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学生讲义

教育的本质是和更优秀的人在一起

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Lecture 5 Spectroscopy in Organic Chemistry

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Intensive Teaching and Practicing

Point 1：Mass spectrometry

Spectroscopy can help us determine the real structure of organic compounds. We shall first consider structure determination as a whole and then introduce three different methods:

- mass spectrometry (to determine mass of the molecule and atomic composition)
- nuclear magnetic resonance (NMR) spectroscopy (to determine symmetry, branching, and connectivity in the molecule)
- infrared spectroscopy (to determine the functional groups in the molecule).

1.1 Mass spectrometry by electron impact

In electron impact (EI) mass spectrometry the molecule is bombarded with highly energetic electrons that knock a weakly bound electron out of the molecule. Losing a single electron leaves behind an unpaired electron and a positive charge. The electron that is lost will be one of relatively high energy, and typically one not involved in bonding, for example an electron from a lone pair.

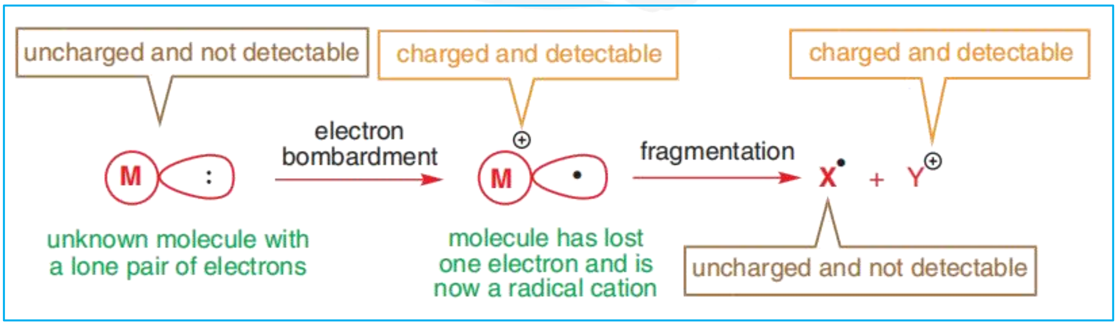


Fig 1 ***《2_Organic Chemistry-Jonathan Clayden》P47***

A typical EI mass spectrum looks like this:

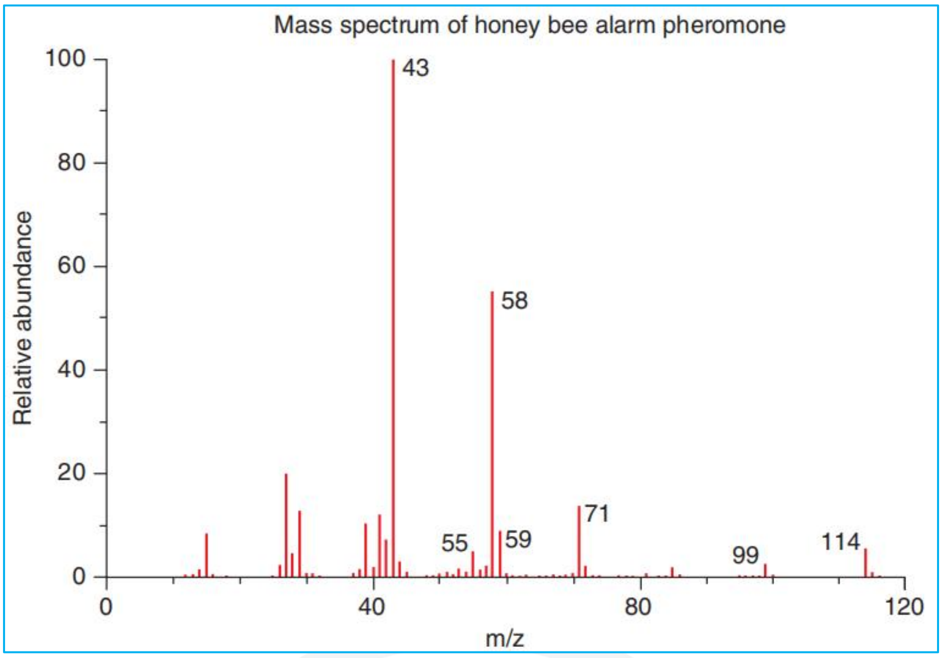


Fig 2 *《2_Organic Chemistry-Jonathan Clayden》P47*

The spectrum you see here indicates that the molecule has a mass of 114 because that is the highest mass observed in the spectrum: the molecule is in fact the volatile ketone heptan-2-one.

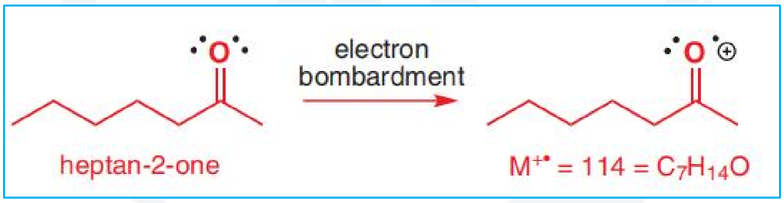


Fig 3 *《2_Organic Chemistry-Jonathan Clayden》P48*

1.2 Mass spectrometry detects isotopes

Most elements can exist as more than one isotope. Usually, one isotope accounts for the vast majority (perhaps >99%) of the atoms of an element. But for some elements, atoms of several isotopes make up a significant cant proportion of the total in a sample. Chlorine, for example, is normally a 3:1 mixture of ^{35}Cl and ^{37}Cl (hence the averaged relative atomic mass of 35.5 for chlorine), while bromine is an almost 1:1 mixture of ^{79}Br and ^{81}Br (hence the average mass of 80 for bromine). Because mass spectrometry weighs individual molecules, there is no averaging: instead it detects the true weight of each molecule, whatever isotope it contains. For example, the molecular ion in the EI mass spectrum of this aryl bromide has two peaks at 186 and 188 of roughly equal intensity. Having two molecular ions of equal intensity separated by 2 mass units is indicative of bromine in a molecule.

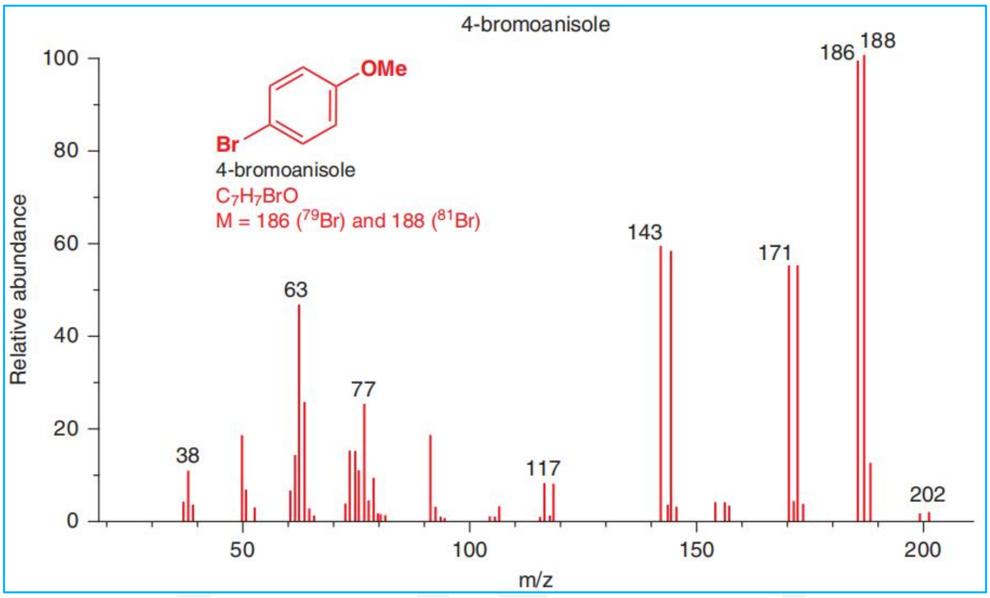


Fig 4 *《2_Organic Chemistry-Jonathan Clayden》P49*

Point 2： Infrared spectra

2.1 Functional groups are identified by infrared spectra

Infrared (IR) spectroscopy, provides a direct way of observing these **functional groups** because it detects the stretching and bending of bonds rather than any property of the atoms themselves. It is particularly good at detecting the stretching of unsymmetrical bonds of the kind found in functional groups such as OH, C=O, NH_2, and NO_2.

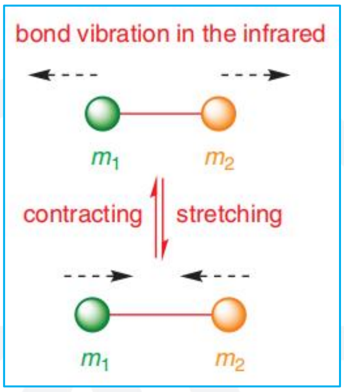
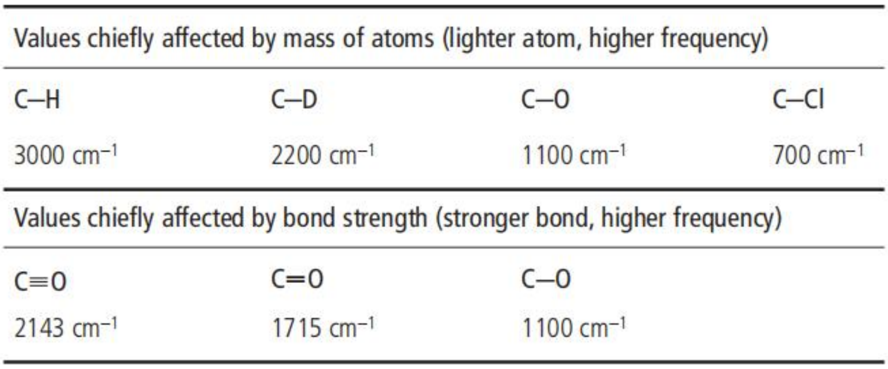


Fig 5 *《2_Organic Chemistry-Jonathan Clayden》P64*

➫Stronger bonds vibrate faster and so do lighter atoms

Infrared spectra are simple absorption spectra. The sample is dissolved in a solvent (or sometimes deposited on the surface of an inert NaCl plate) and exposed to infrared radiation. The wavelength scanned across the spectrum and the amount of infrared energy able to pass through the sample are plotted against the wavelength of the radiation. Just to make the numbers work out nicely, IR spectra don't usually indicate the wavelength but instead a value known as the 'wavenumber', in cm^{-1}, which is simply the number of wavelengths in one centimetre. For a typical bond this will fall between 4000 (short wavelengths, i.e. high frequency) and 500 (long wavelengths, i.e. low frequency). Strong bonds, and light atoms, vibrate fast, so you expect to see these bonds at the high wavenumber end of the spectrum, always plotted at the left-hand end. To illustrate what we mean, here are some typical values for the IR frequencies of a selection of bonds grouped in two ways. Firstly, a series of bonds to increasingly heavy atoms (D, deuterium, has twice the mass of H, and Cl has about twice the mass of O) and secondly a series of bonds of increasing strength.

Firstly, a series of bonds to increasingly heavy atoms (D, deuterium, has twice the mass of H, and Cl has about twice the mass of O) and secondly a series of bonds of increasing strength.



Values chiefly affected by mass of atoms (lighter atom, higher frequency)			
C–H	C–D	C–O	C–Cl
3000 cm^{-1}	2200 cm^{-1}	1100 cm^{-1}	700 cm^{-1}
Values chiefly affected by bond strength (stronger bond, higher frequency)			
C≡O	C=O	C–O	
2143 cm^{-1}	1715 cm^{-1}	1100 cm^{-1}	

2.2 Four important regions of the infrared spectrum

The first region, from **4000 to 2500 cm^{-1} is the region for C–H, N–H, and O–H** bond stretching. Most of the atoms in an organic molecule (C, N, O, for example) are about the same weight (12, 14, 16. . .). Hydrogen is an order of magnitude lighter than any of these and so it dominates the stretching frequency by the large effect it has on the reduced mass, so any bond to H comes right at the left-hand end of the spectrum.

Even the strongest bonds between non-H atoms—triple bonds such as C≡C or C≡N absorb at slightly lower frequencies than bonds to hydrogen: these are in the next region, the **triple bond region from about 2500 to 2000 cm^{-1}**. This and the other two regions of the spectrum follow in logical order of bond strength as the reduced masses are all about the same: C=C and C=O **double bonds appear about 2000–1500 cm^{-1}** and at the right-hand end of the spectrum come **single bonds, below 1500 cm^{-1}**. These regions are summarized in this chart, which you should memorize.

