CIE A Level Chemistry

Your notes

37.3 Carbon-13 NMR Spectroscopy

Contents

Interpreting & Explaining Carbon-13 NMR Spectroscopy

Your notes

Interpreting & Explaining Carbon-13 NMR Spectra

- Nuclear Magnetic Resonance (NMR) spectroscopy is used for analysing organic compounds
- Atoms with odd mass numbers usually show signals on NMR
  - For example isotopes of atoms
  - Many of the carbon atoms on organic molecules are carbon-12
  - A small quantity of organic molecules will contain the isotope carbon-13 atoms
  - These will show signals on a ^{13}C NMR
- In ^{13}C NMR, the magnetic field strengths of carbon-13 atoms in organic compounds are measured and recorded on a spectrum
- Just as in ^{1}H NMR, all samples are measured against a reference compound – Tetramethylsilane (TMS)
- On a ^{13}C NMR spectrum, non-equivalent carbon atoms appear as peaks with different chemical shifts

Chemical shift values (relative to TMS) for ^{13}C NMR analysis table

Hybridisation of carbon atom	Environment of carbon atom	Example	Range of chemical shift (ppm)
sp^3	alkyl	**C**H_3–, **C**H_2–, **C**H–, –**C**–	0 - 50
sp^3	next to alkene / arene	–**C**–C=C, –**C**–Ar*	25 - 50
sp^3	next to carbonyl / carboxyl	**C**–COR, **C**–CO_2R	30 - 65
sp^3	next to halogen	**C**–X	30 - 60
sp^3	next to oxygen	**C**–O	50 - 70
sp^2	alkene / arene	–**C**=C–, –**Ar***–	110 - 160
sp^2	carboxyl	R–**C**OOH, R–**C**OOR	160 - 185
sp^2	carbonyl	R–**C**HO, R–**C**O–R	190 - 220
sp	nitrile	R–**C** ≡ N–	100 - 125

* represents a benzene ring

Features of a ^{13}C NMR spectrum

- ^{13}C NMR spectra display sharp single signals
  - There aren't any complicated spitting patterns as seen with ^{1}H NMR spectra
- The height of each signal is **not** proportional to the number of carbon atoms present in a single molecular environment

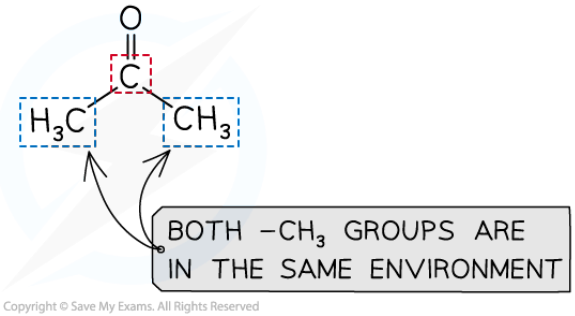
- $CDCl_3$ is used as a solvent to dissolve samples for ^{13}C NMR
  - On spectra, a single solvent peak appears at 80 ppm caused by ^{13}C atoms in the CDCl
  - This can be ignored when interpreting ^{13}C spectra

Your notes

Explaining ^{13}C molecular environments

- On an organic molecule, the carbon-13 environments can be identified in a similar way to the proton environments in ^{1}H NMR
- For example, propanone

Identifying molecular environments in propanone



There are 2 molecular environments in propanone

- There are 2 molecular environments
  - Therefore, 2 signals will be present on its ^{13}C NMR spectrum
- The carbonyl carbon will produce a ^{13}C peak in the range of 190 - 220 ppm
- The 2 methyl groups will produce a ^{13}C peak in the range of 30 - 65 ppm

