

1D Nuclear Magnetic Resonance Spectroscopy

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Introduction

Nuclear Spin and Resonance

Some atomic nuclei have a nuclear spin (I), and the presence of a spin makes these nuclei behave like bar magnets. In the presence of an applied magnetic field the nuclear magnets can orient themselves in $2I + 1$ ways.

Those nuclei with an odd mass number (i.e. those having an odd number of nucleons whether protons or neutrons) **have fractional spins**. Examples are $I = 1/2$ (^1H , ^{13}C , ^{19}F), $I = 3/2$ (^{11}B) & $I = 5/2$ (^{17}O) (Table 1).

Those nuclei with an even mass number composed of odd numbers of protons and neutrons **have integral spins**. Examples are $I = 1$ (^2H , ^{14}N).

Those nuclei with an even mass number composed of even numbers of protons and neutrons **have zero spin** ($I = 0$). Examples are ^{12}C , and ^{16}O .

The five most important nuclei are ^1H and ^{13}C , followed by ^{19}F , ^{29}Si and ^{31}P , all of which have spins of $1/2$. These nuclei, therefore, can take up one of only two orientations, a low-energy orientation aligned with the applied field and a high-energy orientation opposed to the applied field.

Table 1:

Isotope	Natural % Abundance	Spin (I)	Magnetic Moment (μ) [*]	Magnetogyric Ratio (γ) [†]
^1H	99.9844	$1/2$	2.7927	26.753
^2H	0.0156	1	0.8574	4,107
^{11}B	81.17	$3/2$	2.6880	--
^{13}C	1.108	$1/2$	0.7022	6,728
^{17}O	0.037	$5/2$	-1.8930	-3,628
^{19}F	100.0	$1/2$	2.6273	25,179
^{29}Si	4.700	$1/2$	-0.5555	-5,319
^{31}P	100.0	$1/2$	1.1305	10,840

Magnetic nuclei and nonmagnetic nuclei

- All nuclei with an odd number of protons (^1H , ^2H , ^{14}N , ^{19}F , ^{31}P ...) or nuclei with an odd number of neutrons (i.e. ^{13}C) show the magnetic properties required for NMR.
- Nuclei with even number of both protons and neutrons (^{12}C and ^{16}O) do not have the required magnetic properties.

The following features lead to the nmr phenomenon

1. A spinning charge generates a magnetic field, as shown by the animation on the right.

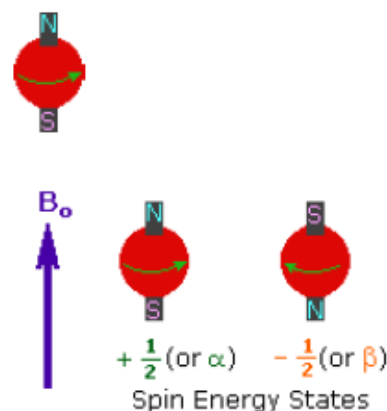
The resulting spin-magnet has a magnetic moment (μ) proportional to the spin.

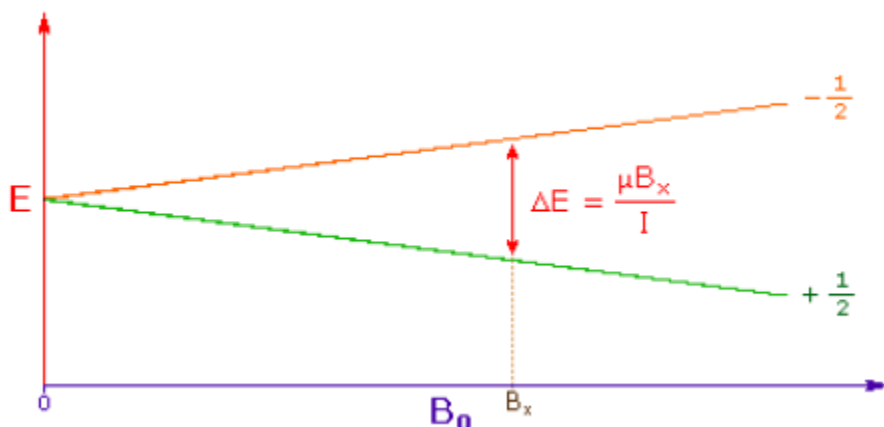
2. In the presence of an external magnetic field (B_0), two spin states exist, $+1/2$ and $-1/2$.

The magnetic moment of the lower energy $+1/2$ state is aligned with the external field, but that of the higher energy $-1/2$ spin state is opposed to the external field.

*Note that the arrow representing the external field points North.

3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The following diagram illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases. At a field equal to B_x a formula for the energy difference is given (remember $I = 1/2$ and μ is the magnetic moment of the nucleus in the field).





Strong magnetic fields are necessary for nmr spectroscopy. The international unit for magnetic flux is the tesla (**T**).

The earth's magnetic field is not constant, but is approximately 10^{-4} T at ground level. Modern nmr spectrometers use powerful magnets having fields of 1 to 20 T. Even with these high fields, the energy difference between the two spin states is less than 0.1 cal/mole.

For nmr purposes, this small energy difference (ΔE) is usually given as a frequency in units of MHz (10⁶ Hz), ranging from 20 to 900 Mz, depending on the magnetic field strength and the specific nucleus being studied.

Irradiation of a sample with radio frequency (rf) energy corresponding exactly to the spin state separation of a specific set of nuclei will cause excitation of those nuclei in the +1/2 state to the higher -1/2 spin state. NMR spectroscopy is therefore the energetically mildest probe used to examine the structure of molecules.

The nucleus of a hydrogen atom (the proton) has a magnetic moment $\mu = 2.7927$, and has been studied more than any other nucleus.

4. For spin 1/2 nuclei the energy difference between the two spin states at a given magnetic field strength will be proportional to their magnetic moments. For the four common nuclei noted above, the magnetic moments are: $^1\text{H } \mu = 2.7927$, $^{19}\text{F } \mu = 2.6273$, $^{31}\text{P } \mu = 1.1305$ & $^{13}\text{C } \mu = 0.7022$. These moments are in nuclear magnetons, which are $5.05078 \cdot 10^{-27} \text{ JT}^{-1}$. The formula in the colored box shows the direct correlation of frequency (energy difference) with magnetic moment (h = Planck's constant = $6.626069 \cdot 10^{-34} \text{ Js}$).

$$\nu = \frac{\mu B_0}{hI} = \frac{4.68 \mu}{h}$$

B_0 is the strength of the applied magnetic field, N_α is the number of nuclei in the low-energy state, and N_β the number in the high-energy state.

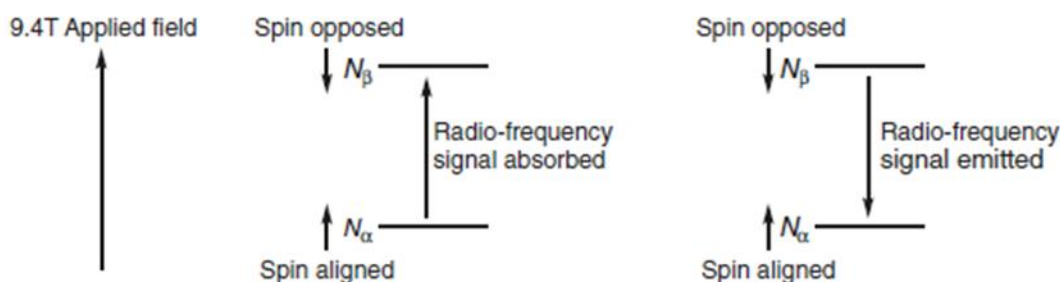


Fig 1: Energy levels for aligned and opposed nuclear spins

A radio-frequency signal applied to the system changes the Boltzmann distribution when the radio frequency matches the frequency ν . It is called the resonance frequency or **Larmor frequency** for that particular nucleus. The effect is to promote nuclei from the low-energy N_α level to the high-energy level N_β (**Fig. 1**).

The Larmor frequency is therefore dependent upon the applied field strength and the nature of the nucleus in question. The frequencies at which nuclei come into resonance at a field strength of 9.4 T (94 kG), at this field strength the common magnetic nuclei come into resonance each in a narrow range close to: 400 MHz for ^1H , 376.3 MHz for ^{19}F , 161.9 MHz for ^{31}P , 100.6 MHz for ^{13}C and 79.4 MHz for ^{29}Si (**Fig 2**).

Because of the widespread use of proton NMR spectroscopy, it is usual to refer to an instrument with this field strength as a 400 MHz instrument. The common nuclei ^{12}C and ^{16}O having $I = 0$ are inactive.

A few other common nuclei have spins, of which ^2H and ^{14}N ($I = 1$) are perhaps the most important.

The higher the field strength, B_0 , the greater the difference between N_α and N_β and so the higher the field strength, the greater the difference in the populations in the N_α and N_β levels, and the more sensitive the instrument. For protons the difference between N_α and N_β , determined by the Boltzmann distribution.

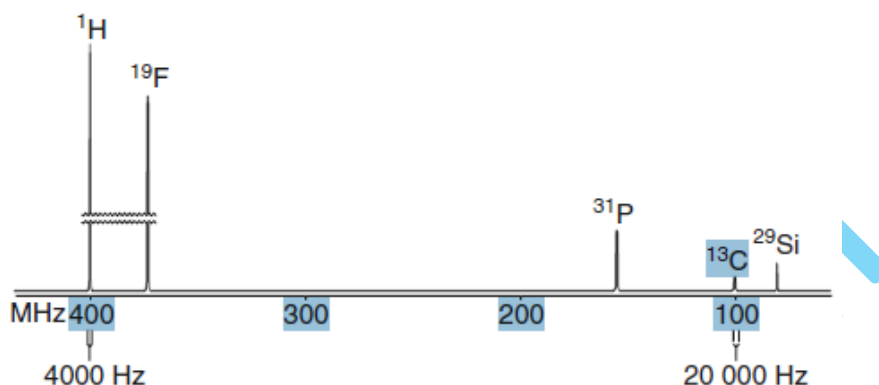


Fig 2: Imaginary NMR spectrum with several different nuclei

Taking a Spectrum

The following discussion is about NMR in the liquid state. Solid state NMR is different in a number of ways. It is not discussed in here, because it is not much used by organic chemists for structure determination.

In order to take an NMR spectrum in the liquid state, the sample is dissolved in a solvent, preferably one that does not itself give rise to signals in the same range as the sample in the NMR spectrum.

Solvents used in ^1H NMR

The most commonly used solvent is CDCl_3 , but more polar solvents like d_8 -THF, CD_3CN , $(\text{CD}_3)_2\text{CO}$, d_6 -DMSO [$(\text{CD}_3)_2\text{SO}$], CD_3OD and D_2O are often used, especially for polar compounds. The solvent itself provides a signal that is used by the computer to calibrate the spectrum, replacing the older system where an internal standard (usually tetramethylsilane) was added for this purpose. Other solvents, like d_8 -THF, d_6 -benzene, d_8 -toluene and d_5 -pyridine are used, the choice of solvent being largely determined by the solubility of the compound under investigation and the extent to which the signals of

individual nuclei are resolved in any one solvent. The solution should be free both of paramagnetic and insoluble impurities, and it should not be viscous, or resolution will suffer. Routinely a good ^1H NMR spectrum might use 5–10 mg, and a good ^{13}C spectrum might use 30 mg, but smaller quantities can still give good spectra with more effort.