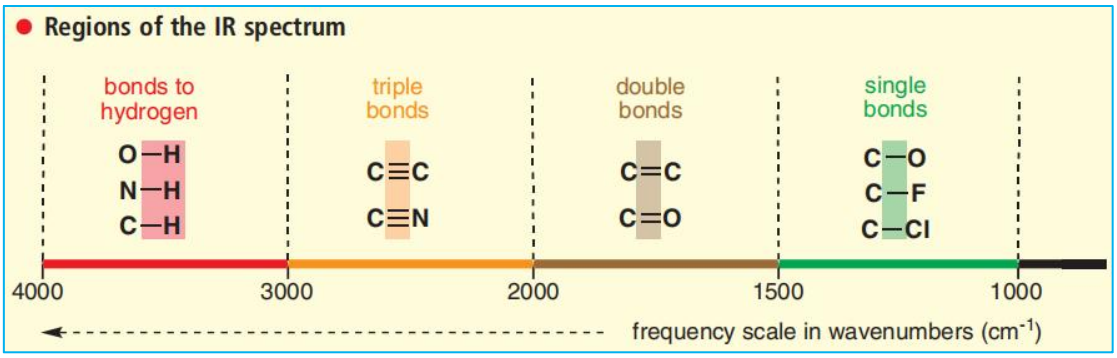


Fig 5 *《2_Organic Chemistry-Jonathan Clayden》P64*

2.2.1 The X–H region (4000–3000 cm^{-1}) distinguishes C–H, N–H, and O–H bonds

Have a look at the shaded portions of the following spectra:

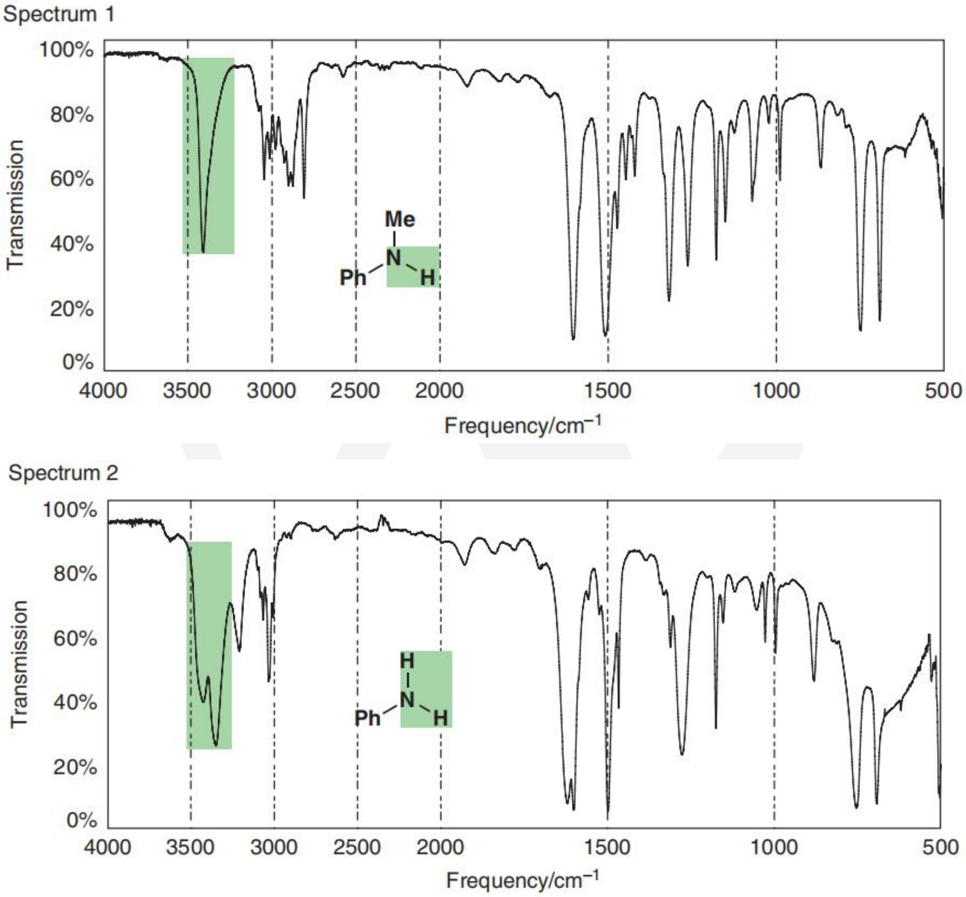


Fig 6 *《2_Organic Chemistry-Jonathan Clayden》P66*

The IR peak of an NH group looks different (spectrum 1) from that of an NH_2 group (spectrum 2). A bond gives an independent vibration only if both bond strength and reduced mass are different from those of neighbouring bonds. In the case of an isolated N–H group, this is likely to be true and we usually get a sharp peak at about 3300 cm−1, whether the NH group is part of a simple amine (R_2NH) or an amide

(RCONHR). The NH_2 group is also independent of the rest of the molecule, but the two NH bonds inside the NH_2 group have identical force constants and reduced masses, and so vibrate as a single unit. Two equally strong bands appear: one for the two N–H bonds vibrating in phase (symmetric) and one for the two N–H bonds vibrating in opposition (antisymmetric). The antisymmetric vibration requires more energy and is at slightly higher frequency.

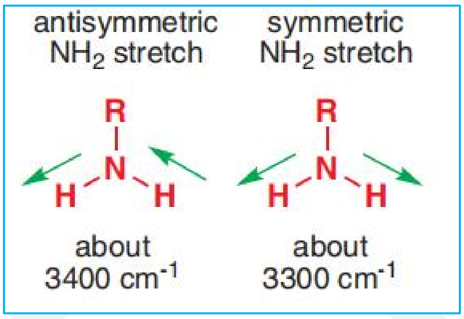


Fig 7 *《2_Organic Chemistry-Jonathan Clayden》P67*

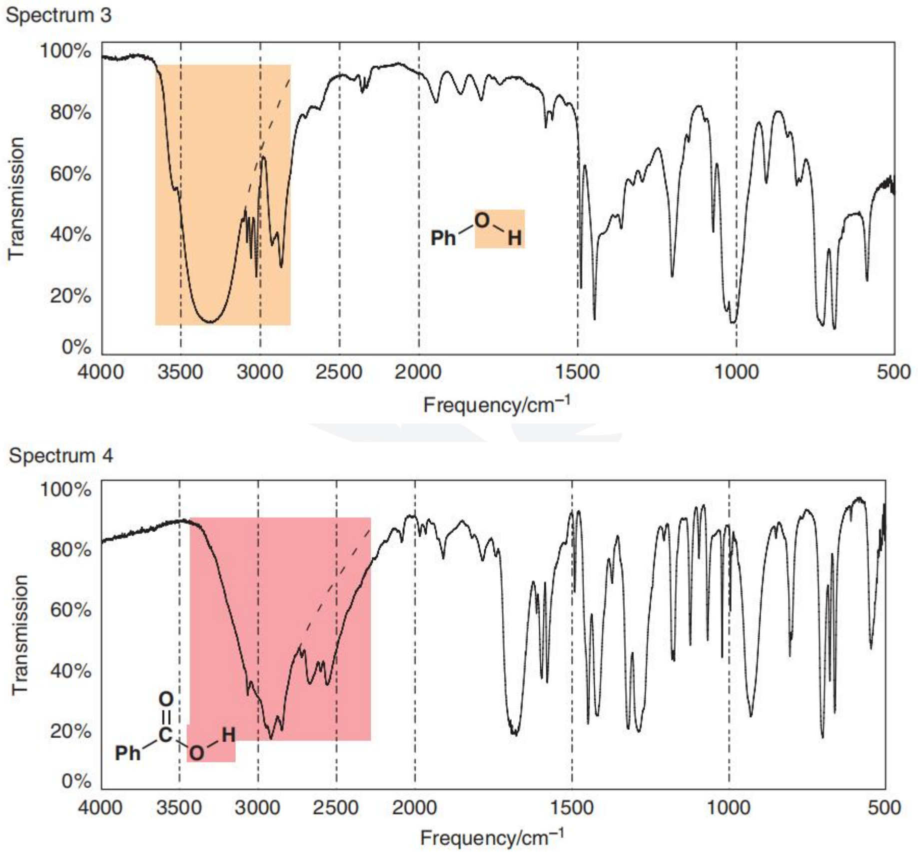


Fig 8 *《2_Organic Chemistry-Jonathan Clayden》P67*

The O–H bands occur at higher frequency, sometimes as a sharp absorption at about 3600 cm^{-1}. More often, as in spectra 3 and 4, you will see a broad absorption at anywhere from 3500 to 2900 cm^{-1}.

Alcohols form hydrogen bonds between the hydroxyl oxygen of one molecule and the hydroxyl hydrogen of another. Carboxylic acids (RCO_2H) form hydrogen-bonded dimers with two strong H bonds between the carbonyl oxygen atom of one molecule and the acidic hydrogen of the other. This leads to differences in O-H bonds absorption spectra.

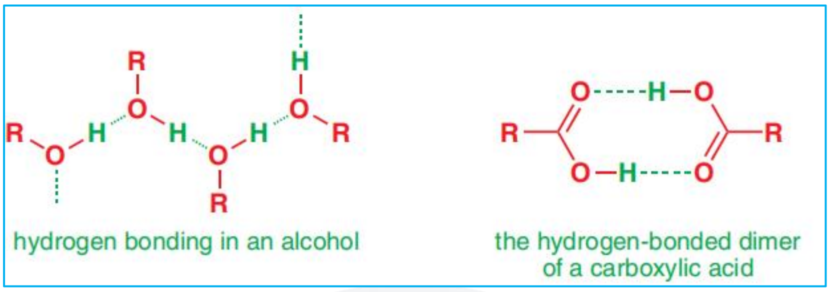


Fig9 *《2_Organic Chemistry-Jonathan Clayden》P68*

Summary:

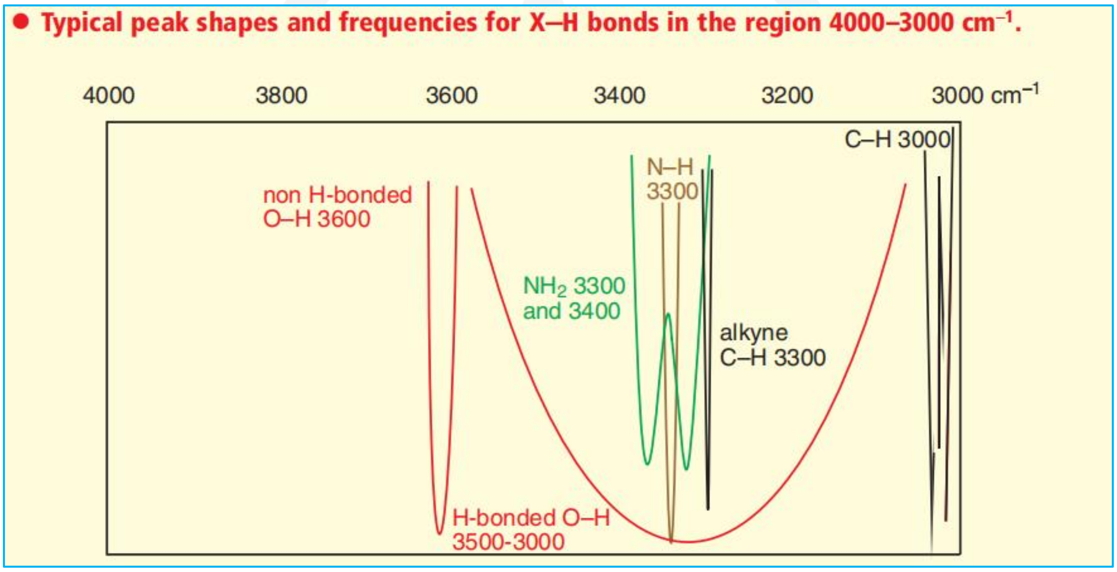


Fig10 *《2_Organic Chemistry-Jonathan Clayden》P69*

2.2.2 The triple bond region (3000–2000 cm^{-1})

When you do see a peak between 2000 and 2500 you can be absolutely certain that the compound is an alkyne (usually at around 2100) or a nitrile (at 2250 cm^{-1}).

Summary:

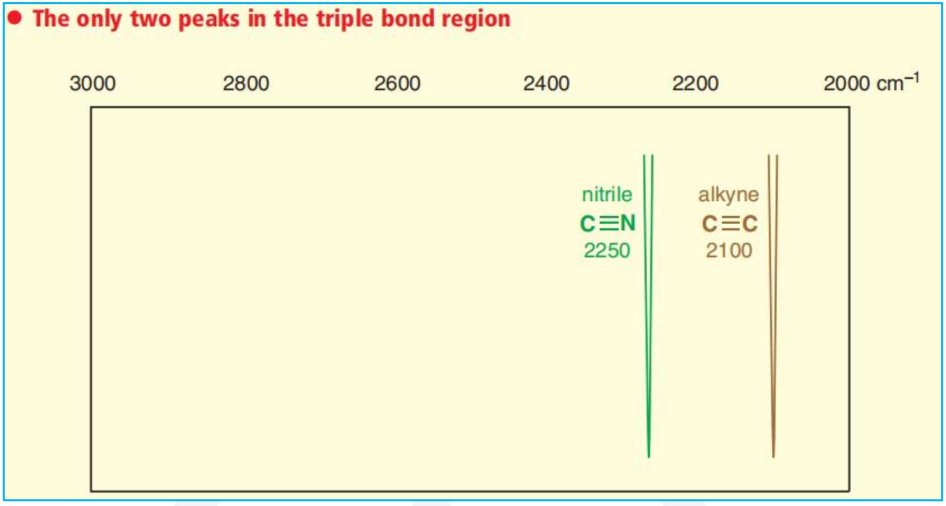


Fig10 ***《2_Organic Chemistry-Jonathan Clayden》P69***

2.2.3 The double bond region (3000–2000 cm^{-1})

Why the nitro group gives two bands is easily understood. Just as with OH and NH_2, it is a matter of how many identical bonds are present in the same functional group. Carbonyl and alkene clearly have one double bond each. The nitro group at first sight appears to contain two different groups, N^+– O^- and N=O, but delocalization means they are identical and we see absorption for symmetric and antisymmetric stretching vibrations. As with NH_2, more energy is associated with the antisymmetric vibration and it occurs at higher frequency (>1500 cm^{-1}).

