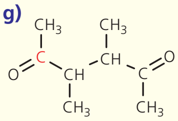


f)

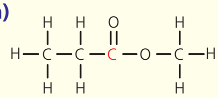


112 skill check

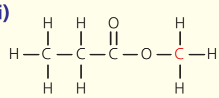
g)



h)

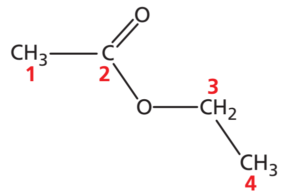


i)

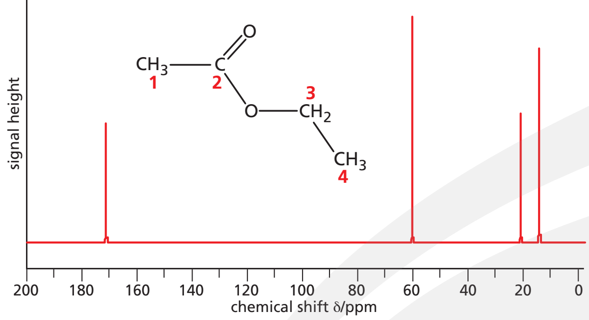


113 ^{13}C nmr of ethyl ethanoate

The spectrum of ethyl ethanoate shows four peaks, one for each of the carbon atoms in the molecule.



114 ^{13}C nmr of ethyl ethanoate



115 ^{13}C nmr of ethyl ethanoate

The peak on the left of the spectrum, at 171ppm, is for carbon 2, and the peak at 60ppm is for carbon 3.

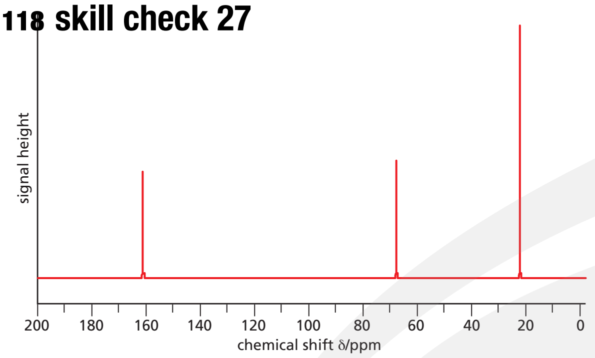
116 ^{13}C nmr of ethyl ethanoate

It is a little more difficult to assign the other two peaks, at 13 and 22ppm, but because the CH_3 next to the C=O is likely to be more deshielded due to the electron-withdrawing effect of the C=O, we can identify carbon 1 with the peak at 22ppm, leaving the peak at 13ppm associated with carbon 4.

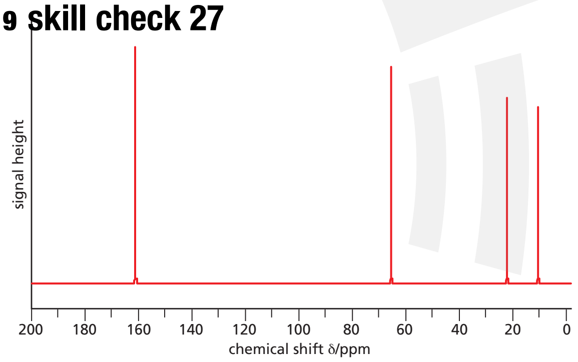
117 skill check 27

Two isomers of ethyl ethanoate are propyl methanoate and prop-2-yl methanoate. Their 13C spectra are shown below. Decide which compound gives which spectrum.

118 skill check 27



119 skill check 27



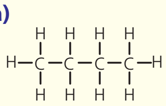
120 H nmr skill check

For each of the compounds below determine:

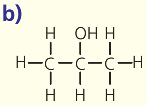
the number of H environments
the relative ratios of the peaks
the splitting of each peak
the chemical shift range of each peak.

121 H nmr skill check

a)



b)



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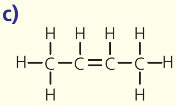
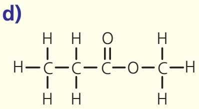


122 H nmr skill check

d)



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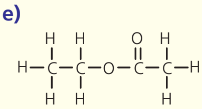

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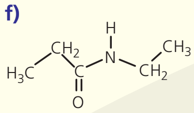
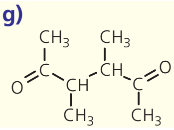


123 H nmr skill check

g)



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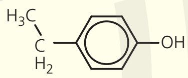

124 H nmr skill check

i)