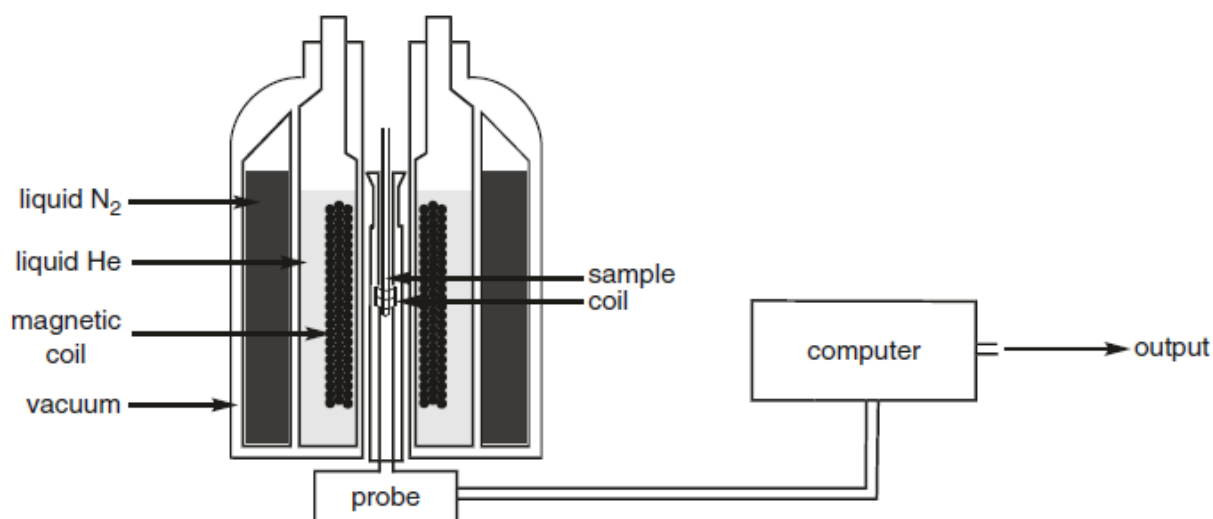


Fig 3: Schematic cross-section of an NMR spectrometer

When the sample is placed in the spectrometer the nuclear magnets settle into the equilibrium distribution, with more in the N_α level than in N_β . This gives the sample a bulk magnetisation represented by the vector M_0 pointing along the axis of the applied field B_0 (**Fig. 4**), which is drawn as the z axis. The RF pulse applied along the x axis tips the magnetisation through an angle θ given by $\theta = \gamma B_1 t_p$, in which B_1 is the magnetic field strength corresponding to the RF frequency.

The angle θ is usually expressed in radians, the strength of the RF pulse (B_1) and the time (t_p) are chosen to make $\theta = 90$.

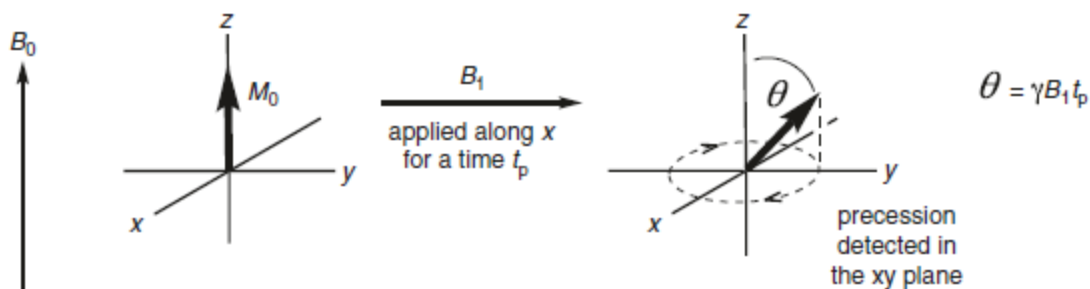


Fig 4: Vector diagram for the basic pulse sequence

The Chemical Shift

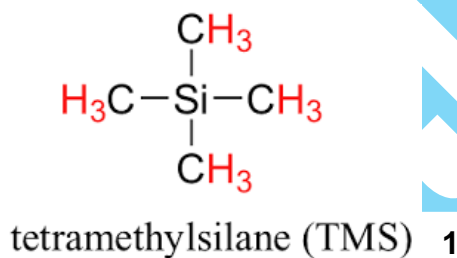
In ^1H NMR spectra taken on a 400 MHz instrument, a narrower range—about 4000 Hz in the neighbourhood of the resonance frequency of 400 MHz—is enough to bring most protons into resonance.

In practice it is inconvenient to characterise the ^1H peaks by assigning its absolute frequency, all very close to 400 MHz: the numbers are cumbersome and much too difficult to measure accurately. Furthermore, they change from instrument to instrument, and even from day to day, as the applied field changes. It is convenient instead to measure the difference of the frequency (ν_s) of the peak from some internal standard (both measured in Hz) and to divide this by the operating frequency in MHz to obtain a field-independent number in a convenient range. Because the spread of frequencies is caused by the different chemical (and hence magnetic) environments, the signals are described as having a chemical shift from some standard frequency. The internal standard used for ^1H spectra is tetramethylsilane (TMS), and the chemical shift scale δ is then defined by Eq.

$$\delta = \frac{\nu_s (\text{Hz}) - \nu_{\text{TMS}} (\text{Hz})}{\text{operating frequency (MHz)}}$$

The chemical shift δ , which measures the position of the signal, will now be the same whatever instrument it is measured on, whether operating at 200 MHz, 400 MHz or 600 MHz. It has no units and is expressed as fractions of the applied field in parts per million (ppm). In a 400 MHz spectrometer, each unit of δ would be 400 Hz on the proton scale and 100 Hz on the carbon scale.

Tetramethylsilane 1 is chosen as the reference point because it is inert, volatile, non-toxic, and cheap, and it has only one signal (^1H), which comes into resonance conveniently at the low-frequency extreme of the frequencies found for most carbon and hydrogen atoms in organic structures. By definition it has a δ value of 0 in ^1H spectra.



The scale on **Fig. 5** shows the common range of δ values within which most protons come into resonance. They are written from right to left, a convention that denotes frequencies as higher and positive on the left and lower on the right. Unfortunately, the left and right sides are hardly ever referred to as being at the high- and low-frequency end of the spectrum. Instead, for historical reasons, they are almost invariably referred to by the value of the applied field which corresponds to this relative frequency. The high-frequency end of the spectrum, on the left with high δ values, is described as being *downfield*, and the right side, with low δ values, is said to be *upfield*.

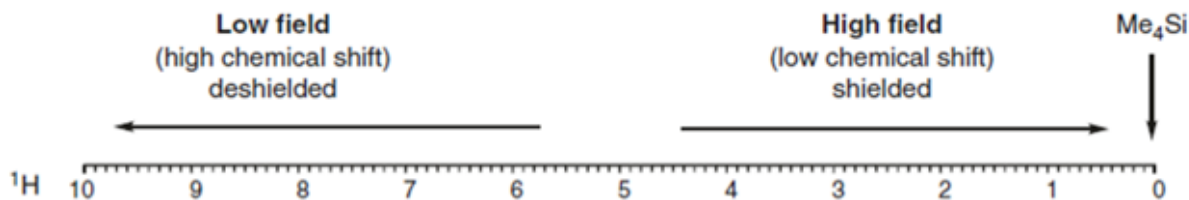


Fig 5: The δ scales for ^1H NMR spectrum

Most instruments only resolve signals when they are 0.5 Hz or more apart. In practice, ^1H signals, spread over a narrower range of 4000 Hz (in a 400 MHz instrument), do quite often give coincident, or near coincident signals from different protons. Resolution gets better with instruments working at higher field, but coincidence, or at any rate overlap, is still common.

Shielded nucleus vs de-shielded nucleus

Shielding:

The higher the electron density around the nucleus, the higher the opposing magnetic field to B_0 from the electrons, the greater the shielding. Because the proton experiences lower external magnetic field, it needs a lower frequency to achieve resonance, and therefore, the chemical shift shifts upfield (lower ppm).

Deshielding:

If the electron density around a nucleus decreases, the opposing magnetic field becomes small and therefore, the nucleus feels more the external magnetic field B_0 , and therefore it is said to be deshielded. Because the proton experiences higher external magnetic field, it needs a higher frequency to achieve resonance, and therefore, the chemical shift shifts downfield (higher ppm).

Factors Affecting the Chemical Shift

1. The Inductive Effect

In a uniform magnetic field, the electrons, which have a high magnetogyric ratio, surrounding a nucleus circulate, setting up a secondary magnetic field opposed to the applied field at the nucleus (**Fig. 6**, where the solid curves indicate the lines of force associated with the induced field and the dashed circle the circulating electrons). As a result, nuclei in a region of high electron population experience a field proportionately weaker than those in a region of low electron population. As a result, the levels N_α and N_β are not split as far apart, and the frequency of the transition between them is reduced. Equally one can say that a higher field has to be applied to bring them into resonance. However, it is explained, whether by referring to the frequency or the field, such nuclei are said to be *shielded* by the electrons.

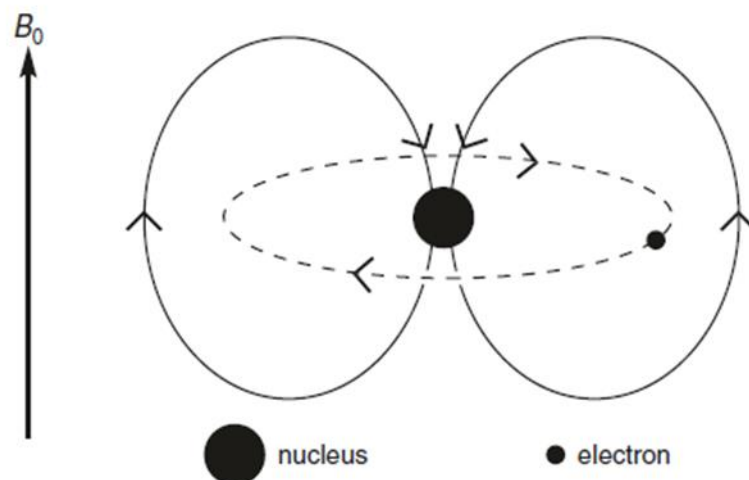


Fig 6: Shielding of a nucleus by the current induced in an electron cloud

Thus, a high electron population shields a nucleus and causes resonance to occur at relatively high field (i.e. at low frequency, with low values of δ). Likewise, a low electron population causes resonance to occur at relatively low field (i.e. at high frequency, with high values of δ), and the nucleus is said to be *deshielded*. The extent of the effect can be seen in the positions of resonance of the ^1H nuclei of the methyl group attached to the various atoms listed in **Table 2**.

- The electropositive elements (Li, Si) shift the signals upfield because they supply electrons.
- The electronegative elements (N, O, F) shift the signals downfield, because they withdraw electrons.

Table 2: Chemical shifts for methyl groups attached to various atoms in CH_3X

CH_3X	δ_{H}	CH_3X	δ_{H}
CH_3Li	-1.94	CH_3OH	3.39
$(\text{CH}_3)_4\text{Si}$	0.0	$(\text{CH}_3)_2\text{S}$	2.09
CH_4	0.23	$(\text{CH}_3)_2\text{Se}$	2.00
CH_3Me	0.86	CH_3F	4.27
CH_3Et	0.91	CH_3Cl	3.06
CH_3NH_2	2.47	CH_3Br	2.69
$(\text{CH}_3)_3\text{P}$	1.43	CH_3I	2.13

- Hydrogen is more electropositive than carbon, with the result that every replacement of hydrogen by an alkyl group causes a downfield shift in the resonance of that carbon atom and any remaining hydrogens attached to it. Thus, methyl, methylene, methine, and fully substituted carbons (and their attached protons) come into resonance at successively lower fields (**2–6**).

CH ₄	MeCH ₃	Me ₂ CH ₂	Me ₃ CH	Me ₄ C
δ_H 0.23	δ_H 0.86	δ_H 1.33	δ_H 1.68	
2	3	4	5	6

- Every replacement of hydrogen by an electronegative element causes a larger downfield shift, more or less additive, in the resonance of the carbon atom and any remaining hydrogens attached to it. Thus, the carbon and the attached protons of methyl chloride, dichloromethane, chloroform, and carbon tetrachloride come into resonance at successively lower fields (**7–10**).