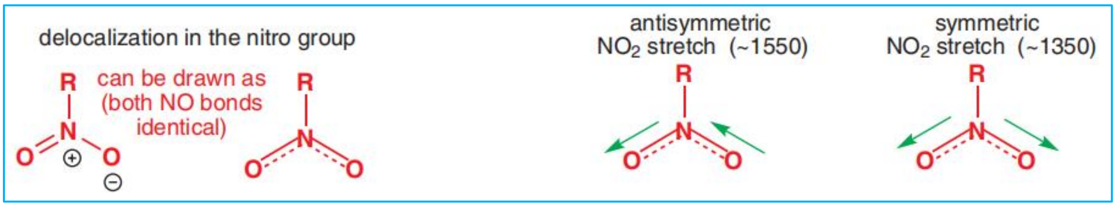


Fig10 ***《2_Organic Chemistry-Jonathan Clayden》P69***

Arenes, being rings, have a much more complex pattern of vibration that cannot be analysed simply, However, it’s worth noting that arene C=C bonds come at lower frequency (<1600 cm^{-1}) than alkene C=C bonds (>1600 cm^{-1}).

You’ve already seen the IR spectra of the three carbonyl compounds below in this chapter. It’s easy to identify the C=O peak in each spectrum—C=O peaks are always intense (you will see why in a minute) and come somewhere near 1700 cm^{-1}.

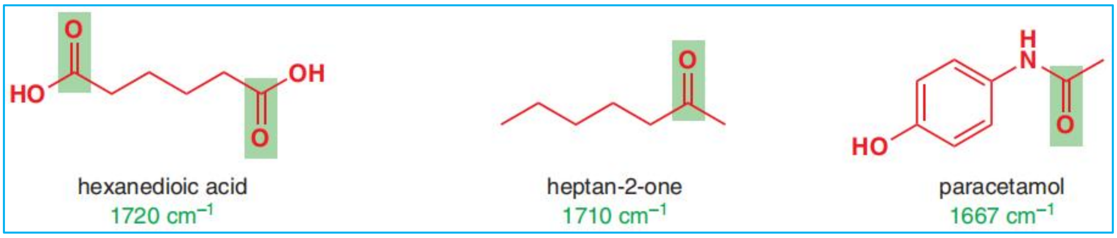


Fig11 ***《2_Organic Chemistry-Jonathan Clayden》P70***

Summary:

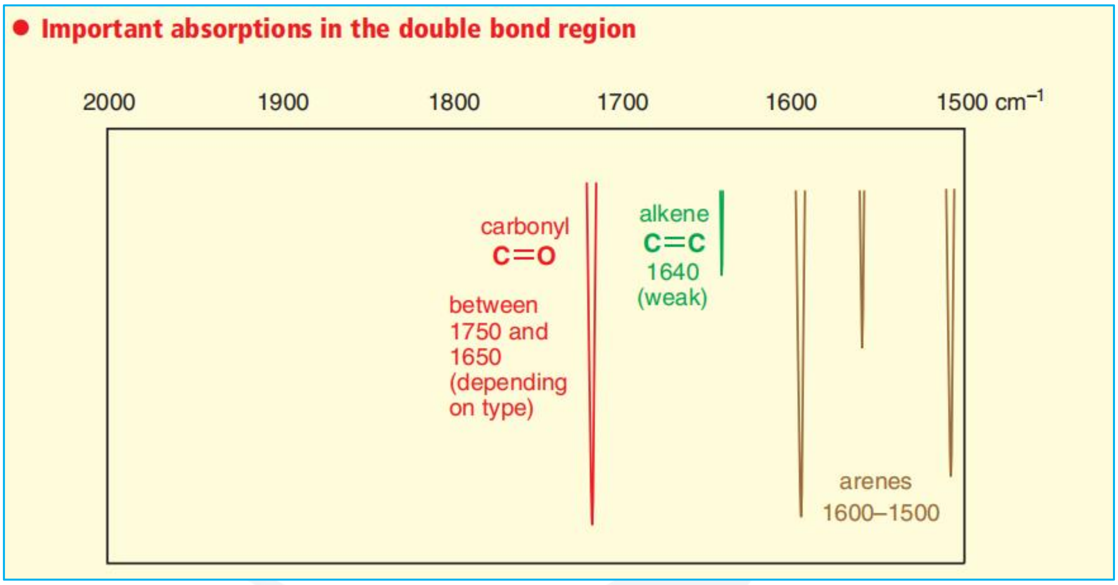
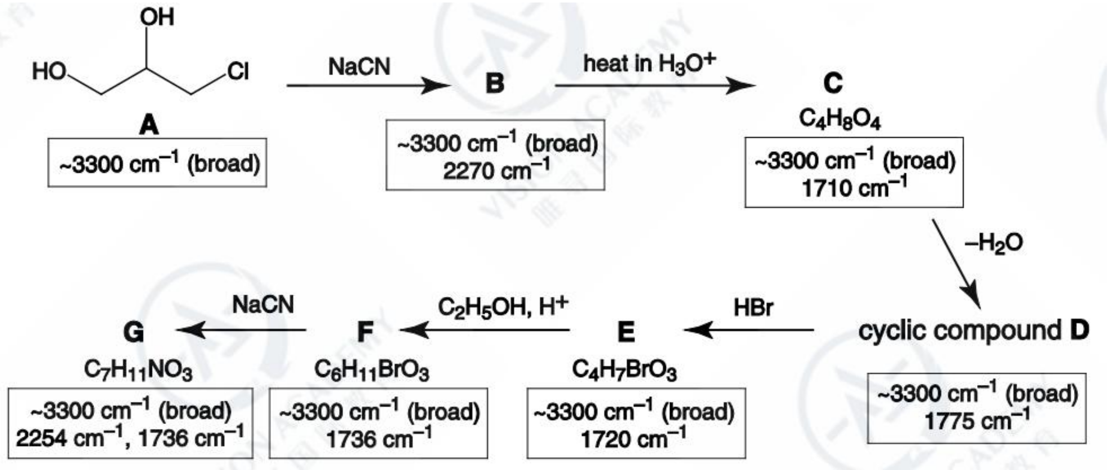
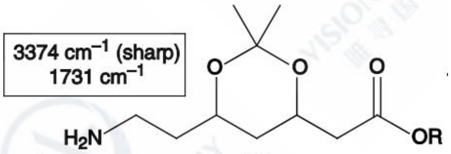


Fig11 ***《2_Organic Chemistry-Jonathan Clayden》P70***

Example 1.*(source,UKChO,2012,4a)*

Given in the boxes are the most characteristic IR stretching frequencies of the intermediates in the synthesis. No stretches due to any C–C or C–H bonds are included; stretching frequencies due to single bonds other than bonds to hydrogen do not show up in the range listed. You are not expected to know these stretching frequencies, but through careful reasoning, you should be able to use them to help work out the structures of the unknowns.





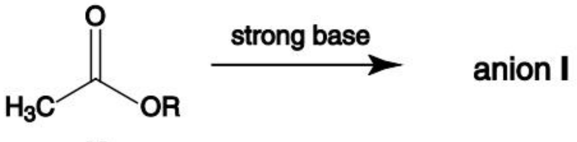
M

(a) Give the structures for the compounds **B** to **G** and, over the course of the whole question, complete the table of IR absorptions found in compounds **A** to **M**.

Absorption/cm^{-1}	~3300 (broad)	?	2250-2275	?	1700-1740
bond	?	C=O in a small ring	?	N-H	?

Exercise 1.*(source,UKChO,2012,4b-4c)*

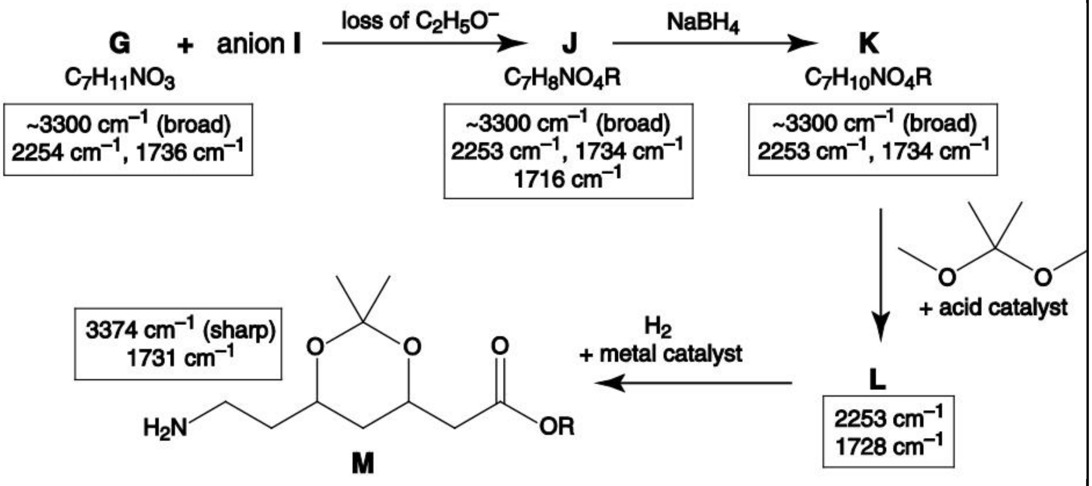
Ester **H** is deprotonated by strongbases to give the reactive carbon nucleophile, anion **I**. The R group in the structure is an alkyl chain which remains unchanged throughout the entire synthesis.



H

(b) Draw the structure for the anion **I**.

The synthesis continues as shown below:



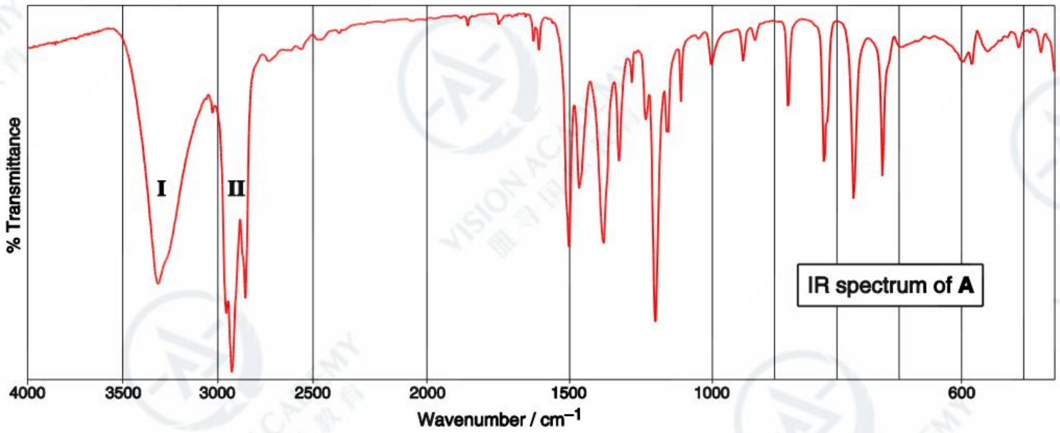
(c) Give the structures for the compounds **J**, **K** and **L**.

Exercise 2.(source,UKChO,2014,4e)

Combustion analysis of Compound **A** indicates that it contains only carbon, hydrogen and oxygen.

In compound **A**, stretching in some of the bonds contained in the X substituents contributes to characteristic peaks in the IR spectrum of this compound (shown below). These characteristic peaks are marked **I** and **II** on the spectrum.

(e) Suggest which bond stretches are responsible for **I** and **II**.



Point 3：The ^{13}C NMR spectrum

3.1 Nuclear magnetic resonance

In a molecule such as propanol, the hydrogen atom of the hydroxyl group is clearly different from the hydrogen atoms of its carbon skeleton, for example. NMR (actually ^{1}H, or proton, NMR) can easily distinguish between these two sorts of hydrogens by detecting the environment the hydrogen’s nucleus finds itself in. Moreover, it can also distinguish between all the other different sorts of hydrogen atoms present. Likewise, carbon (more precisely ^{13}C) NMR can easily distinguish between the three different carbon atoms. Some nuclei with singular mass numbers such as ^{1}H、 ^{13}C and ^{15}N can produce nuclear magnetic resonance spectra.

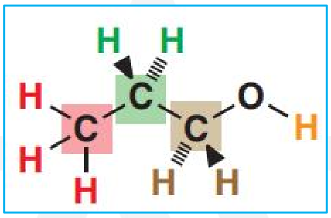


Fig 3.1

^{1}H NMR distinguishes the coloured hydrogens ^{13}C NMR distinguishes the boxed carbons.

A ^{1}H or ^{13}C nucleus in a magnetic field can have two energy levels, and energy is needed to flip the nucleus from the more stable state to the less stable state. But since the amount of energy needed is so small, it can be provided by low-energy electromagnetic radiation of radio-wave frequency. Radio waves flip the nucleus from the lower energy state to the higher state. Turn off the radio pulse and the nucleus returns to the lower energy state. When it does so, the energy comes out again, and this (a tiny pulse of radio frequency electromagnetic radiation) is what we detect.

The sample is irradiated with a short pulse of radiofrequency energy. This disturbs the equilibrium balance between the two energy levels: some nuclei absorb the energy and are promoted to a higher energy level.

When the pulse finishes, the radiation given out as the nuclei fall back down to the lower energy level is detected using what is basically a sophisticated radio receiver.