Carbon-13 NMR spectrum for propanone

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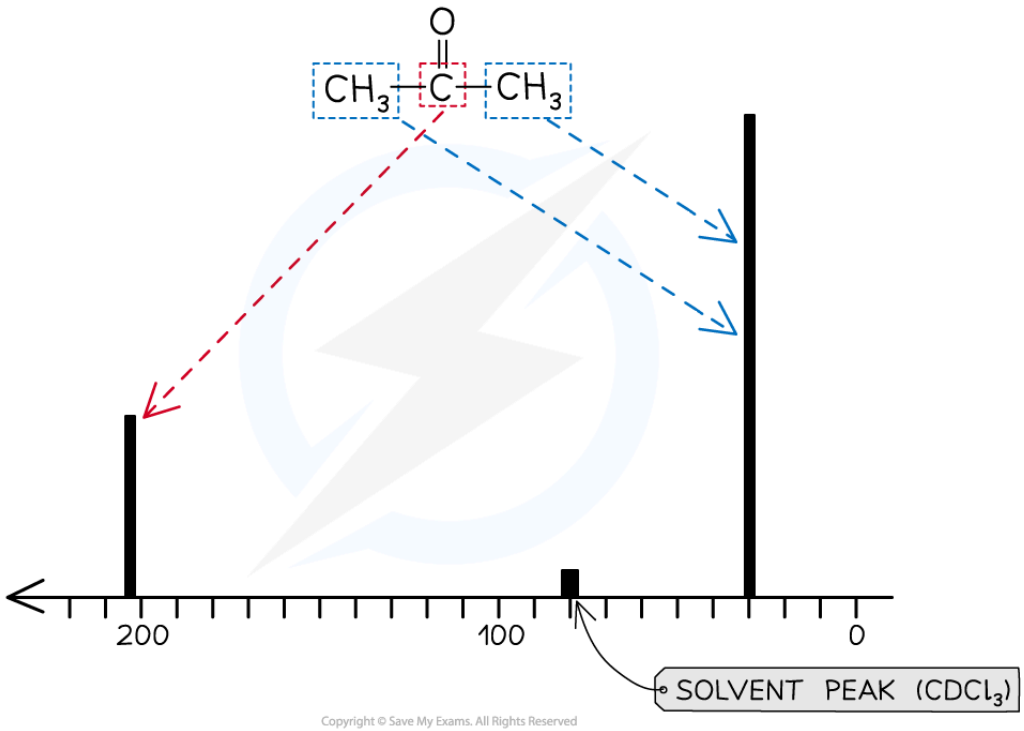


The ^{13}C NMR of propanone shows 2 signals for the 2 molecular environments

Predicting Carbon-13 NMR Spectra

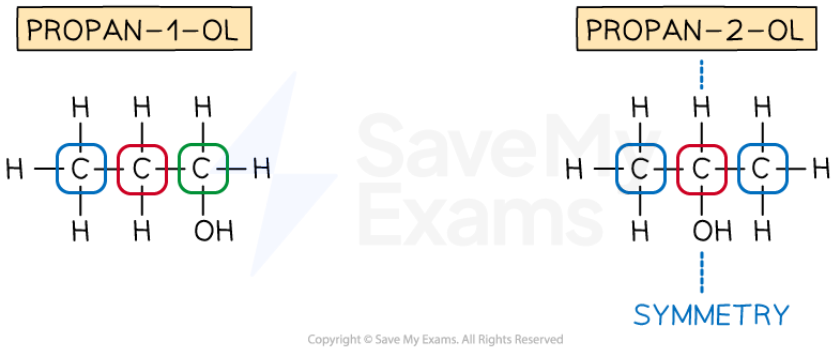
Your notes

Predicting Carbon-13 NMR Spectra

Predicting ^{13}C molecular environments

- The key to carbon-13 NMR spectroscopy is identifying different carbon environments
  - It can help to look for symmetry in the molecules
- For example, propanol
  - There are 2 isomers of propanol: propan-1-ol and propan-2-ol
  - Since both isomers contain 3 carbons, the maximum possible number of ^{13}C NMR peaks is 3
  - Propan-1-ol
    - There is no symmetry or equivalent carbons in a molecule of propan-1-ol
    - Therefore, there will be 3 peaks in the ^{13}C NMR spectrum of propan-1-ol
  - Propan-2-ol
    - There is a line of symmetry through the second carbon with the hydroxyl / OH group attached
    - This means that the CH_3 groups on either side are equivalent
    - Therefore, there will be 2 peaks in the ^{13}C NMR spectrum of propan-2-ol

Identifying molecular environments in propanol



Propan-1-ol has no symmetry / equivalent carbons in its structure, while propan-2-ol has symmetry and, therefore, 2 equivalent carbons

- For example, pentane-1,4-diol
  - Since pentane-1,4-diol contains 5 carbons, the maximum possible number of ^{13}C NMR peaks is 5
  - There are 2 carbons with hydroxyl / OH groups attached but these are not equivalent
    - Carbon-1 is CH_2OH with a neighbouring CH_2
    - Carbon-4 is CHOH with a neighbouring CH_2 and a neighbouring CH_3
    - This means that there is no symmetry within the molecule and, therefore, no equivalent carbons
    - So, there will be 5 peaks in the ^{13}C NMR spectrum of pentane-1,4-diol