CH ₄	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
δ_H 0.23	δ_H 3.06	δ_H 5.33	δ_H 7.24	
2	7	8	9	10

2. Anisotropy of Chemical Bonds

Chemical bonds are regions of high electron population that can set up magnetic fields. These fields are stronger in one direction than another (they are anisotropic), and the effect of the field on the chemical shift of nearby nuclei is dependent upon the orientation of the nucleus in question with respect to the bond. The anisotropy in π -bonds is especially effective in influencing the chemical shift of nearby protons, as illustrated in **Fig. 7**. When a double bond (**Fig. 7a**) is oriented at right angles to the applied field B_0 , the electrons in it are induced to circulate in the plane of the double bond (dashed ellipse in **Fig. 7a**), creating a magnetic field opposed to the applied field at the centre and augmenting it at the periphery. The effect of the induced field is to shift signals from any hydrogens in the augmented region downfield, identified with minus signs (–) in **Fig. 7** to symbolise deshielding.

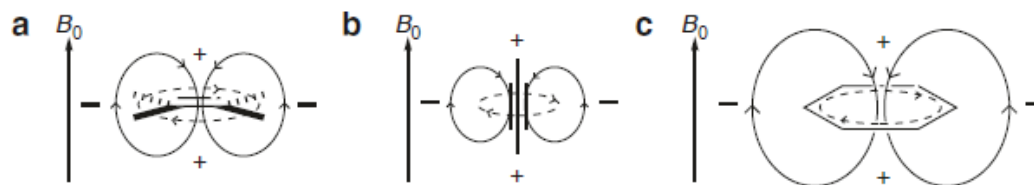


Fig 7: Anisotropic fields created in π conjugated systems

Table 3: Chemical shifts for ^1H NMR, on and near multiple bonds

Compound	δ_{H}	Compound	δ_{H}
CH_3H	0.23	CH_3CHO	2.20
$\text{CH}_3\text{CH}=\text{CH}_2$	1.71	CH_3COMe	2.09
$\text{CH}_3\text{C}\equiv\text{CH}$	1.80	CH_3CN	1.98
$\text{CH}_2=\text{CH}_2$	5.25	MeCHO	9.80
$\text{HC}\equiv\text{CMe}$	1.80	Me_2CO	—
$\text{MeC}\equiv\text{CMe}$	1.75	MeCN	—

Thus, **olefinic hydrogen atoms** are shifted downfield relative to their saturated counterparts. But the observed downfield shift is large (**Table 3, column 2**), and only partly because of the anisotropy effect; it is also caused by the fact that trigonal carbons are more electronegative (because of their higher s-character) than are tetrahedral carbon atoms.

The anisotropic effect also shifts the signals from **allylic hydrogens and carbons** downfield, but to a lesser extent (**Table 3, Compound 2**).

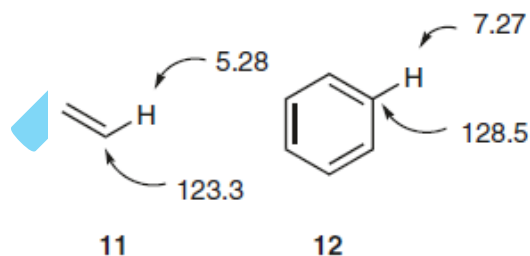
A carbonyl group has a similar large effect on the hydrogen bonded to it in aldehydes, where the anisotropy is augmented by the inductive effect of the electronegative oxygen atom (**Table 3, Compound 10**). The carbonyl group has a smaller effect upon the carbon atoms attached to it and on the protons attached to those carbon atoms (**Table 3, column 4, compound 7**). Olefinic and carbonyl carbons suffer large downfield shifts relative to their saturated equivalents, although simple models that rationalise these shifts are less easily conveyed. Nevertheless, it is clear that carbonyl carbons and their directly attached protons—which suffer not only the influences experienced by olefinic carbons and their

directly attached protons, but also experience the electronegativity of the oxygen atom exhibit remarkably large chemical shifts (**Table 3, compound 10**).

Triple bonds are noticeably different: they experience an anisotropy set up by electrons circulating around the triple bond with cylindrical symmetry (**Fig. 7b**), which has the opposite effect from that produced by the π -bond of an alkene or a carbonyl group.

The net effect on the chemical shift of acetylenic protons and carbons is for them to come into resonance in between the protons and carbons of alkenes and alkanes (**Table 3, compounds 3, 5 and 6**).

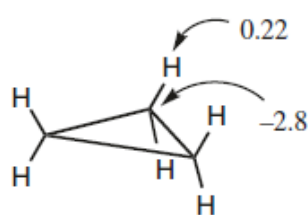
An even larger anisotropic effect is produced by the π -system of **aromatic rings**. The circulating electrons are now called a *ring current*, and they create a relatively strong magnetic field (**Fig. 7c**). The effect of the induced field is to deshield substantially the hydrogens attached to the aromatic ring **12**, which generally come into resonance 1.5–2 ppm. downfield from the corresponding olefinic signals in ethylene **11**.



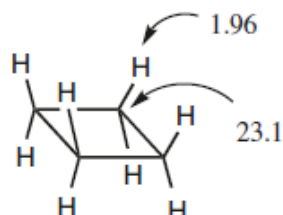
The magnetic field induced in double bonds, and especially in aromatic rings, can have a profound effect on the chemical shift of nuclei held anywhere in their neighbourhood, not just those in and attached directly to them. The precise orientation can make a large difference, so that the NMR spectra of complex structures with aromatic rings in them can be hard to predict.

Cyclopropanes present a special case, because both the carbon and proton resonances appear at exceptionally high field, above the usual range for methylene groups, and even above the range for most methyl groups. One explanation is that it is a consequence of a ring current: in cyclopropane itself **13** the three *cis* vicinal C–H bonds are able to conjugate with each other, just as p-orbitals conjugate with each other. The cyclic six-electron conjugated system gives rise to a ring current, and both the carbons and the protons sit in the shielding region of the magnetic field induced by that ring current. Substitution by alkyl groups and by electronegative elements moves the resonances downfield in the usual way.

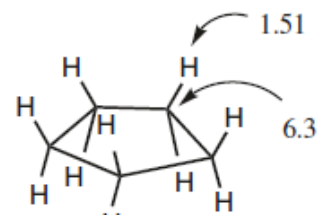
The antiaromatic conjugation of four C–H bonds in cyclobutane **14** is much less effective, because of puckering in the ring, but the effect is discernible in the opposite direction cyclobutane protons come into resonance at slightly lower field than comparable methylene protons, as in cyclopentane **15**, which has chemical shifts similar to those of open-chain compounds. Cyclopentane is not flat but is constantly changing its conformation.



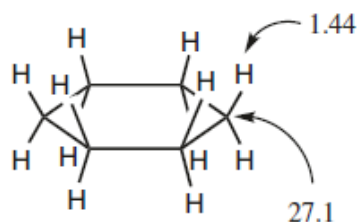
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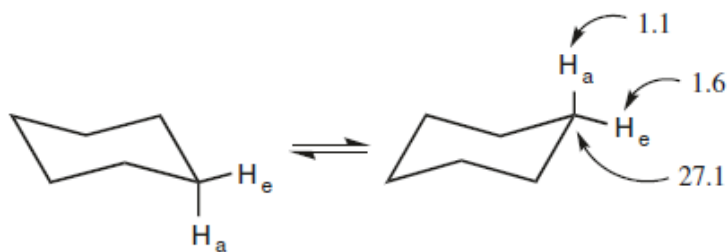
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15



16

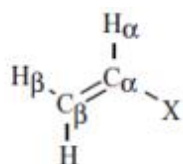


Similarly, cyclohexane **16** is not flat, but is constantly flipping between chair conformations that exchange the positions of the axial and equatorial protons. At room temperature the protons effectively experience the average field of the two environments, and come into resonance at δ 1.44 as though it were a flat molecule. At -100° , however, the flipping is slowed down so that the difference between the axial and the equatorial environments is revealed, with the axial protons coming into resonance upfield (δ 1.1) of the equatorial (δ 1.6). The upfield shift of the axial protons may reflect the presence of a weak ring current from the three axial C–H bonds, effectively placing the axial protons ‘inside’ and the equatorial protons ‘outside’. Rigid cyclohexanes, where the axial and equatorial protons retain their distinction, show the same trend, with axial protons apt to be upfield of equatorial protons, but other influences can come into play.

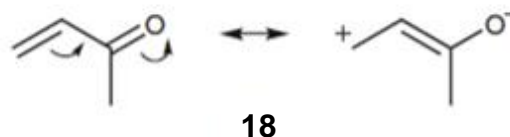
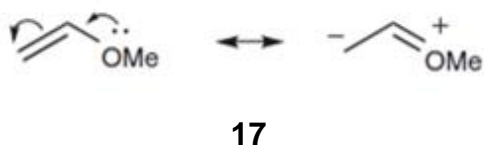
3. Polar Effects of Conjugation

When a double bond carries a polar group, the electron distribution is displaced. The displacement is usually understood as a combination of inductive effects, which operate in the σ -framework (and simply fall off with distance) and conjugative effects, which operate in the π -system (and alternate along a conjugated chain). The effects in the π -system can be illustrated simplistically with curly arrows on the canonical structures for methyl vinyl ether **17** and methyl vinyl ketone **18**. The curly arrows illustrate the effect on a C=C double bond with a π -donor **17** and a π -acceptor group **18**, and molecular orbital calculations of the electron distribution in π -systems support this simple picture.

Table 4: Conjugative effects on the chemical shifts of substituted alkenes



X	Electronic nature	$\delta_{H\beta}$	$\delta_{H\alpha}$
H	Reference compound	5.28	5.28
Me	Weak π - and σ -donor	4.88	5.73
OMe	π -Donor, σ -acceptor	3.85	6.38
Cl	σ -Acceptor, weak π -donor	5.02	5.94
Li	π -Acceptor, σ -donor		
SiMe ₃	π -Acceptor, σ -donor	5.87	6.12
CH=CH ₂	Simple conjugation	5.06	6.27
COMe	π -Acceptor, weak σ -acceptor	6.40	5.85

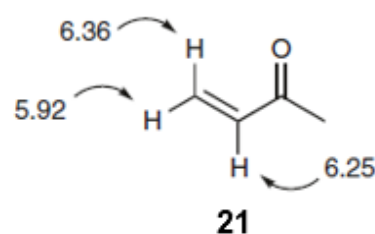
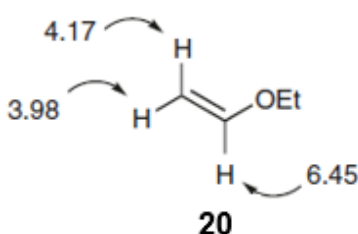
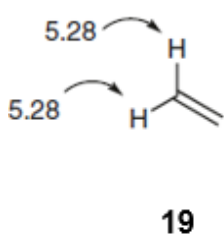


These displacements of electron population naturally affect the position of resonance of nearby nuclei, as shown in **Table 4**.

- The π -donor groups (Me < MeO < Me₂N) on π -systems shield the β -nuclei, as implied by the canonical structure on the right for **17**, causing an upfield shift relative to their position in ethylene. The β -hydrogen atom *trans* to the substituent to move further upfield as in ethyl vinyl ether **20**, relative to ethylene **19**, than the hydrogen atom *cis* to it.
- The effects of π -acceptor groups (Li, SiMe₃ and COMe) on π -systems are not so easily explained using inductive effects and resonance structures like **18**. Because of the way the substituent interacts with the π -system, affecting the anisotropic field surrounding the π -bond. **A carbonyl group**, as in methyl vinyl ketone **21**, causes the β -hydrogen *cis* to the carbonyl group to be shifted further downfield

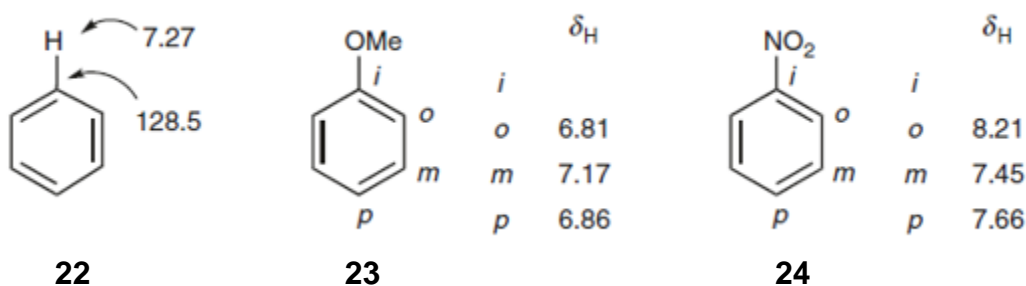
than the hydrogen *trans* to it, probably because of a direct contribution through space from the anisotropic field induced in the carbonyl group.