After lots of computation, the results are displayed in the form of intensity (i.e. number of absorptions) against frequency. Here is an example

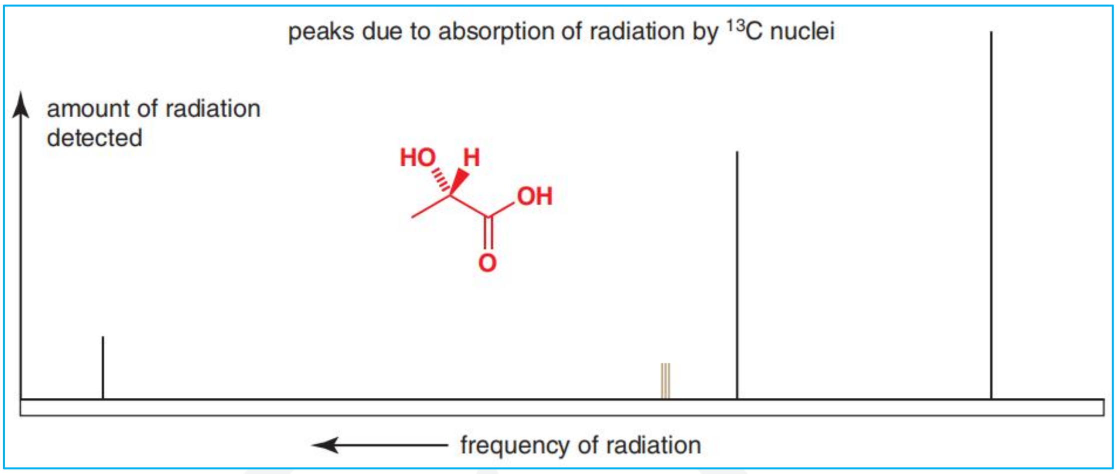


Fig 3.2 *《2_Organic Chemistry-Jonathan Clayden》P54*

3.2 Chemical shift

The variation in frequency for different carbon atoms must mean that the energy jump from ‘nucleus-aligned-with’ to ‘nucleus-aligned-against’ the applied magnetic field must be different for each type of carbon atom. The reason is that the ^{13}C nuclei in question experience a magnetic field that is not quite the same as the magnetic field that we apply. Each nucleus is surrounded by electrons, and in a magnetic field these will set up a tiny electric current. This current will set up its own magnetic field (rather like the magnetic field set up by the electrons of an electric current moving through a coil of wire or solenoid), which will oppose the magnetic field that we apply. The electrons are said to **shield** the nucleus from the external magnetic field. If the electron distribution varies from ^{13}C atom to ^{13}C atom, so does the local magnetic field experienced by its nucleus, and so does the corresponding resonating frequency.

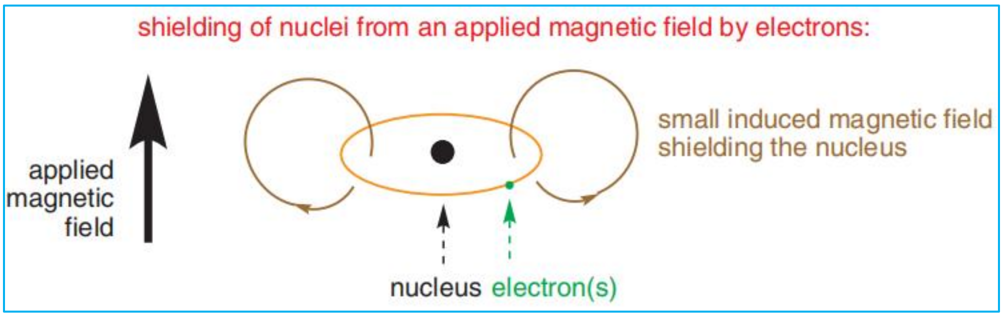


Fig 3.3 *《2_Organic Chemistry-Jonathan Clayden》P54*

● Changes in the distribution of electrons around a nucleus affect:

- **the local magnetic field that the nucleus experiences**
- **the frequency at which the nucleus resonates**
- **the chemistry of the molecule at that atom**

This variation in frequency is known as the chemical shift. Its symbol is δ.

As an example, consider ethanol (right). The red carbon attached to the OH group will have a smaller share of the electrons around it compared to the green carbon since the oxygen atom is more electronegative and pulls electrons towards it, away from the red carbon atom.

The magnetic field that the red carbon nucleus feels will therefore be slightly greater than that felt by the green carbon, which has a greater share of the electrons, since the red carbon is less shielded from the applied external magnetic field—in other words it is **deshielded**. Since the carbon attached to the oxygen feels a stronger magnetic field (it is more 'exposed' to the field as it has lost some of its electronic shielding) there will be a greater energy difference between the two alignments of its nucleus. The greater the energy difference, the higher the resonant frequency (energy is proportional to frequency). So for ethanol we would expect the red carbon with the OH group attached to resonate at a higher frequency than the green carbon, and indeed this is exactly what the ^{13}C NMR spectrum shows.

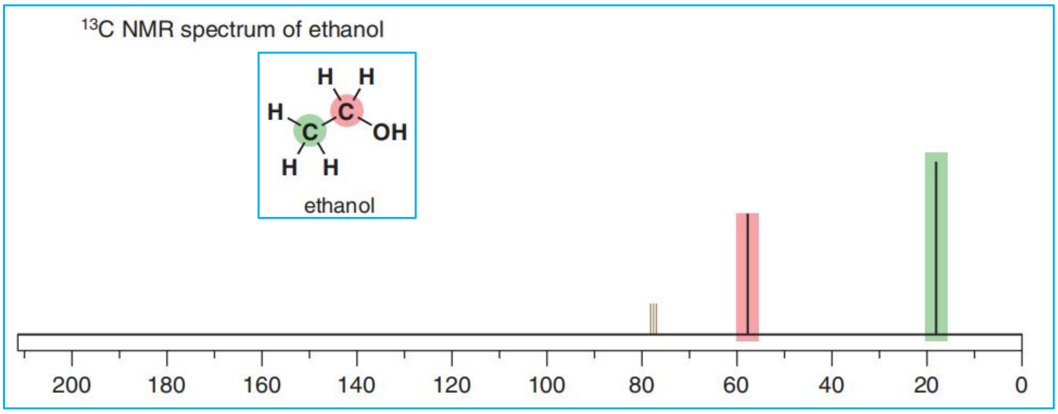


Fig 3.4 *《2_Organic Chemistry-Jonathan Clayden》P55*

3.3 Regions of the ^{13}C NMR spectrum

We can also work out what sort of chemical environment the carbon atoms are in. All ^{13}C spectra can be divided into four major regions: saturated carbon atoms (0–50 ppm), saturated carbon atoms next to oxygen (50–100 ppm), unsaturated carbon atoms (100–150 ppm), and unsaturated carbon atoms next to oxygen, i.e. C=O groups (150 to about 200 ppm).

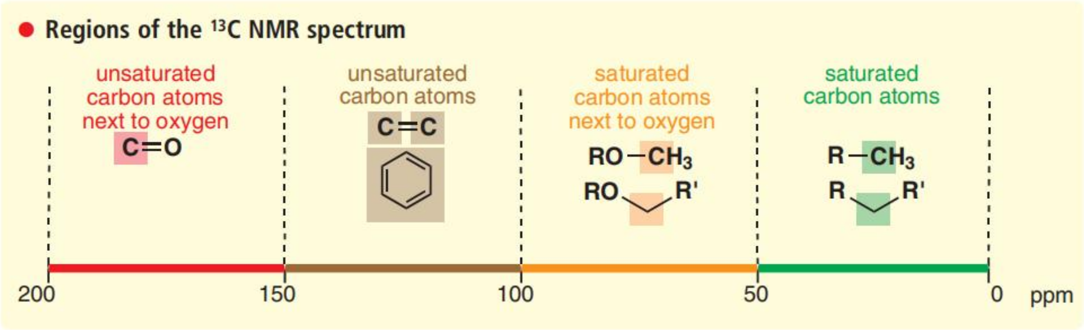


Fig 3.4 *《2_Organic Chemistry-Jonathan Clayden》P57*

3.4 The ^{13}C NMR spectra of some simple molecules

First compound, hexanedioic acid, has the simple NMR spectrum shown here. Because of the symmetry of the molecule, the two carboxylic acids are identical and give one peak at 174.2 ppm. By the same token C2 and C5 are identical, and C3 and C4 are identical. These are all in the saturated region 0–50 ppm but the carbons next to the electronwithdrawing CO_2H group will be more deshielded than the others. So we assign C2/C5 to the peak at 33.2 ppm and C3/C4 to 24.0 ppm.

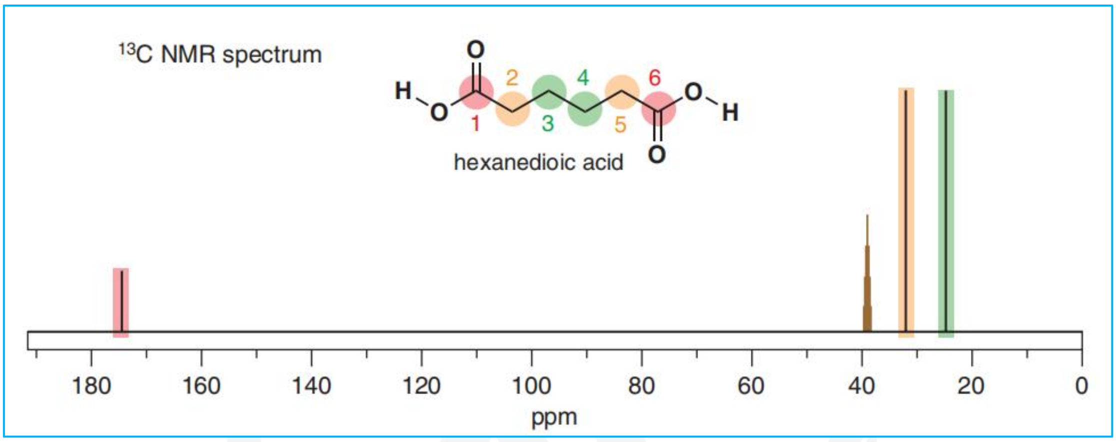


Fig 3.5 *《2_Organic Chemistry-Jonathan Clayden》P57*

The second compound is the bee pheromone. It has no symmetry so all its seven carbon atoms are different. The carbonyl group is easy to identify (208.8 ppm) but the rest are morediffifi cult. The two carbon atoms next to the carbonyl group come at lowest field, while C7 is at highest fifi eld (13.9 ppm). It is important that there is the right number of signals at about the right chemical shift. If that is so, we are not worried if we cannot assign each frequency to a precise carbon atom (such as atoms 4, 5, and 6, for example). As we said before, don’t be concerned with the *intensities* of the peaks.

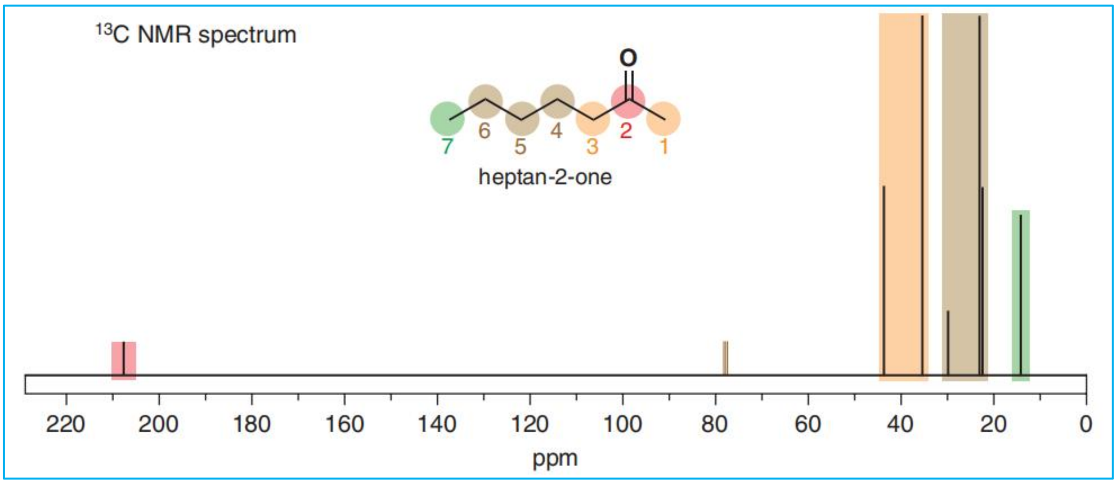


Fig 3.6 ***Organic Chemistry-Jonathan Clayden》P58***

The third compound is BHT : its formula is $C_{15}H_{24}O$ and the first surprise in its NMR spectrum is that there are only seven signals for the 15 carbon atoms. There is obviously a lot of symmetry; in fact the molecule has a plane of symmetry vertically as it is drawn here, and the coloured blobs indicate pairs or groups of carbons related to each other by symmetry which therefore give only one signal. The very strong signal at $\delta = 30.4$ ppm belongs to the six identical methyl groups on the *t*-butyl groups (coloured red) and the other two signals in the 0–50 ppm range are the methyl group at C4 and the brown central carbons of the *t*-butyl groups. In the aromatic region there are only four signals as the two halves of the molecule are the same. As with the last example, we are not concerned with exactly which is which— we just check that there are the right number of signals with the right chemical shifts.