Identifying molecular environments in pentane-1,4-diol

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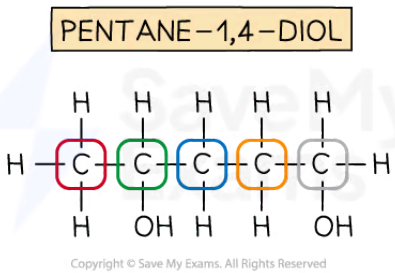
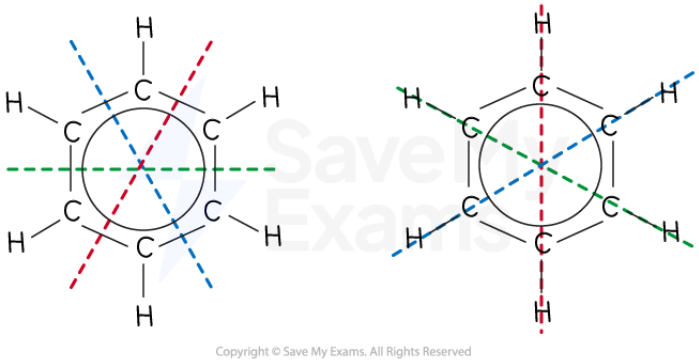


Pentane-1,4-diol has no symmetry / equivalent carbons in its structure

- The same principle of carbon environments also applies to aromatic compounds
- For example, benzene
  - Since benzene contains 6 carbons, the maximum possible number of ^{13}C NMR peaks is 6
  - The benzene molecule has several lines of symmetry leading to the fact that all of the carbons are equivalent
  - So, there will be 1 peak in the ^{13}C NMR spectrum of benzene

Identifying molecular environments in benzene



Benzene has symmetry / equivalent carbons in its structure

Examiner Tip

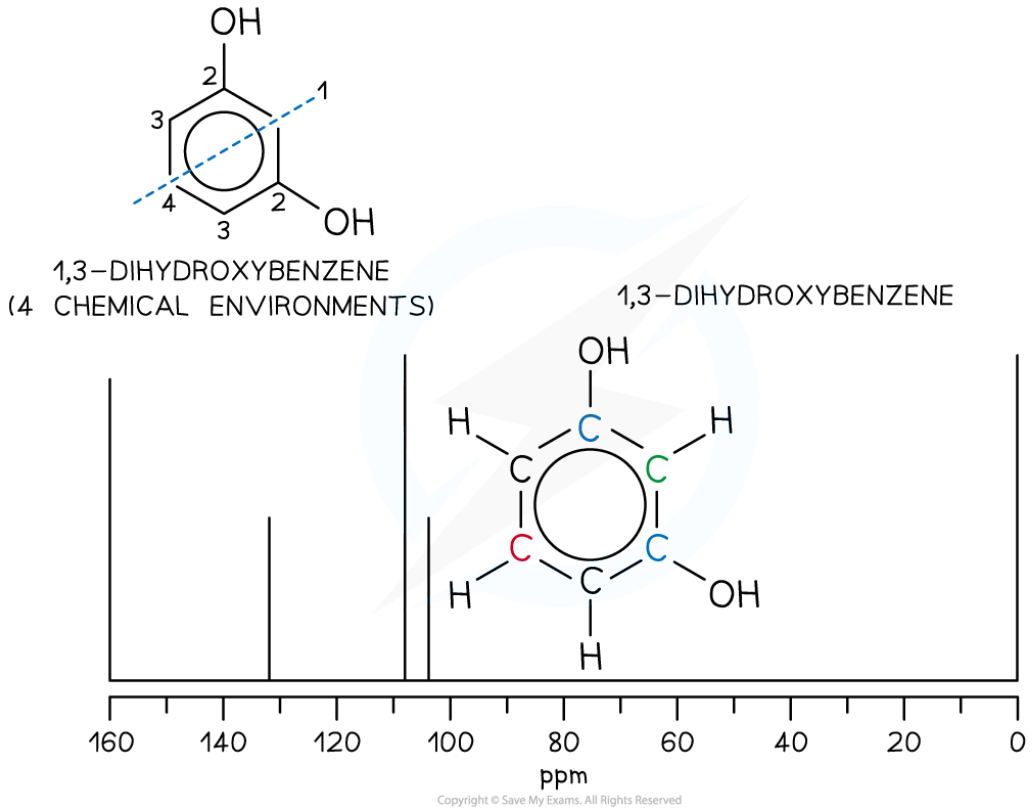
- Counting the number of ^{13}C resonances should be the first step in analysing a spectrum
- For example, it is possible to differentiate the three isomers of dihydroxybenzene quickly be considering the symmetry of the molecules and therefore the number of resonances expected in their spectra.

Worked example

Predict the number of peaks / resonances in the ^{13}C spectrum of 1,3-dihydroxybenzene.

Answer:

- There are 4 chemical environments
- Therefore, there will be four peaks / resonances in the ^{13}C spectrum



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