- Electronegative elements simultaneously induce a downfield shift of the α nuclei. Largely because of the inductive effect.
- Electropositive substituents give rise to downfield shifts on trigonal carbons, both α and β , in contrast to the upfield shifts they induce on tetrahedral carbons.



Polar groups attached directly to a benzene ring cause upfield and downfield shifts more or less in the same way as they do on a simple double bond.

- **The effects of a π -donor** and σ -withdrawing are seen in anisole **23**, where the signals of the *ortho* and *para* hydrogens are shifted upfield by the methoxy group, relative to the signals of benzene **22**. **The effect of the π -acceptor group** in nitrobenzene **24** is less straightforward, just as the electron-withdrawing groups are on an alkene: the *ortho* and the *para* hydrogen are shifted downfield, as one might expect. The downfield shift of the *ortho* hydrogen is probably greater than that on the *para* hydrogen because of a through-space effect, analogous to that of the acetyl group on the *cis* hydrogen in methyl vinyl ketone **21**.



The overall pattern that has emerged from the discussion so far is summarised in **Fig. 8**, which gives the approximate ^1H chemical shifts in and adjacent to many of the common functional groups.

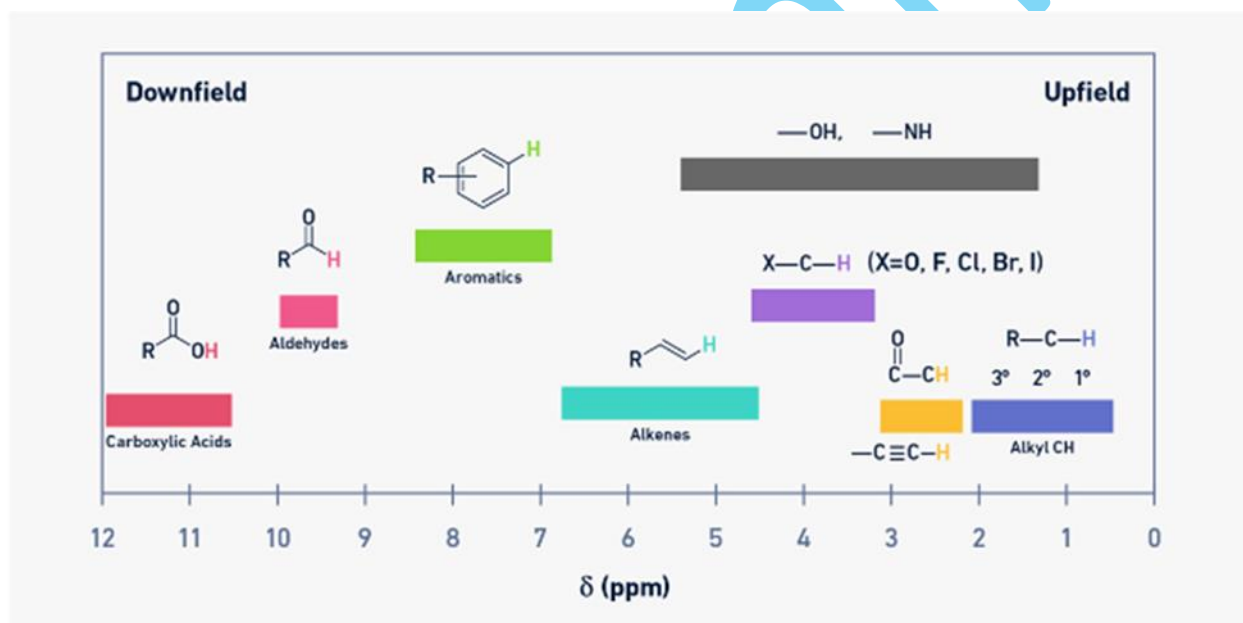


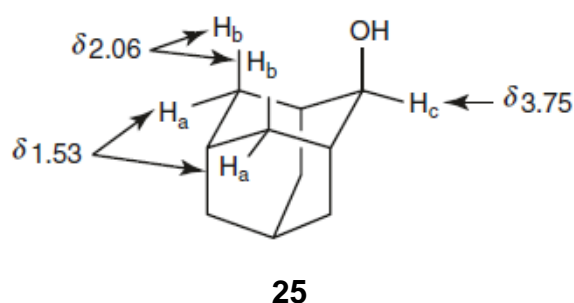
Fig 8: ^1H NMR chart showing the typical chemical shift values for different types of hydrogen atoms

4. Van der Waals Forces

When a substituent, especially an electronegative element, is pressed close to a hydrogen atom (closer than the sum of their Van der Waals radii), the electron population around the proton is pushed away (it is a form of weak hydrogen bonding). The proton is overall deshielded, and comes into resonance at unusually low field, as in the ^1H NMR

spectrum of 2-adamantanol **25**, where the signal from the two protons H_b appears downfield from the broad, largely unresolved signal (δ 1.89–1.69) from all the other CHs (the ‘methylene envelope’), except, of course, for H_c, which is bonded to a carbon carrying an electronegative element.

The proximity-induced displacement of the electrons has the opposite effect on a second proton if there is one bonded to the same carbon atom. This proton is shielded, and as a result the signal from the two protons H_a in adamantanol appears upfield of all the other CHs.



5. Isotope Effects

Replacing a lighter isotope by a heavier one causes an upfield shift in the signals from nearby atoms. The effect is most easily seen when a proton is replaced by a deuterium atom.

6. Estimating a Chemical Shift

The inductive, conjugative and anisotropic effects in polyfunctional molecules are more or less additive, so that we can, for example, see that the proton signals in the ¹H spectrum of **Fig. 9** are in appropriate places.

The signal from the C-3 and C-5 methyl groups (at δ 2.31) appears downfield from that of the methyl group in propene (δ 1.71, **See Table 3, Compound 2**), because the methyl groups are adjacent to a benzene ring and suffer some of the effect of the ring current, which is typically responsible for a downfield shift of about 0.6 ppm. The methylene group attached to C-1 of the benzene ring simultaneously suffers the effects of being adjacent to the benzene ring and of being adjacent to an electronegative element.

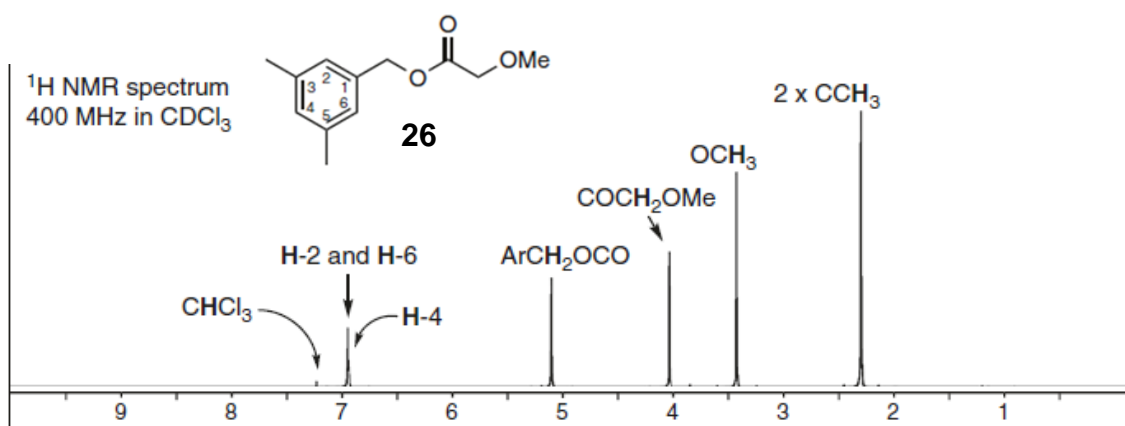


Fig 9: ^1H NMR spectra of the ester **26**

We can expect it to be downfield by about 1.4 ppm. for the effect of being benzylic and about 2.8 ppm. for being next to an ester oxygen, making a total of 4.2 ppm. downfield from the position of a simple methylene group (δ 1.33, **Me₂CH₂** (**Compound 4**)). Thus, we can expect it to give a signal at δ 5.5, and it actually comes into resonance at δ 5.11. Similarly, the methylene group between the carbonyl group and the methoxy group might be expected to be shifted downfield by the carbonyl group by 0.9 ppm. and by the methoxy group by 2.1 ppm., giving an estimate of δ 4.3, close to the observed value of δ 4.05. The methoxy group (at δ 3.45) is a little downfield of the position for methanol (at δ 3.39, **MeOH**, **See Table 2**), principally because of the anisotropic effect of the nearby carbonyl group.

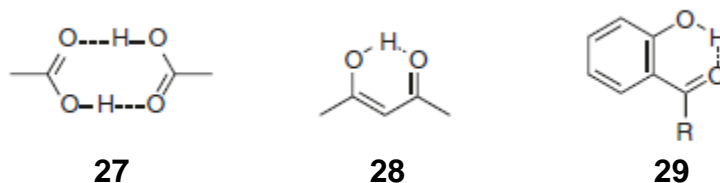
Finally, the aromatic protons at δ 6.97 are a little upfield of the signal from benzene (δ 7.27), because they are *ortho* to two alkyl groups and *para* to another. Alkyl groups, which are mildly electron-donating, shift an *ortho* or *para* proton upfield by about 0.2 ppm.

7. Hydrogen Bonds

A hydrogen atom involved in hydrogen bonding is sharing its electrons with two electronegative elements. As a result, it is itself deshielded, and comes into resonance at low field.

The position of resonance of the OH and NH protons of alcohols and amines is unpredictable, because the extent to which the hydrogen atoms are involved in hydrogen bonding is both unpredictable and concentration dependent. The usual range is δ 0.5–4.5 for alcohols, δ 1.0–4.0 for thiols, and δ 1.0–5.0 for amines. The much stronger

intermolecular hydrogen bonding in carboxylic acid dimers **27** leads to very low-field absorption in the δ 9–15 range, and the corresponding intramolecular hydrogen bonding of enolised β -diketones **28** and *o*-hydroxycarbonyl compounds **29** is similar (δ 15.4 for acetylacetone **28** itself). These are out of the range of the usual ^1H NMR spectral width, and may have to be looked for specially.



Fortunately, it is easy to identify the signal from a hydrogen atom bonded to an electro-negative element, in spite of the uncertainty about where it will appear in a ^1H NMR spectrum: if the sample in CDCl_3 solution is shaken with a drop of D_2O the OH, NH, and SH hydrogens exchange rapidly with the deuterons, the HDO floats to the surface, out of the region examined by the spectrometer, and the signal of the OH, NH, or SH disappears from the spectrum (or, quite commonly, is replaced by a weak signal close to δ 4.8 from suspended droplets of HDO). This technique is known as a D_2O shake. It does not always work for amide NHs, which need some acid catalysis to exchange rapidly.

8. Solvent Effects and Temperature

The common solvents in NMR spectroscopy are used in deuterated form, in order not to introduce extra signals, but most of them have residual signals from incomplete deuteration.

Chemical shifts are little affected by changing solvent from CCl_4 to CDCl_3 (± 0.1 ppm.), but change to more polar solvents—such as acetone, methanol, or DMSO does have a noticeable effect, ± 0.3 ppm. for protons. Benzene can have an even larger effect, ± 1 ppm. for protons, because it weakly solvates areas of low electron population; since the benzene has a powerful anisotropic magnetic field (**See Fig. 7**), solute atoms lying to the

side of or underneath the solvating benzene ring can experience significant shielding or deshielding relative to their position in an inert solvent like CDCl_3 .