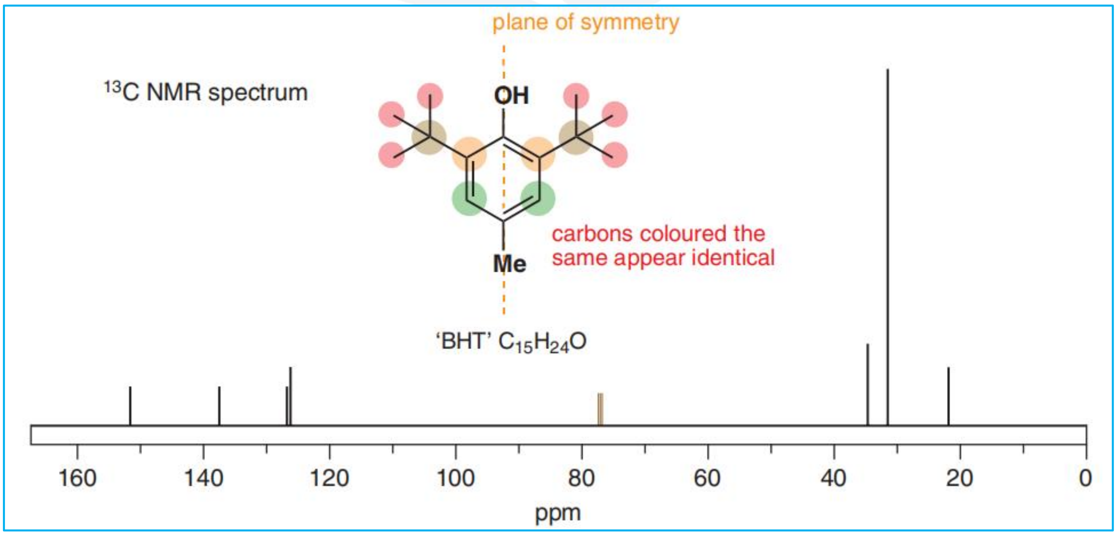
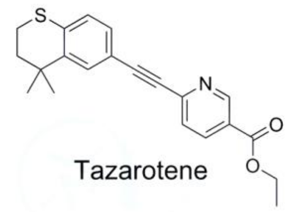


Fig 3.7 ***Organic Chemistry-Jonathan Clayden》P58***

Example 2.(*source,UKChO,2014,3*)

(f) How many signals would you expect to see in the ^{13}C NMR spectrum of tazarotene?



(*source,UKChO,2014,3g*)

Tazarotene is actually a pro-drug, meaning it is metabolised to its active form when inside the body.

The active form has a molar mass of 323.41 g mol^{-1} and two fewer signals in its ^{13}C NMR spectrum than tazarotene.

(g) Suggest a structure for the active form of the drug.

Point 4：The ^{1}H NMR spectrum

^{1}H NMR spectra have many similarities with ^{13}C NMR spectra: the scale runs from right to left and the zero point is given by the same reference compound. However, the scale is much smaller, ranging over only about 10 ppm instead of the 200 ppm needed for carbon.

Proton NMR differs from ^{13}C NMR in a number of ways.

- ^{1}H is the major isotope of hydrogen (99.985% natural abundance), while ^{13}C is only a minor isotope (1.1%).
- ^{1}H NMR is quantitative: the area under the peak tells us the number of hydrogen nuclei, while ^{13}C NMR may give strong or weak peaks from the same number of ^{13}C nuclei.
- Protons interact magnetically (‘couple’) to reveal the connectivity of the structure, while ^{13}C is too rare for coupling between ^{13}C nuclei to be seen.
- ^{1}H NMR shifts give a more reliable indication of the local chemistry than that given by ^{13}C spectra.

Hydrogen nuclei in a magnetic field have two energy levels: they can be aligned either with or against the applied magnetic field.

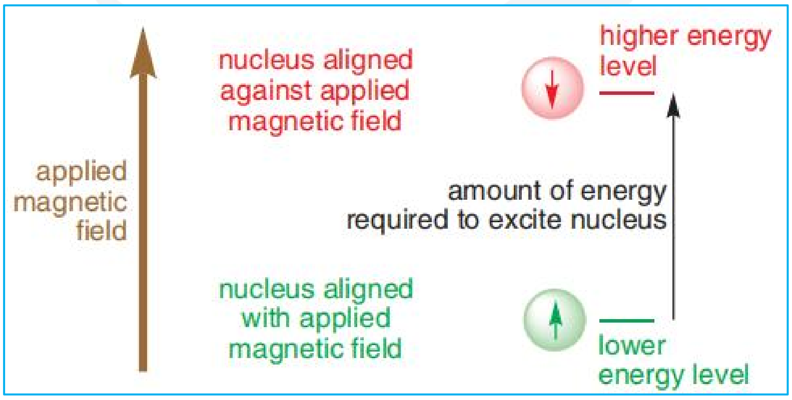


Fig 4.1 ***Organic Chemistry-Jonathan Clayden》P270***

4.1 Integration tells us the number of hydrogen atoms in each peak

You know that the position of a signal in an NMR spectrum tells us about its environment. In ^{1}H NMR the size of the peaks is also important: the area under the peaks is exactly proportional to the number of protons:

Note:

Generally， NMR instruments are equipped with integrator, which can make the integral curve of peak area.The area under the peaks is computed and recorded as a line,and the height of the curve is directly proportional to the proton’s number.

Like this:

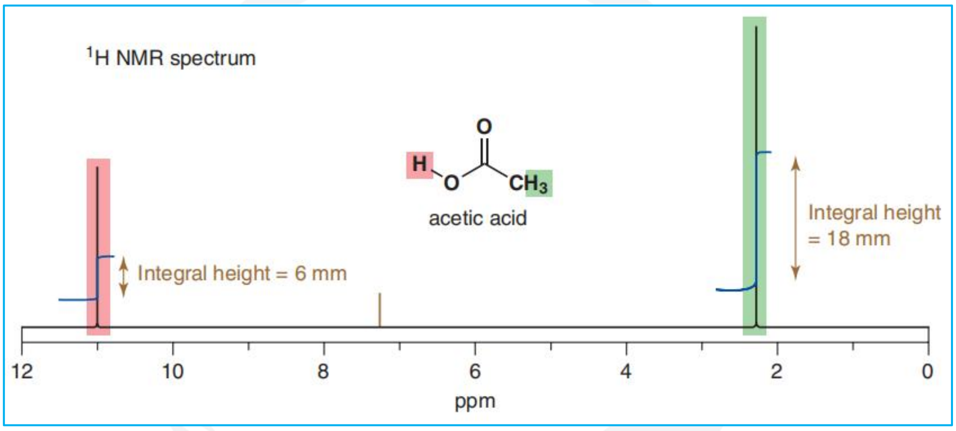


Fig 4.2 ***Organic Chemistry-Jonathan Clayden》P271***

In this next example it is easy to assign the spectrum simply by measuring the steps in the integral. There are two identical methyl groups (CMe$_2$) with six Hs, one methyl group by itself with three Hs, the OH proton (1 H), the CH$_2$ group next to the OH (two Hs), and finally the CH$_2$CH$_2$ group between the oxygen atoms in the ring (four Hs).

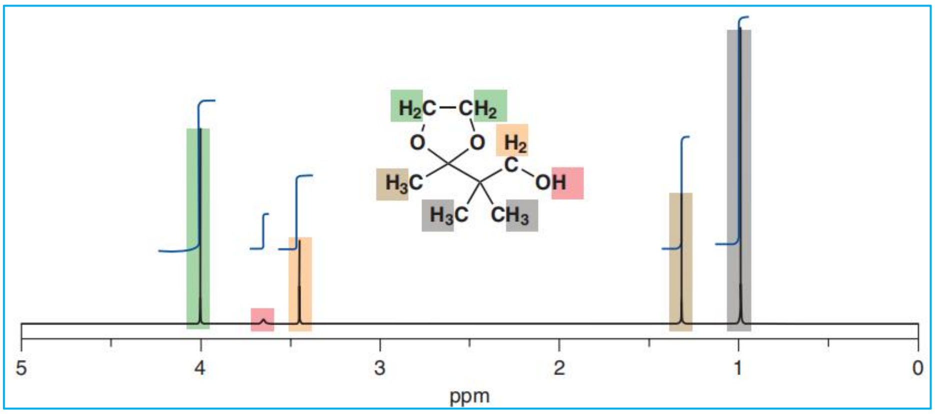


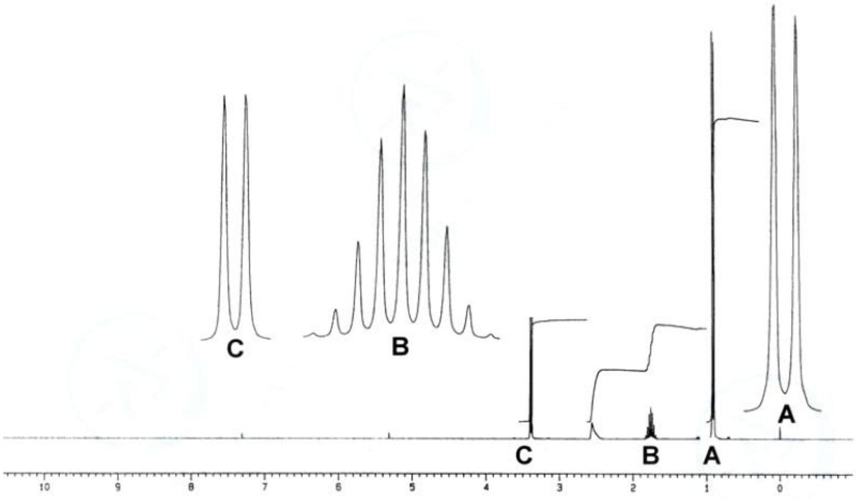
Fig 4.2 ***Organic Chemistry-Jonathan Clayden》P271***

Example 3.*(Source,UKChO,2011,4)*

Your task is to identify compounds **1-7** using the information given below.

In your answer booklet, you should draw the **skeletal** formula of each compound and give the systematic names of compounds **1- 4**.

- Compounds **1-7** all have the same molecular formula, $\mathbf{C_4H_{10}O}$, but have different chemical, structural and spectroscopic properties.
- Compounds **5, 6,** and **7** have lower boiling points than compounds **1-4**.
- Compounds **1-4** have a broad absorption at 3300 cm^{-1} in their infra-red spectra.
- Compound **2** can exist as optical isomers.
- The ^1H NMR spectrum of compound **3** is shown below:



- The ^1H NMR spectra of compounds **4** and **5** each consist of two distinct signals.

- The ^1H NMR spectrum of compound **5** gives the following data:

Chemical Shift/ppm	Splitting pattern	Relative intensity
1.21	triplet	3
3.47	quartet	2

- The ^{13}C NMR spectrum of compound **6** contains four distinct signals, whereas the ^{13}C NMR spectrum of compound **7** shows only three.

> **Information about NMR spectroscopy .**
>
> ----*(The introduction to **NMR** spectroscopy in the original title is omitted here, and only useful information is retained)*
>
> For example, the spectrum for compound **3** shown opposite, indicates that there are 4 different ^1H environments. The relative intensities of the peaks are 2:1:1:6.
>
> The *splitting patterns* for peaks **A**, **B** and **C** are shown in larger scale.

4.2 Coupling in the proton NMR spectrum

4.2.1 Nearby hydrogen nuclei interact and give multiple peaks

As mentioned above, we expect that the ^1H NMR spectrum of 1,1,2-tribromoethane should have two peaks, but in fact, its spectrum has five peaks, as shown in the figure below.

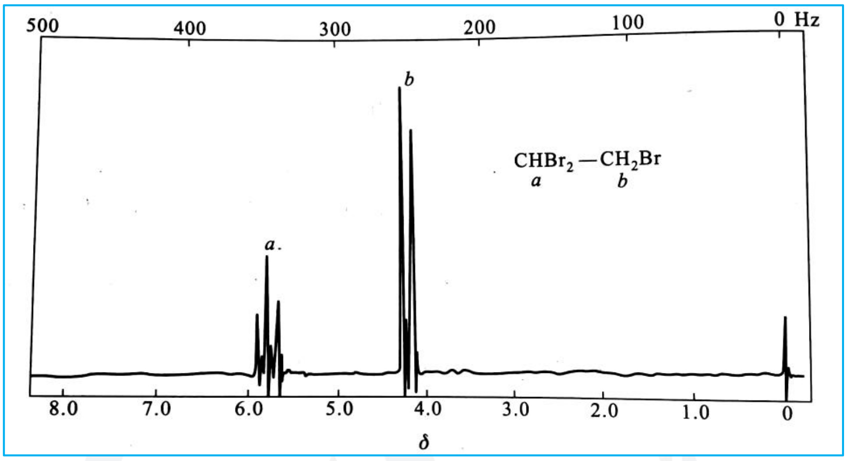


Fig 4.3 *The ^1H NMR spectrum of 1,1,2-tribromoethane*

The absorption peak of Ha is divided into three(triple peak, represented by ‘t’) and the absorption peak of Hb is divided into two(double peak, represented by ‘d’). This situation is called ‘splitting’. More detailed information about the structure can be obtained from the signal splitting.

Splitting is caused by the small magnetic field generated by the spin of hydrogen nuclei on adjacent carbon atoms in the molecule. The spin of each hydrogen nucleus has two orientations. The influence of different orientations on the magnetic induction intensity of the external magnetic field can be slightly strengthened or slightly weakened.

The hydrogen nucleus is also affected by the magnetic field generated by the spin of the adjacent hydrogen nucleus. This interaction is called spin coupling.