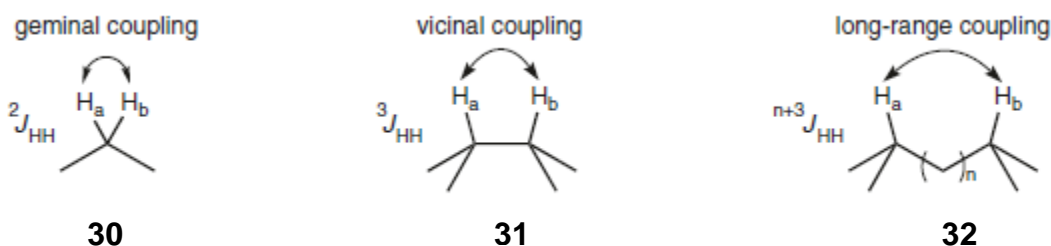
Pyridine can be even more effective. This solvent-induced shift can be used to separate two signals which overlap.

The resonance position of most signals is little affected by temperature. Hydrogen-bonded protons from OH, NH, and SH groups come into resonance at a higher field at higher temperatures, because the degree of hydrogen bonding is reduced. The major effect that temperature has is on signals from protons undergoing exchange from one environment to another during the time. If the exchange is rapid, the protons experience an average environment, and temperature has no effect. But if the exchange rate is slow, the proton signals are broadened and the degree of broadening is temperature dependent.

^1H – ^1H Coupling: Multiplicity and Coupling Patterns

When two nuclei with $I = 1/2$ are coupled, for proton-proton coupling. Three types of coupling.

1. Two-bond coupling **30** is called geminal coupling.
2. Three-bond coupling **31** is called vicinal coupling.
3. Coupling through more than three bonds **32** is called long-range coupling.



^1H – ^1H Vicinal Coupling ($^3J_{\text{HH}}$)

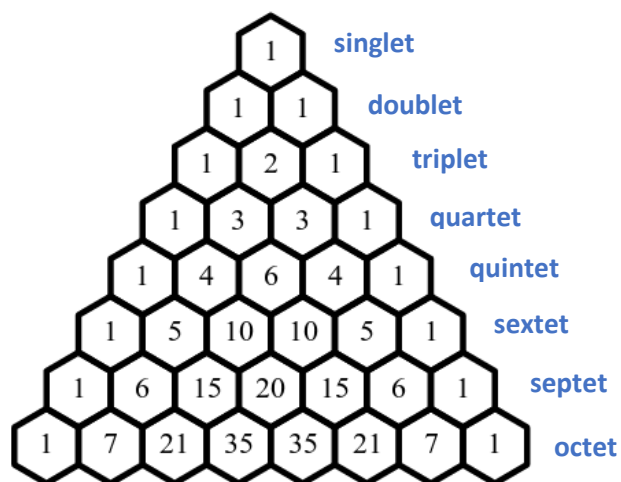
Coupling from H_a to H_b in **31** tells us something about connectivity when we are trying to put together a structure.

In proton NMR spectra, we see doublets, triplets, and quartets whenever a proton is coupled equally to one, two or three protons, respectively.

Multiplicity in Proton NMR

The number of lines in a peak is always one more ($n+1$) than the number of hydrogens on the neighboring carbon. **Table 5** summarizes coupling patterns that arise when protons have different numbers of neighbors.

In other words: The rule is a nucleus, equally coupled to n others, will give rise to a signal with ($n+1$) lines, and the intensities are given by the numbers in (Pascal's triangle).



Pascal's Triangle

Table 5: Summarizes coupling patterns in the proton signals that arise when protons have different numbers of neighbors

Number of lines	Ratio of lines	Term of peak	Number of neighbors
1	-	singlet	-
2	1:1	doublet	1
3	1:2:1	triplet	2
4	1:3:3:1	quartet	3
5	1:4:6:4:1	quintet	4
6	1:5:10:10:5:1	sextet	5
7	1:6:15:20:15:6:1	septet	6
8	1:7:21:35:35:21:7:1	octet	7
9	1:8:28:56:70:56:28:8:1	nonet	8

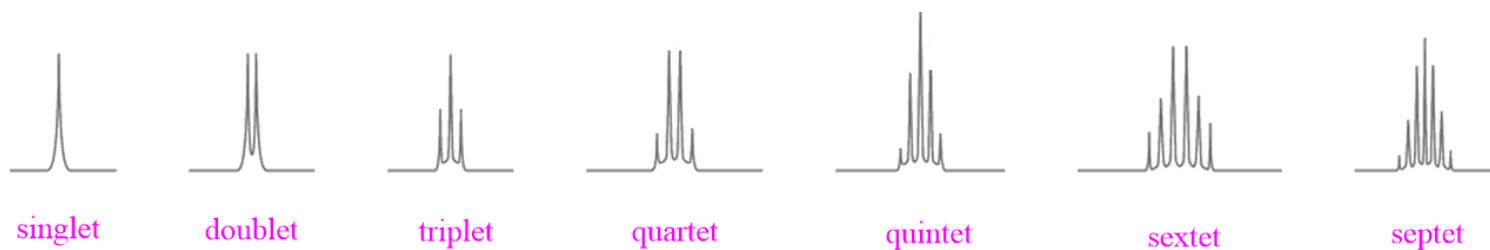


Fig 10: Multiplicity or splitting patterns results

Table 6: Splitting patterns for different protons attached to different carbons

Splitting pattern for H _x	Structure	Splitting pattern for H _y
	$\begin{array}{c} \text{--- C --- C ---} \\ \quad \\ \text{H}_x \quad \text{H}_y \end{array}$	
	$\begin{array}{c} \text{H}_x \\ \\ \text{--- C --- C --- H}_y \\ \\ \text{H}_x \end{array}$	
	$\begin{array}{c} \text{H}_x \quad \text{H}_y \\ \quad \\ \text{--- C --- C ---} \\ \quad \\ \text{H}_x \quad \text{H}_y \end{array}$	
	$\begin{array}{c} \text{H}_x \\ \\ \text{H}_x \text{--- C --- C --- H}_y \\ \\ \text{H}_x \end{array}$	
	$\begin{array}{c} \text{H}_x \quad \text{H}_y \\ \quad \\ \text{H}_x \text{--- C --- C ---} \\ \quad \\ \text{H}_x \quad \text{H}_y \end{array}$	
	$\begin{array}{c} \text{H}_x \\ \\ \text{H}_x \text{--- C --- C --- H}_y \\ \quad \\ \text{H}_x \quad \text{H}_x \text{--- C --- H}_x \\ \\ \text{H}_x \end{array}$	
	$\begin{array}{c} \text{H}_x \\ \\ \text{H}_x \text{--- C --- C ---} \\ \\ \text{H}_x \end{array}$	

Coupling constant

The signal splitting in proton spectra is usually small, ranging from fractions of a Hz to as much as 18 Hz, and is designated as J (referred to as the coupling constant) **Fig. 11**. In the **1,1-dichloroethane 33** example **Fig. 12** all the coupling constants are 6.0 Hz, so the coupling constant is simply the difference between two adjacent sub-peaks in a split signal.

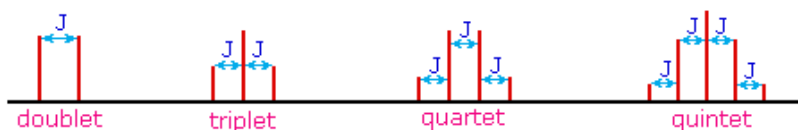


Fig 11: Four patterns are displayed in this illustration

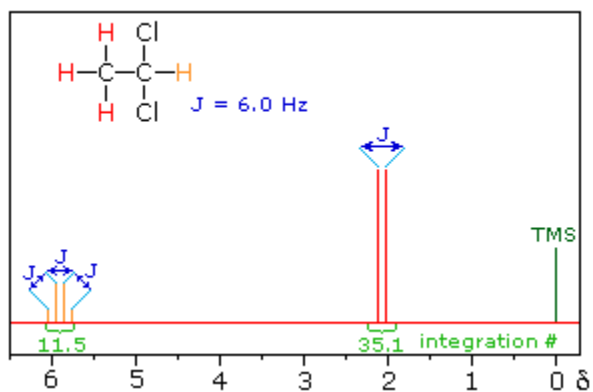


Fig 12: 1,1-dichloroethane **33**

Table 7: Magnitude of Some Typical Coupling Constants

Structural Type	J (Hz)	Structural Type	J (Hz)
	0 (unless in a rigid ideal orientation)		12 to 18
$\text{H}_3\text{C}-\text{CH}_2-\text{X}$	6 to 8		7 to 12
	5 to 7		0.5 to 3
	2 to 12 (depends on dihedral angle and the nature of X and Y)		3 to 11 (depends on dihedral angle)
	0.5 to 3		2 to 3
	12 to 15 (must be diastereotopic)		o 6 to 9 m 1 to 3 p 0 to 1

The splitting patterns shown in **Figures 10, 11** display the ideal or (**First-Order**) arrangement of lines. This is usually observed if the spin-coupled nuclei have very different chemical shifts ($\Delta\nu$ is large compared to J).

Complex-first order splitting: occurs when a nucleus spin-couples with 2 or more sets of nearby nuclei that have different J values, the $n+1$ rule is not obeyed and **complex splitting patterns** often result (see **table 8**).

(**Fig 13a & 13b**) Show the difference between **First-Order & Complex-first order splitting**

Second order behavior: If the coupled nuclei have similar chemical shifts, the splitting patterns are distorted. Two examples **34 & 35** that exhibit minor 2nd order distortion are shown below **Figures 14, 15**.

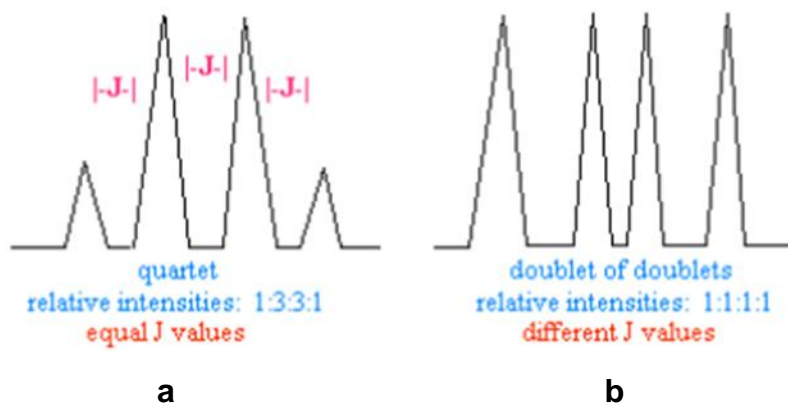


Fig 13: a) First order splitting and **b)** non-first order splitting patterns

Spectrum of 1,3-dichloropropane, even though the chemical shift difference between the A and B protons in the 1,3-dichloroethane spectrum is fairly large (140 Hz) compared with the coupling constant (6.2 Hz), some distortion of the splitting patterns is evident.

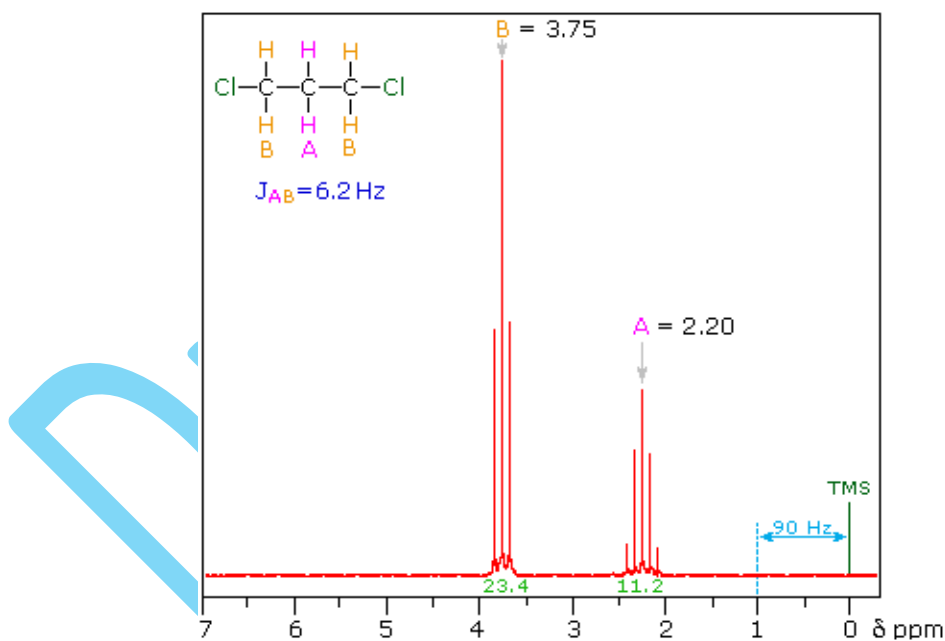


Fig 14: 1,3-dichloropropane 34 spectrum at a frequency of 90 MHz

We would expect the nmr spectrum of two spin coupled protons A&B to display a pair of doublets. However, if the ratio of $\Delta\nu$ to J (both in Hz) decreases to less than 10 a significant distortion of this expected pattern will take place, as shown in the following diagram.

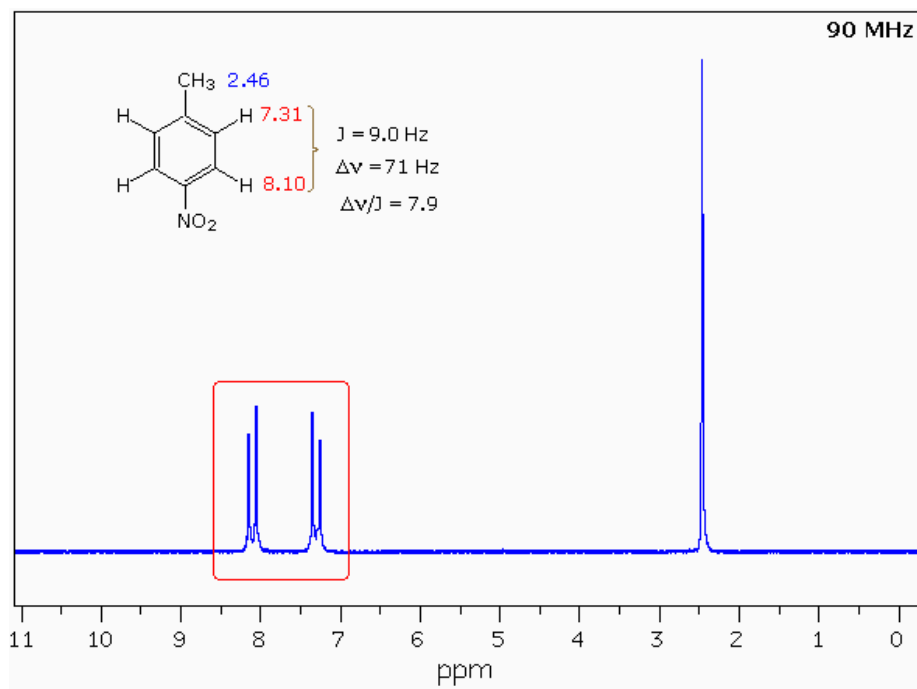


Fig 15: *p*-Nitro toluene **35** spectrum at a frequency of 90 MHz

The expanded signals in **Fig. 16** show the coupling of the characteristically low-field aldehyde proton in diphenylacetaldehyde **36** with the proton on the α -carbon. Ignoring for the moment the confused-looking signals in the δ 7.5–7.0 region from the aromatic protons, we can see that the signal from each of the two protons is split equally into a doublet by the other, and the **pattern** is described as being that of a **coupled AX system**. The convention used is to label protons close in chemical shift with the letters A, B and C, those far away in chemical shift with the letters X, Y and Z, and those intermediate with the letters M, N and O.

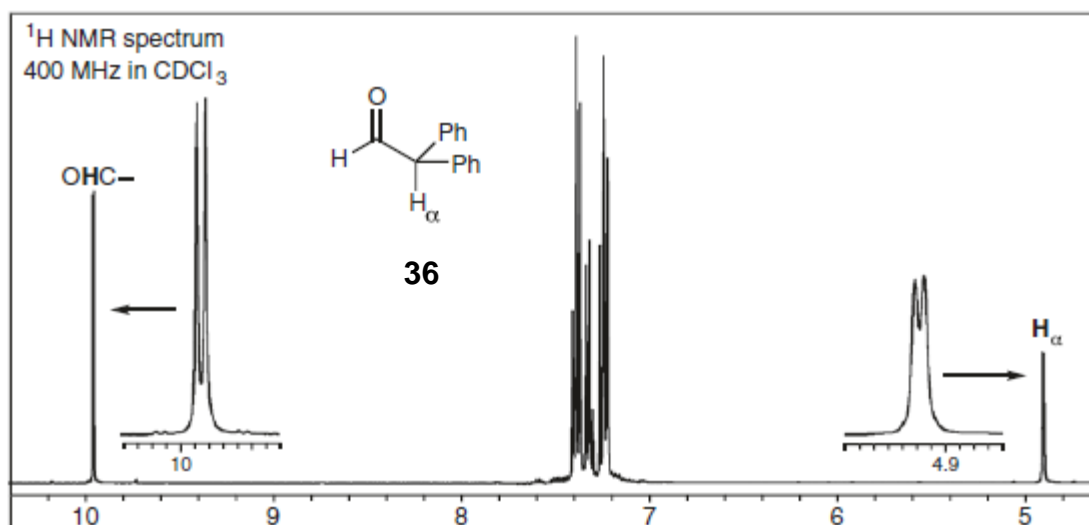


Fig 16: ¹H NMR spectrum of diphenylacetaldehyde

Figure 9 shows the ¹H NMR spectrum of **3,5-dimethylbenzyl methoxyacetate 26**, a compound which gives rise to signals over most of the usual chemical shift range, free of the complication of coupling, which we shall come to later. In the ¹H NMR spectrum is not fully resolved, because the signal at δ 6.96 from the hydrogen atom on C-4 can only just be seen as a shoulder on the side of the signal from the two identical hydrogen atoms on C-2 and C-6 at δ 6.97. H-4 is in a different chemical environment from H-2 and H-6, but the environments are so similar that their chemical shifts are barely resolved. Each of the remaining lines corresponds to one of the five significantly different kinds of hydrogen atoms.

The solvent in this case is deuteriochloroform (CDCl₃). In the ¹H NMR spectrum, there is a small residual signal at δ 7.25 from the presence of incompletely deuterated chloroform.

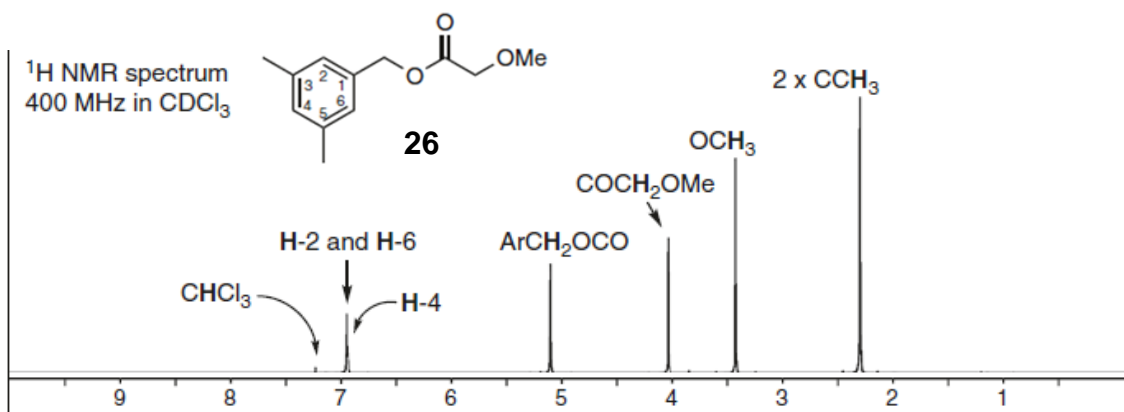


Fig 9: ¹H NMR spectra of the ester **26**

The absorption of a signal in a ¹H NMR spectrum is generally proportional to the number of protons coming into resonance at the frequency of that signal. The area under the peaks is therefore proportional to the number of protons being detected. This is illustrated in **Fig. 9**, which shows two ways in which the area under the peak can be presented.

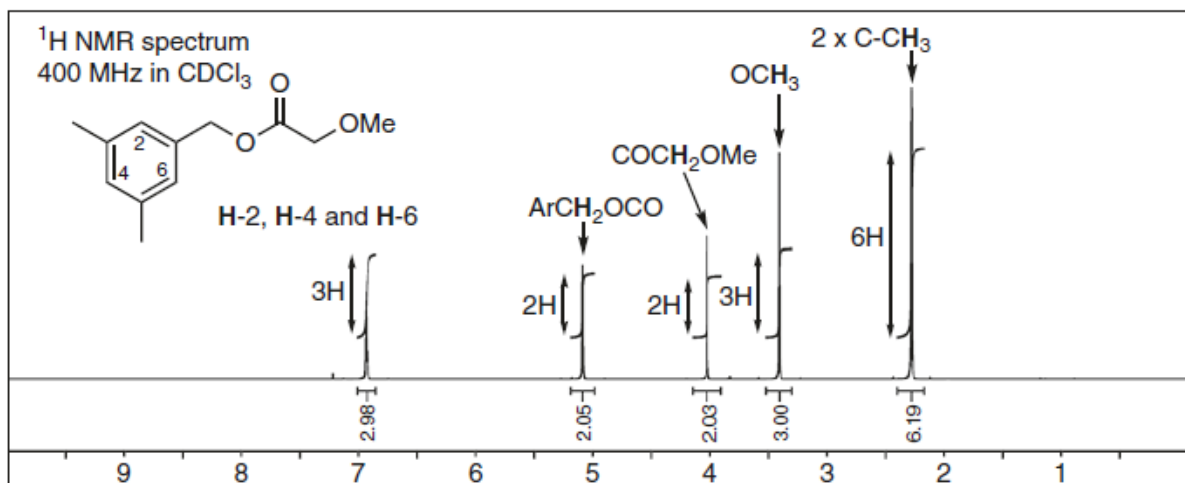


Fig 9: Integration traces

Fig. 17 shows the **AX₃ system** in the ¹H NMR spectrum of 2-chloropropionic acid **37**. The mid-field signal centred at δ 4.44 is the signal from the methine hydrogen H_α, downfield because it has a carbonyl group and an electronegative element attached to the methine carbon. It resonates as a 1:3:3:1 quartet because the methine hydrogen is coupled to the three identical hydrogens H_β of the methyl group. Likewise, the upfield signal centred at δ 1.725 is the signal from the methyl hydrogens H_β with a chemical shift slightly downfield from the position of a normal C-Me group, because it has an electronegative element on the next carbon. It appears as a doublet because the three hydrogens of the methyl group are coupled to the single methine hydrogen, and are split into two by it.