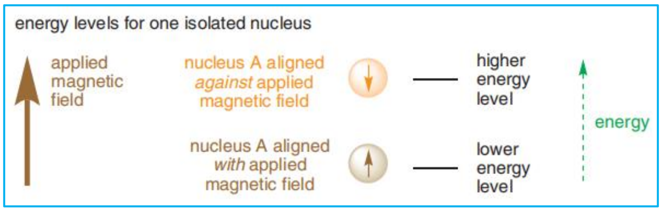


Fig 4.4 ***Organic Chemistry-Jonathan Clayden》P287***

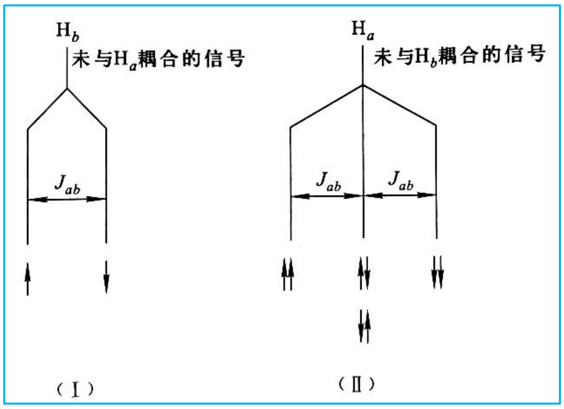


Fig 4.5

> Note:
>
> Generally , the number of splits of a signal depends on the number of adjacent hydrogen. If there are n equal adjacent hydrogen, the signal is split into (n + 1) peaks

☛Coupling constants

In each group of peaks, the distance between small peaks is in Hertz (Hz), which is called **coupling constant(which is called *J*).**

4.2.2 The intensities of the splitting pattern

There are two groups of peaks in the ^{1}H NMR spectrum of CH_3CH_2I. The quartet with larger δ value corresponds to H_a, and the other group of triplet is H_b on —CH_3

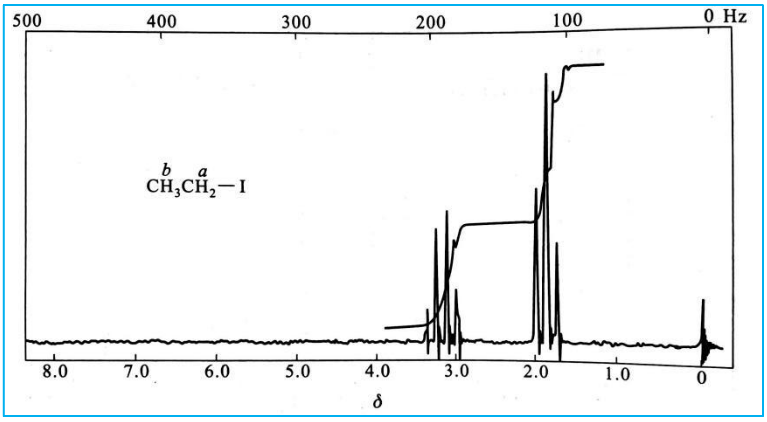


Fig 4.6 *The ^{1}H NMR spectrum of CH_3CH_2I*

Similar to the spectrum of 1,1,2-tribromoethane, the signal of H_b is split into triple peaks by Ha, and its intensity ratio should be 1:2:1. H_a is affected by three adjacent H_b. The spin orientations of the three Hb can be combined in the following four ways:

(1) ↑↑↑ (all strengthen)
(2) ↑↑↓ ↑↓↑ ↓↑↑ (one strengthen)
(3) ↑↓↓ ↓↑↓ ↓↓↑ (one weakened)
(4) ↓↓↓ (all weakened)

The result is a 1:3:3:1 quartet.If there are more protons involved, we continue to get more complex systems.However, it is time-consuming to obtain the intensity ratio of the post splitting peak by this method.

Any hydrogen is divided into multiple peaks by adjacent ***n*** equivalent hydrogen cracks, and the theoretical intensity ratio between the multiple peaks is the coefficient ratio of each item after expansion of $(x + y)^{\boldsymbol{n}}$.The intensities can all be deduced simply from **Pascal's triangle**, which gives the coefficients in a binomial expansion.

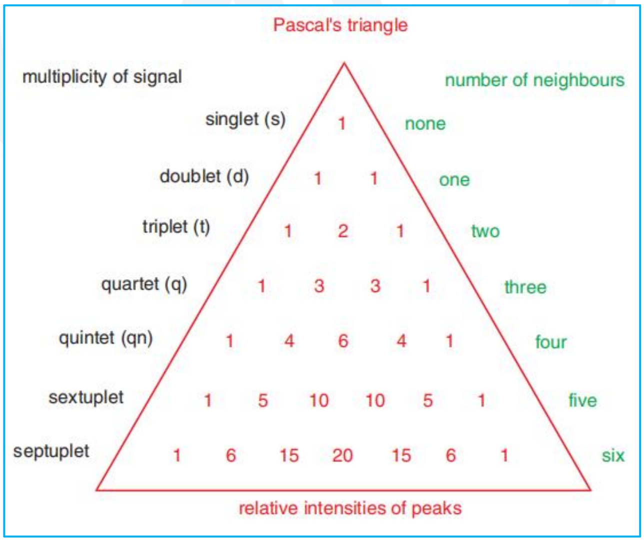


Fig 4.7 ***Organic Chemistry-Jonathan Clayden》 P291***

You can read off from the triangle what pattern you may expect when a proton is coupled to *n* equivalent neighbours. There are always *n* + 1 peaks with the intensities shown by the triangle. **All numbers except 1 are the sum of the two diagonally opposite numbers in the upper row.** You will often meet ethyl groups (CH_3CH_2X), where the CH_2 group couples to three identical protons and appears as a 1:3:3:1 quartet and the methyl group as a 1:2:1 triplet. In isopropyl groups, $(CH_3)_2CHX$, the methyl groups appear as a 6H doublet and the CH group as a septuplet.

Let's see another simple example: the four-membered cyclic ether oxetane. Its NMR spectrum has a 4H triplet for the two identical CH_2 groups next to oxygen and a 2H quintet for the CH_2 in the middle. Each proton HX 'sees' four identical neighbours (HA) and is split equally by them all to give a 1:4:6:4:1 quintet. Each proton HA 'sees' two identical neighbours HX and is split into a 1:2:1 triplet. The combined integral of all the lines in the quintet together is 2 and of all the lines in the triplet is 4.

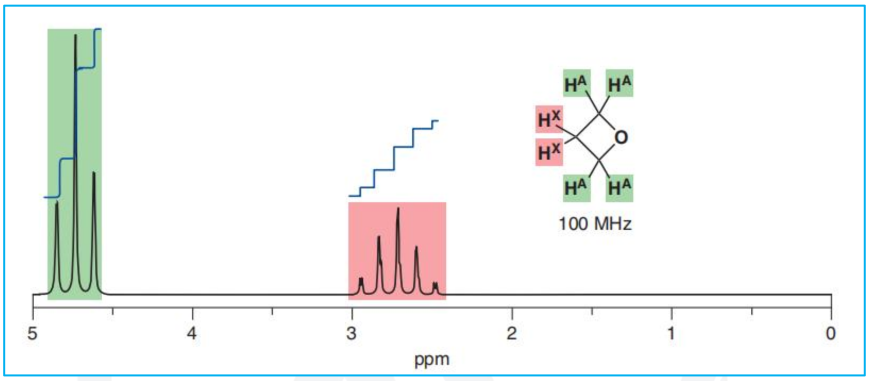


Fig 4.8 ***Organic Chemistry-Jonathan Clayden》P292***

In all of these molecules, a proton may have had several neighbours. What happens when call those neighbours have different coupling constants?Chrysanthemic acid, the structural core of the insecticides produced by pyrethrum flowers, gives an example of the simplest situation— where a proton has two different neighbours.

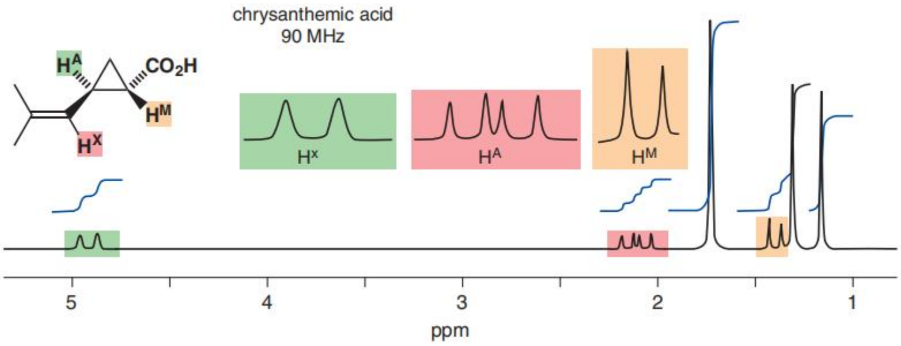


Fig 4.9 ***Organic Chemistry-Jonathan Clayden》P292***

Chrysanthemic acid has a carboxylic acid, an alkene, and two methyl groups on the threemembered ring. Proton H^A has two neighbours, H^X and H^M. The coupling constant to H^X is 8 Hz, and that to H^M is 5.5 Hz. We can construct the splitting pattern as shown below.

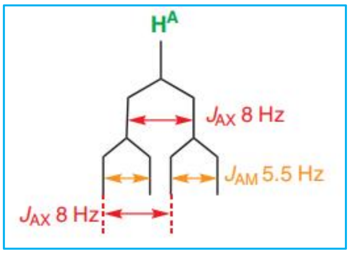
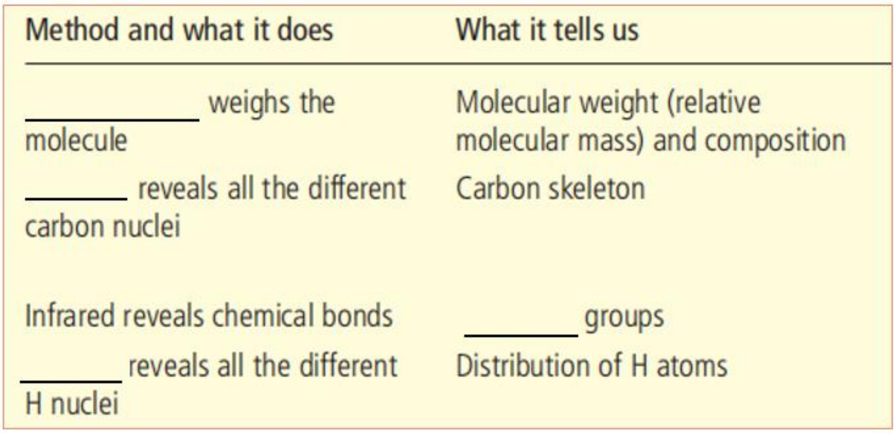


Fig 4.10 ***Organic Chemistry-Jonathan Clayden》P293***

The result is four lines of equal intensity called a **double doublet** (or sometimes a **doublet of doublets**), abbreviation dd. The smaller coupling constant can be read off from the separation between lines 1 and 2 or between lines 3 and 4, while the larger coupling constant is between lines 1 and 3 or between lines 2 and 4. The separation between the middle two lines is not a coupling constant. You could view a double doublet as an imperfect triplet where the second coupling is too small to bring the central lines together: alternatively, look at a triplet as a special case of a double doublet where the two couplings are identical and the two middle lines coincide.

Summary

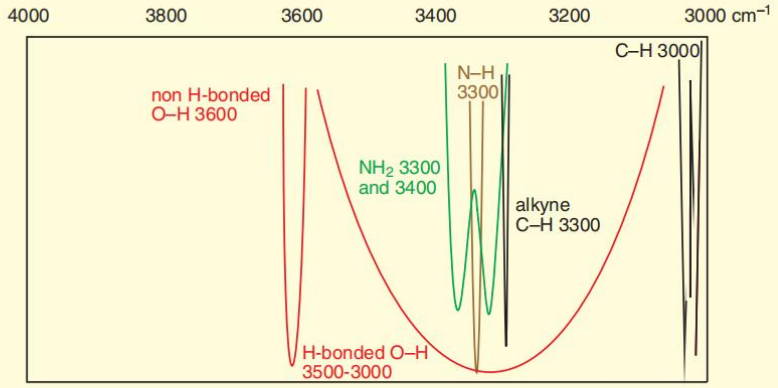
1、What each spectroscopic method tells us



Method and what it does	What it tells us
____________ weighs the molecule	Molecular weight (relative molecular mass) and composition
_______ reveals all the different carbon nuclei	Carbon skeleton
Infrared reveals chemical bonds	________ groups
_______ reveals all the different H nuclei	Distribution of H atoms

2、About the infrared spectra,this diagram is very important.

● Typical peak shapes and frequencies for X–H bonds in the region 4000–3000 cm^{-1}.



3、In NMR,the integral area of the peak is directly ____________ to the ^{13}C atoms or protons in the chemical environment.