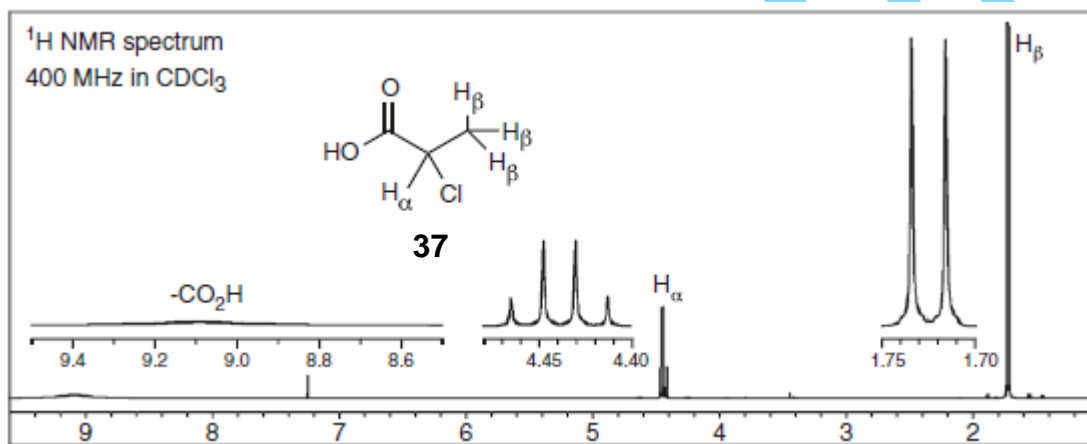


Fig 17: ¹H NMR spectrum of 2-chloropropionic acid

The three methyl hydrogens, because of the free rotation about the C–C bond, experience identical magnetic environments and they come into resonance at exactly the same place. The methyl protons are, in fact, coupled to each other, but coupling between protons with identical chemical shifts does not show up in NMR spectra.

The upfield doublet is three times as intense as the downfield quartet and three times as intense as the broad signal from the carboxylic acid proton.

In summary, the mid-field signal is a one-proton quartet because the proton that gives rise to it is equally coupled to three protons, and the upfield signal is a three-proton doublet because the protons that give rise to it are coupled to one proton.

The spectrum in **Fig. 18** of ethyl propionate **38** twice over illustrates **the characteristic appearance of A_2X_3** signals from ethyl groups. The three protons of the methyl groups couple equally with the two protons of the neighbouring methylene groups. Likewise, the two protons of the methylene groups couple equally with the three protons of the neighbouring methyl groups. This pattern of an upfield three-proton 1:2:1 triplet and a downfield two-proton 1:3:3:1 quartet is characteristic of an ethyl group in which the methylene protons are not coupled to anything else. The chemical shifts of the methylene groups δ 4.19 and 2.38 are strongly indicative of the nature of the atom to which they are bonded oxygen for the former and carbon for the latter.

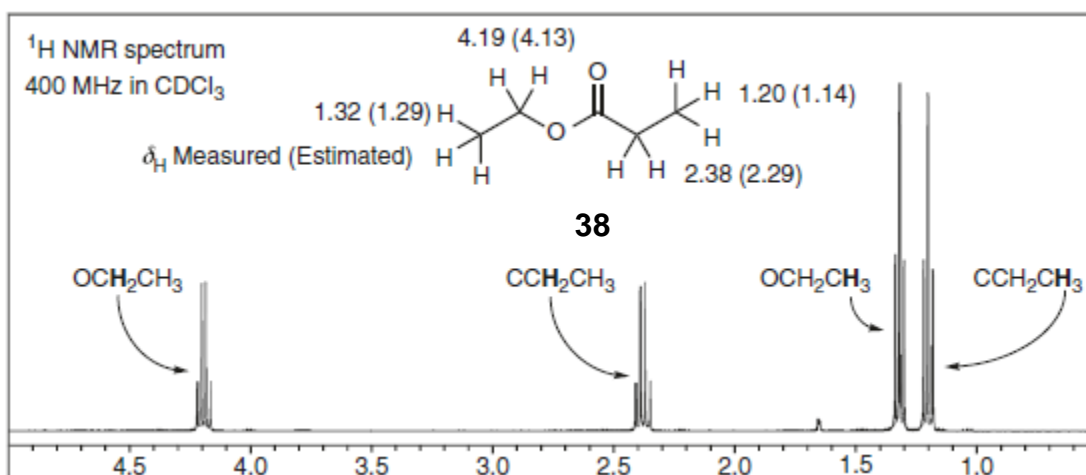


Fig 18: ¹H NMR spectrum of ethyl propionate

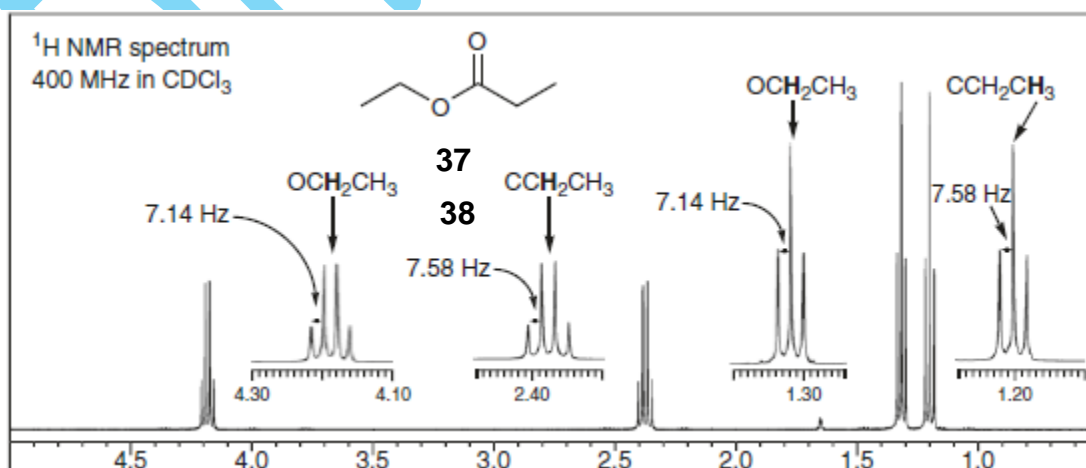


Fig 18: ¹H NMR spectrum of ethyl propionate in more detail

Moving on to larger multiplets, the $A_2X_2A_2$ spectrum of oxetane **39** in **Fig. 19** shows the downfield four-proton triplet from the pair of identical methylene groups flanking the central methylene group, which gives rise to the clean 1:4:6:4:1 quintet. The triplet is downfield, because the methylene groups giving rise to this signal are adjacent to the oxygen atom. Note that the quintet here has base-line resolution and lines in the proper proportions. All the couplings in oxetane **39** are coincidentally equal.

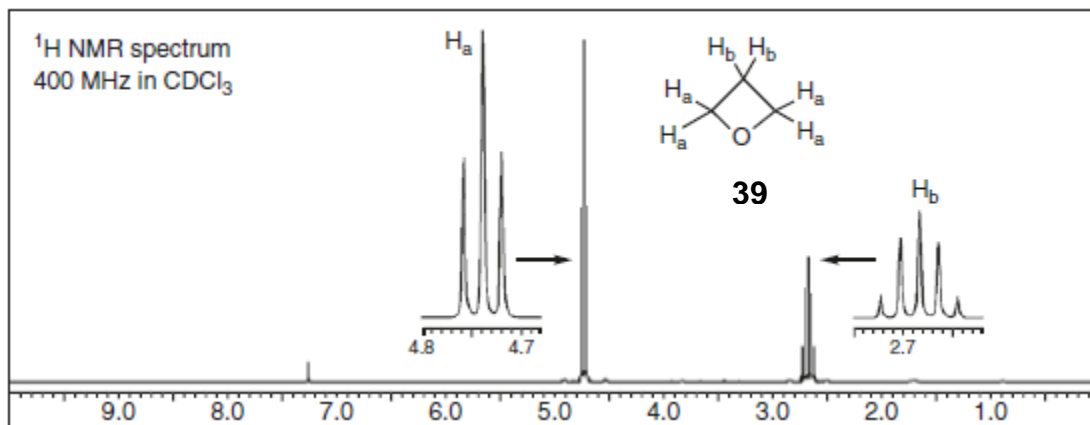


Fig 19: ^1H NMR spectrum of oxetane

Figure 20 shows a slightly more complicated example in the spectrum of 1-nitropropane **40**. The protons H_c on the methyl group give rise to a three-proton signal at high field (δ 1.04) as a triplet, because they are adjacent to a methylene group. The protons on the methylene group H_a give rise to a two-proton triplet at low field (δ 4.37). The chemical shift is appropriate for a methylene group next to an electronegative element, and the multiplicity is appropriate for protons coupling to another methylene group. The protons of the methylene group in the middle H_b give rise to a two-proton 1:5:10:10:5:1 sextet at δ 2.06. The chemical shift is appropriate for a methylene group between two alkyl groups, but not far from an electronegative group.

The multiplicity is appropriate for protons coupling equally to a total of five protons. Actually, the coupling constant J_{ab} (7.0 Hz) is slightly smaller than J_{bc} (7.5 Hz), but the difference is not resolved in the sextet, showing up only as a slight broadening of the lines and resolution that does not reach the base line.

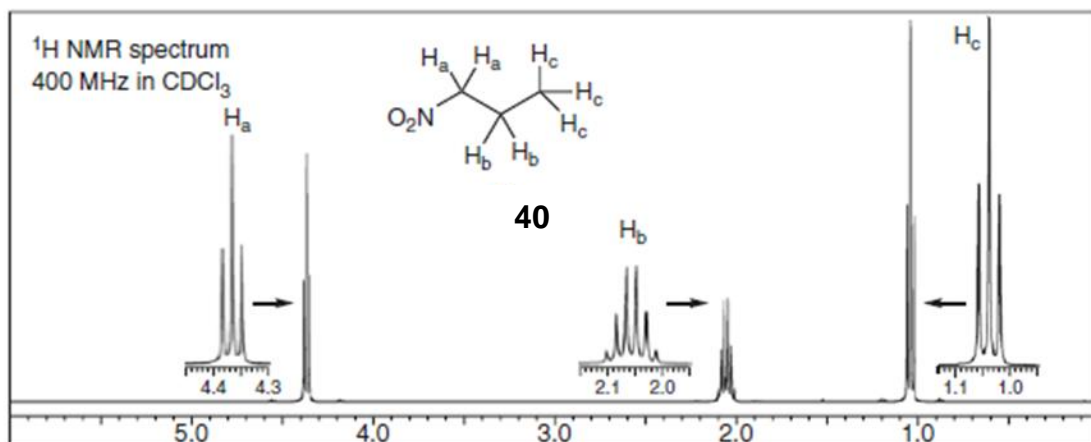


Fig 20: ¹H NMR spectrum of 1-nitropropane

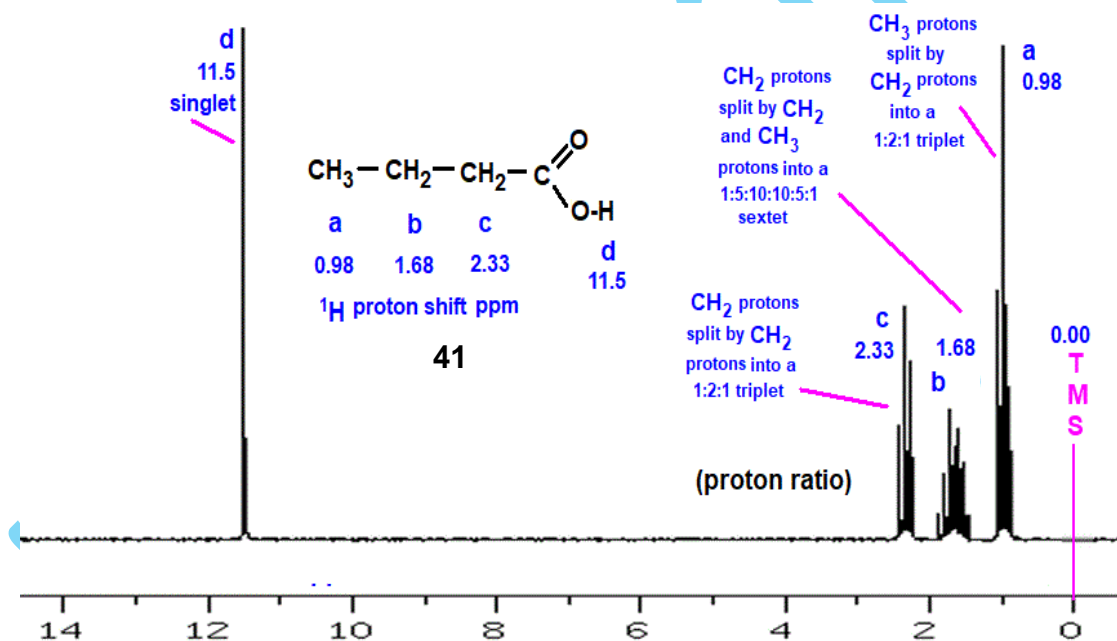


Fig 21: ¹H NMR spectrum of butanoic acid 41

In the spectra in **Figs. 17, 18, 19, 20** and **21** the coupling constants have all been very much the same, either inherently, as in the spectra of 2-chloropropionic acid **37** (**Fig 17**) and ethyl propionate **38** (**Fig 18**), or accidentally, as in the spectra in oxetane **39** (**Fig 19**), where the *cis* and *trans* couplings were equal, and nitropropane **40** (**Fig 20**), where the

coupling J_{ab} is almost the same as J_{bc} . The coupling constant ${}^3J_{HH}$ = 6–8 Hz in these four spectra is typical of coupling constants in freely rotating alkyl chains (**See Table 7**). However, the coupling constant for the mutually coupled doublets in diphenylacetaldehyde **36** shown in (**Fig. 16**) is noticeably smaller, J = 2.6 Hz (**See Table 7**).