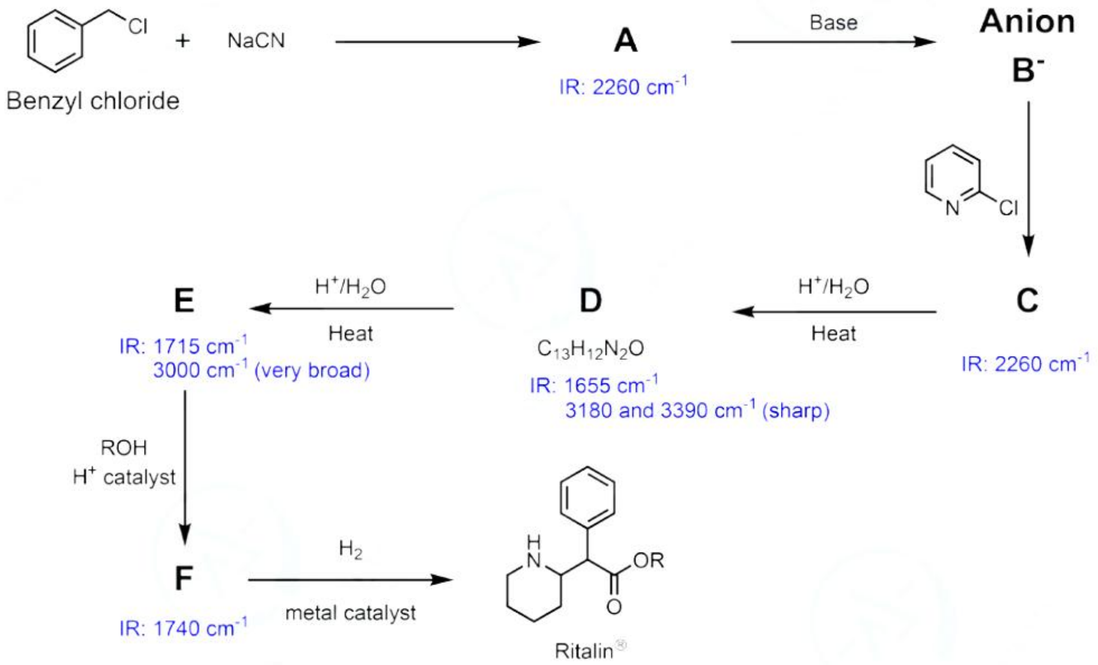
4、Generally , the number of splits of a signal depends on the number of adjacent hydrogen. If there are **n** equal adjacent hydrogen, the signal is split into _____ peaks.

5、The theoretical intensity ratio between the multiple peaks is the coefficient ratio of each item after expansion of $(x + y)^n$.The intensities can all be deduced simply from **Pascal’s triangle**

QUIZ

Question 1.*(source,UKChO,2015,3a-3f)*

Ritalin is synthesised according to the scheme below. Some of the characteristic IR stretching frequencies of the intermediates are shown.



(a) The synthesis begins with the reaction of benzyl chloride and sodium cyanide to form Compound **A**. Draw the structure of Compound **A**.

(b) Compound **A** is then deprotonated to form **Anion B$^-$** . Draw the structure of **Anion B$^-$**.

(c) Draw the structures of Compounds **C**, **D**, **E** and **F**. For Compound **F** you do not need to worry about the specific identity of R.

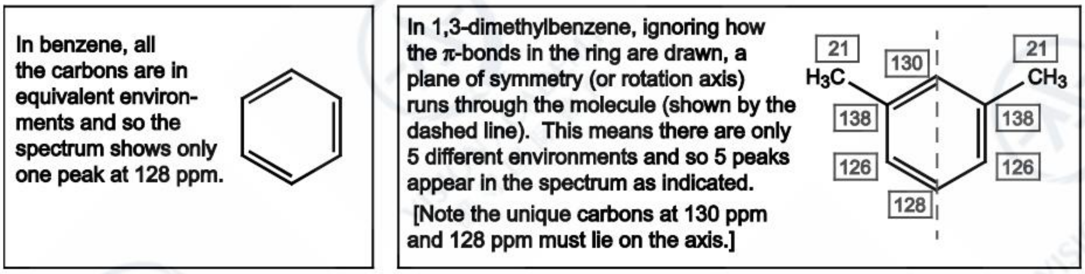
(f) For each of the following IR stretching frequencies from this scheme, draw the functional group responsible and indicate with an arrow which of the bonds are vibrating.

(i) 1655 cm^{-1} **(ii)** 1715 cm^{-1} **(iii)** 1740 cm^{-1} **(iv)** 2260 cm^{-1}

(v) 3000 cm^{-1} (very broad) **(vi)** 3180 and 3390 cm^{-1} (sharp)

Question 2.*(source,UKChO,2016,3d)*

The types of DBE may be revealed using spectroscopic techniques, such as NMR. In ^{13}C NMR, the number of signals in the spectrum depends on the number of different carbon environments in a structure. For example, in benzene, each carbon atom is equivalent and so the spectrum shows only one peak, whereas in 1,3-dimethylbenzene there are 5 different environments as shown below:



In benzene, all the carbons are in equivalent environments and so the spectrum shows only one peak at 128 ppm.

In 1,3-dimethylbenzene, ignoring how the π-bonds in the ring are drawn, a plane of symmetry (or rotation axis) runs through the molecule (shown by the dashed line). This means there are only 5 different environments and so 5 peaks appear in the spectrum as indicated.

[Note the unique carbons at 130 ppm and 128 ppm must lie on the axis.]

Carbon atoms in the following environments typically give peaks in the regions indicated:

- *Triple-bonded alkyne carbons: 70-100 ppm*
- *Double-bonded alkene carbons: 100-160 ppm*
- *Carbons with four single bonds to carbons or hydrogens: 0-50 ppm*

In the rather unusual allene group, $R_2C=C=CR_2$, the central carbon gives a peak over 200 ppm, and the carbons attached directly to the central allene carbon, flanking it either side, now fall in the same region as the triple-bonded carbons, i.e.

- *Allene central carbon: >200 ppm*
- *Allene flanking carbons: 70-100 ppm*

Using advanced NMR techniques, in addition to telling how many carbon atoms are in a particular environment, it is also possible to tell how many hydrogen atoms are attached to a particular carbon. We may denote this as (CH_3), (CH_2), (CH), or (C) for carbons with 3, 2, 1, or 0 hydrogens attached. The spectrum for 1,3-dimethylbenzene may be summarised as:

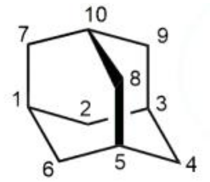
$$2 \times 138\ (C),\ 130\ (CH),\ 128\ (CH),\ 2 \times 126\ (CH),\ 2 \times 21\ (CH_3).$$

(a) The following data are taken from the ^{13}C NMR spectra of isomers with the formula C_8H_8 which has **five** DBE. For each spectrum, first complete the table in your answer booklet and hence suggest how many triple bonds, double bonds, and rings each compound contains. Then suggest a skeletal structure consistent with the data. [You do not need to assign values to particular carbons.]

Spectrum	Signals / ppm
A	8 × 132 (CH)
B	8 × 47 (CH)
C	4 × 96 (C), 4 × 20 (CH_2)
D	2 × 210 (C), 134 (C), 113 (CH_2), 2 × 93 (CH), 2 × 79 (CH_2)
E	147 (C), 2 × 138 (CH), 2 × 131 (CH), 2 × 127 (CH), 112 (CH_2)
F	142 (CH), 136 (CH), 127 (CH_2), 120 (CH_2), 117 (CH), 112 (CH), 91 (C), 89 (C)
G	2 × 146 (C), 2 × 127 (CH), 2 × 122 (CH), 2 × 30 (CH_2)
H	154 (C), 151 (C), 2 × 136 (CH), 2 × 128 (CH), 2 × 37 (CH_2)
I	157 (C), 101 (CH_2), 2 × 26 (CH), 4 × 19 (CH)

Question 3.*(source,UKChO,2017,4c)*

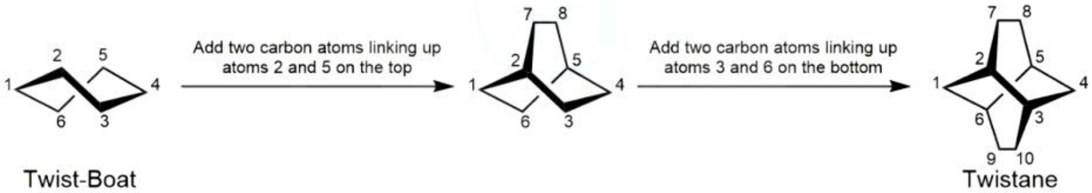
(c) How many signals are there in the ^{13}C NMR spectrum of adamantane (i.e. how many unique environments of carbon are there)?



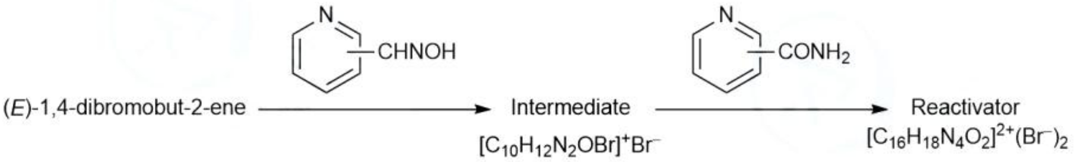
Adamantane

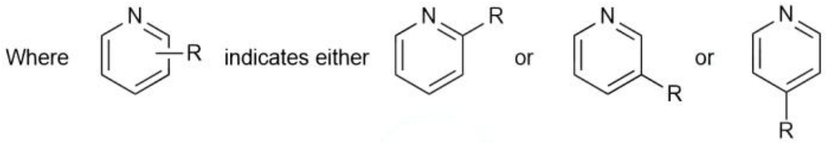
(source,UKChO,2017,4e)

(e) How many signals are there in the ^{13}C NMR spectrum of twistane?



Question 4.*(source,UKChO,2019,3g)*





The most potent reactivator **Y** had 12 signals in its ^{13}C NMR and was obtained from intermediate **X** that had 8 signals in its ^{13}C NMR.

(g) Draw the structures of **X** and **Y**.

Question 5.*(source,UKChO,2019,2h)*

Transition metal complexes can be identified using a range of spectroscopic techniques, one of which is nuclear magnetic resonance (NMR). Just as ^{1}H and ^{13}C nuclei can be excited in an NMR experiment, so can transition metal nuclei. An NMR spectrum can be run if the spin (*I*) is not zero. Nuclei such as 195Pt and 103Rh give useful spectra, however, other nuclei such as 105Pd lead to very broad lines and are unsuitable for NMR experiments.

Coupling of transition metal nuclei to other nuclei can cause signals to split, similar to the doublets, triplets and quartets seen in ^{1}H NMR.

Number of peaks into which the resonance is split = $(2N \times I) + 1$

where N = *number of equivalent nuclei*

I = *spin of nuclei coupled to*

^{195}Pt has spin $I = ½$. ^{1}H can be considered as 100% abundant and has spin $I = ½$. ^{16}O can be considered as 100% abundant and has spin $I = 0$. ^{1}H nuclei are not seen to couple to the platinum in ^{195}Pt NMR.

Platinum complexes, such as $[Pt(NH_3)_4]^{2+}$ and *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$, can be formed in electroplating baths. A 195Pt NMR of a mixture of the two complexes exhibits signals at $\delta = -2576$ and -1555 ppm. These signals are split because the platinum nuclei couple to either ^{14}N ($I = 1$) or ^{15}N ($I = 1/2$). The signals can be assigned from their splitting pattern.

(h) Calculate the number of lines the ^{195}Pt signal is split into by nitrogen in the ^{195}Pt NMR of:

(i) *cis*-$[Pt(^{14}NH_3)_2(H_2O)_2]^{2+}$

(ii) $[Pt(^{14}NH_3)_4]^{2+}$

(iii) $[Pt(^{15}NH_3)_4]^{2+}$

(source,UKChO,2019,2i)

The line intensities for ^{195}Pt NMR resonances split by nuclei with $I = 1$ can be derived from the coefficients in the expansion of the polynomial $(x^2 + xy + y^2)^n$, where n is the number of equivalent coupling ^{14}N atoms.

Therefore:

$n = 1$ $(x^2 + xy + y^2)^1 = x^2 + xy + y^2$

$n = 2$ $(x^2 + xy + y^2)^2 = x^4 + 2x^3y + 3x^2y^2 + 2xy^3 + y^4$

$n = 3$ $(x^2 + xy + y^2)^3 = x^6 + 3x^5y + 6x^4y^2 + 7x^3y^3 + 6x^2y^4 + 3xy^5 + y^6$

This leads to a Pascal-like triangle

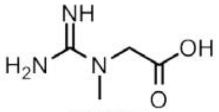
n = 0				1			
n = 1			1	1	1		
n = 2		1	2	3	2	1	
n = 3	1	3	6	7	6	3	1

(i) Calculate the intensities of the splitting pattern in the ^{195}Pt NMR of

(i) *cis*-$[Pt(^{14}NH_3)_2(H_2O)_2]^{2+}$

(ii) $[Pt(^{14}NH_3)_4]$

Question 7.*(source,UKChO,2013,5d)*



creatine

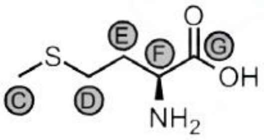
The chemical structure of creatine and these amino acids can be analysed by ^{1}H NMR. As these are polar molecules, the NMR spectra are run in D_2O solvent. In D_2O, protons attached to nitrogen or oxygen atoms undergo rapid exchange with deuteriums from the solvent. This means that by the time the NMR is run, all N-H bonds have been replaced by N-D bonds and all O-H bonds by O-D bonds. As signals from deuterium atoms are not observed in ^{1}H NMR spectra, no signals from N-H or O-H groups in the molecule are seen in the spectrum. The number of signals observed depends on the symmetry of the molecule. Each hydrogen atom in a unique environment gives rise to a signal at a different chemical shift in the spectrum. Occasionally, signals from two different environments can appear on top of one another when the difference in chemical shifts between the environments is very small.

The area under each signal is proportional to the number of protons in that environment. This is shown by an integral trace (the stepped line on the spectrum). The height of each step is proportional to the area under that signal.

The appearance of the signals can be complicated by coupling. If the hydrogen atom(s) are within three bonds of another hydrogen which is in a different environment, instead of appearing as a single peak, its signal is split into a number of peaks. If the hydrogen under consideration is within three bonds of **n** hydrogens in a different environment from itself, it will be split into **(n + 1) equally spaced** peaks. The ratio of the area under the peaks is given by the number in Pascal's triangle (shown on the right). Due to rapid exchange of any protons/deuteriums bonded to oxygen or nitrogen atoms with the solvent, no coupling is seen to protons/deuteriums bonded to oxygen or nitrogen atoms.

n	Intensities of peaks
0	1
1	1 : 1
2	1 : 2 : 1
3	1 : 3 : 3 : 1
4	1 : 4 : 6 : 4 : 1

(d) Consider the amino acid methionine. Complete the table in the answer booklet for carbons **C**, **D** and **F** in methionine to suggest the appearance of the overall signal from the protons bonded to that carbon atom.



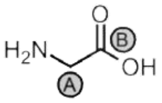
methionine

(source,UKChO,2013,5e)

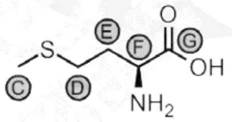
(e) Usually all protons attached to the same carbon atom are in the same chemical environment; however, this is not always the case. Two protons on the same carbon atom that are in different chemical environments are called diastereotopic protons.

These are most often observed where the carbon under consideration is bonded to an asymmetric carbon atom. An asymmetric carbon atom has four different chemical groups attached to it.

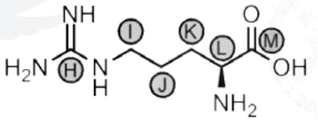
Consider glycine, methionine and arginine. In these three amino acids, write the letters of all such carbons whose diastereotopic protons would be observed as different signals in their spectra.



glycine



methionine



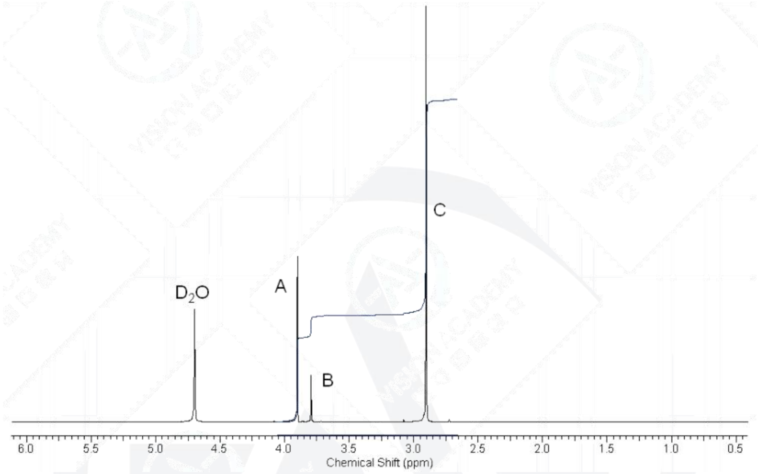
arginine

(source,UKChO,2013,5g)

In the body, creatine is in equilibrium with a cyclic molecule called creatinine, by the following equation. The position of equilibrium varies with pH.

$$\text{creatine} \overset{K}{\rightleftharpoons} \text{creatinine} + \text{H}_2\text{O}$$

Creatinine is a metabolic waste product that is not used by the body. It is filtered out in the kidneys. The ^{1}H NMR spectrum in D_2O of a creatine/creatinine solution is shown below. Three signals are observed. Creatinine gives rise to signal A. Creatine gives rise to signal B. Both creatine and creatinine give rise to signal C.



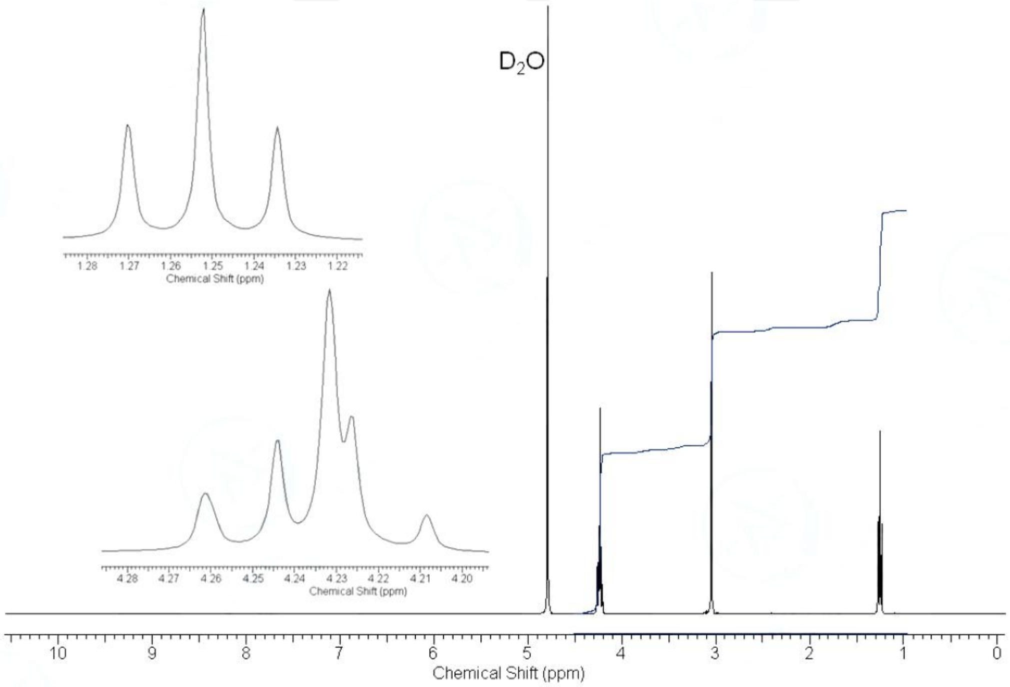
(g) Assuming this sample has reached equilibrium, calculate a value for the equilibrium constant, *K*, at this pH and temperature. Show clearly how you worked this out. You may ignore the concentration of water in your calculation.

(source,UKChO,2013,5h)

(h)A problem with creatine supplementation is that a lot of the creatine taken does not get absorbed by the body. Recently, supplements containing derivatives of creatine have been marketed. These are usually more lipophilic (dissolve more easily in fats) in an effort to improve uptake into the body.

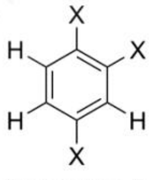
The ^{1}H NMR spectrum in D_2O of one of these supplements is shown below. Some regions of the spectrum have been expanded on the left hand side of the figure to help with your analysis.

This supplement exists in an ionised form at pH 1 but does not exist in an ionised form at pH 12. Suggest a structure for this supplement.



Question 8.*(source,UKChO,2014,4f)*

In compound **A**, two of the three X substituents are the same (i.e. the substituents are Xa, Xa and Xb).

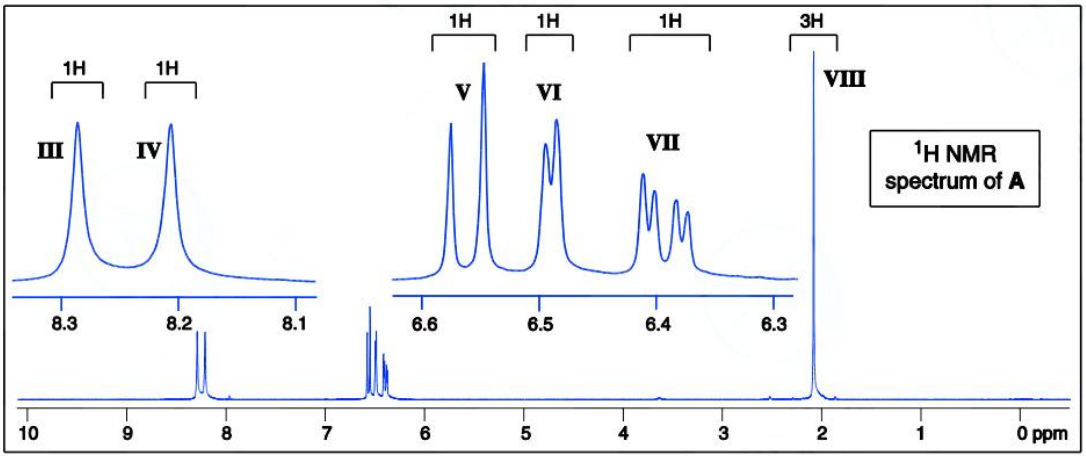


Compound **A**

The ^{13}C NMR spectrum of compound **A** contains seven signals.

The ^{1}H NMR spectrum of compound **A** is shown below.

Peaks III and IV in the ^{1}H NMR spectrum disappear on addition of D_2O to the sample.

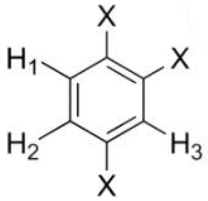


(f) **(i)** Suggest an identity for the two identical substituents (Xa and Xa).

(ii) Suggest an identity for the other substituent (Xb).

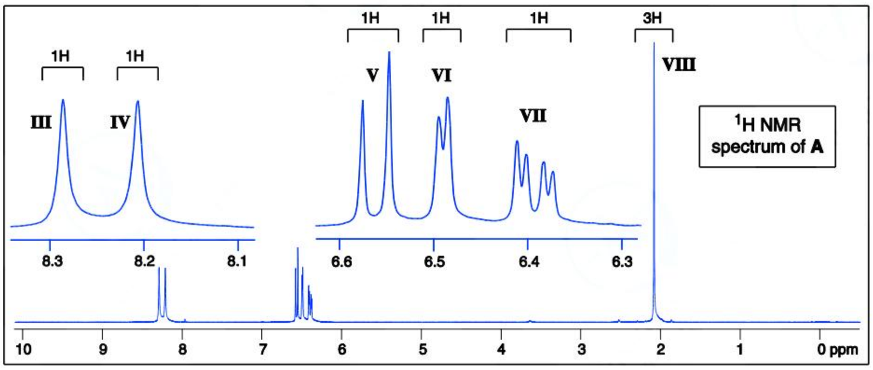
(source,UKChO,2014,4g)

The protons on the benzene ring in compound **A** (H_1, H_2 and H_3) can be assigned by analysis of their coupling constants in the 1H NMR spectrum. The splitting that is observed in the spectrum due to coupling between two non-equivalent benzene ring protons in a 1,2-relationship to each other, is considerably larger than the splitting observed due to coupling between two non-equivalent benzene ring protons in a 1,3-relationship. The splitting due to coupling between two non-equivalent benzene ring protons in a 1,4-relationship is generally too small to be observed.



(g) Assign one of the signals **III-VIII** in the ^{1}H NMR spectrum of **A** to each of the protons H_1, H_2 and H_3. Bombardier beetles also use a simpler organic compound, **C** for the same purpose. Compound **C** is a relative of compound **A** where one of the X substituents is replaced by a hydrogen atom, making a disubstituted benzene.

The ^{1}H NMR spectrum of compound **C** only contains two signals.



(source,UKChO,2014,4h)

Bombardier beetles also use a simpler organic compound, **C** for the same purpose.

Compound **C** is a relative of compound **A** where one of the X substituents is replaced by a hydrogen atom, making a disubstituted benzene.

The ^{1}H NMR spectrum of compound **C** only contains two signals.

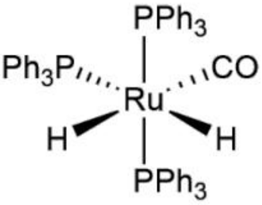
(h) Suggest a structure for compound **C** and hence also a structure for compound **A**.

(source,UKChO,2014,4i)

(i) Suggest a structure for compound **B** and a structure for compound **D**.

Question 9.*(source,UKChO,2021,3i)*

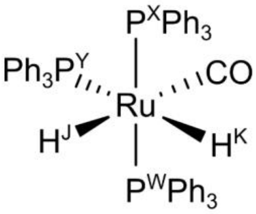
This catalyst can be analysed by ^{31}P NMR. ^{31}P is 100% abundant and is a spin ½ nucleus like ^{1}H. The ^{31}P NMR is run in a way that means no coupling between ^{31}P and ^{1}H is observed. The only coupling which is observed is between ^{31}P nuclei in different environments.

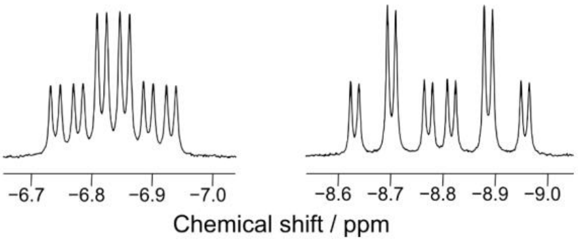


(i) What is observed in the ^{31}P NMR spectrum of this catalyst? Tick the correct answer.

(source,UKChO,2021,3j)

In the ^{1}H NMR spectrum, the two hydrides appear at negative chemical shifts and have complex coupling patterns. The couplings observed for these signals arise from coupling through two bonds to either ^{1}H or ^{31}P, (i.e. either ^{1}H–Ru–^{1}H, or ^{1}H–Ru–^{31}P) and are measured in Hz. The coupling constant between two nuclei that are *trans* is usually larger than between two nuclei that are *cis*.





The signal at −6.83 ppm is a 'triplet of doublets of doublets'. The signal is split into a triplet with the largest coupling constant of 31 Hz, further split into a doublet with coupling constant of 15 Hz, further split into a doublet with coupling constant of 6 Hz.

The signal at −8.80 ppm is a 'doublet of triplets of doublets'. The signal is split into a doublet with the largest coupling constant of 74Hz, further split into a triplet with coupling constant of 28Hz, further split into a doublet with coupling constant of 6Hz.

(j) Complete the table to assign the values of the coupling constants in Hz to the following pairs of nuclei (H_J–H_K, H_J–P_W, H_J–P_X, H_J–P_Y, H_K–P_W, H_K–P_X, H_K–P_Y).

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