When a multiplet is split again by coupling to other protons with a different coupling constant, more complicated patterns emerge (**See Table 8, Figs 22-23**) than the doublets, triplets, quartets, quintets and sextets that we have seen in (**Figs. 16-21**).

Dr. Tahani

Table 8: First-order Splitting Patterns of Some Common Spin Systems

Complex 1st order spin systems

Entry	Structure	Notation and Pattern for H_a $J_{ab} = J_{ac}$	Entry	Structure	H_a Multiplets
1		d 	7		dd
2		t 	8		t
3		t 	9		dd
4		q 	10		dt
5		q 	11		ddd
6		sp 	12		dq

For example, in the spectrum of propionaldehyde **42** in **Fig. 22** the methylene protons are not the quintet that would be produced by coupling equally to the four neighbouring protons. Instead, the coupling between the methylene protons and the aldehyde proton has a coupling constant of 1.3 Hz, whereas the coupling constant to the methyl protons is 7.5 Hz. The methylene signal is therefore a double quartet, made up in the pattern shown above the expanded signal for H_a . Note how the two coupling constants can be measured in each of the participating signals, the smaller coupling constant both in the aldehyde triplet and in the double quartet, and the larger coupling constant both in the methyl triplet and in the double quartet.

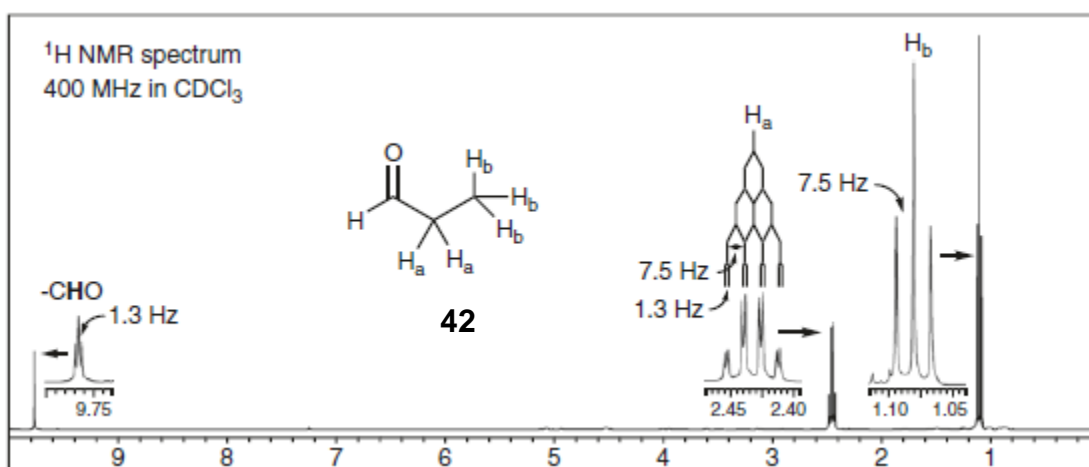


Fig 22: ¹H NMR spectrum of propionaldehyde

The proton H_c on the double bond of allyl bromide **43**, centred at δ 6.03, is doubled by coupling to the *trans* proton H_a , doubled again with a different coupling constant by coupling to the *cis* proton H_b , and it is further coupled to the two protons H_d on the methylene group (**Fig. 23**). Since the three coupling constants are all different, it is a double, double, triplet, and could give rise to as many as 12 lines. The actual appearance of this signal is shown in **Fig. 23**, together with the analysis in the descending tree-like drawing above the spectrum. Because the couplings J_{cd} (7.5 Hz) and J_{cb} (10 Hz) add up to a number very close to J_{ca} (17 Hz), several lines almost perfectly coincide. Only 10

lines are resolved, instead of the full complement of 12 expected for a double-double triplet with three different coupling constants.

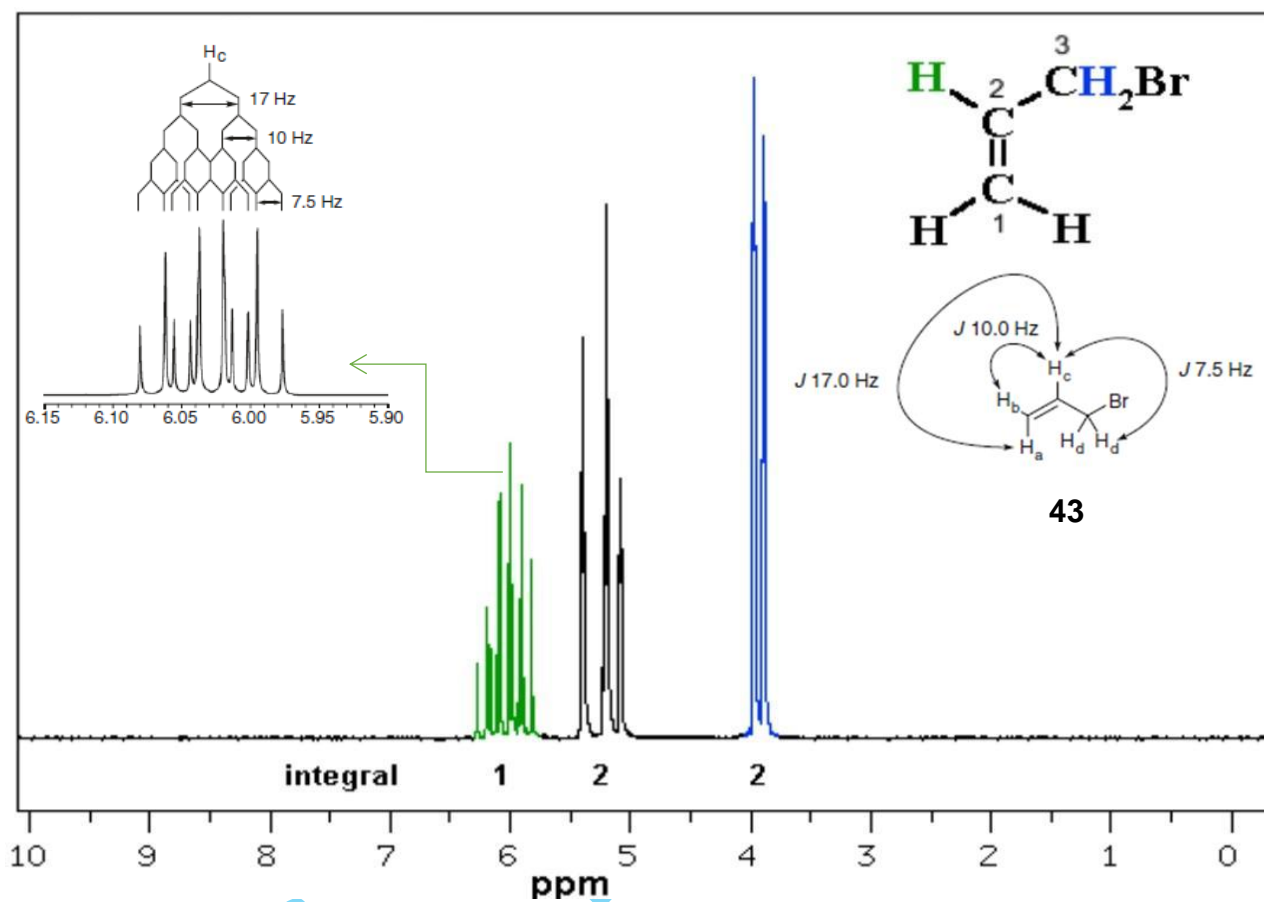


Fig 23: ^1H NMR spectrum of allyl bromide showing the **double double triplet** from H_c protons

It is lazy to report a signal like the one shown in **Fig. 23** simply as a multiplet, when its components can be analysed with a little thought. Recognising the patterns in this signal is helped if you can pick out the 1:2:1 triplet feature repeated along the multiplet. It is most easily picked out as the first, second and fourth lines, reading from the left or from the right. Once a feature like the triplet is recognised, its doubling by the 10 Hz separation of the first and third lines, and redoubling by the 17 Hz separation of the first and fifth lines, is easier to build up into the full tree.

First order splitting

- In all the spectra considered so far the separation of the signals (in Hz) has been much greater than the coupling constants (in Hz).

- Coupling in which the coupling constant ***J*** is **small** relative to the chemical shift difference between the coupling partners ($\Delta\nu \gg J$) is called **weak coupling**.

- They have all been A_nX_m systems.

- Produces “normal” splitting patterns that have equal *J* values, obey *n*+1 rule.

- The simplest examples showing deviations from first-order spectra, and the most simple of all is an AB system, consisting of two mutually coupled protons A and B, which are not coupled to any other protons.

Second order splitting or (Non first order)

- The chemical shifts are close together.

- Coupling in which the coupling constant ***J*** is **large** relative to the chemical shift difference between the coupling partners is called **strong coupling** ($\Delta\nu > J$) or ($\Delta\nu \sim J$) or ($\Delta\nu/J \leq 10$).

- They have all been A_nB_m systems.

- The splitting patterns are distorted

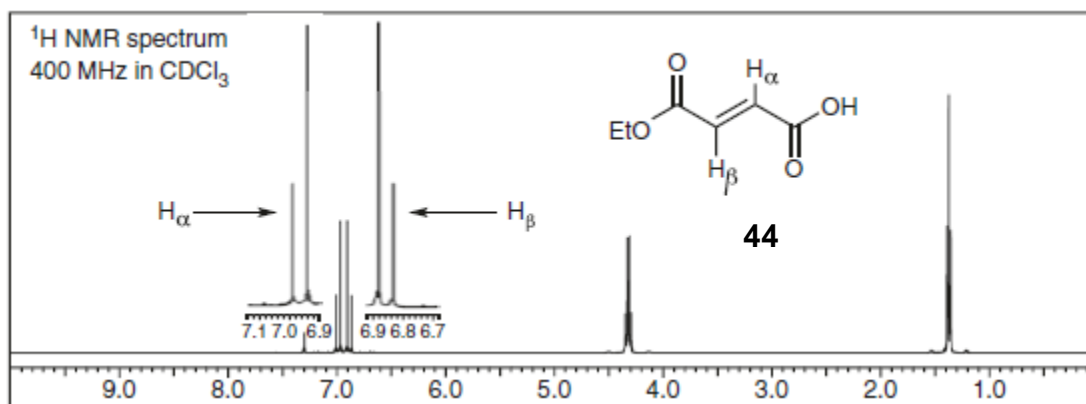


Fig 24: ¹H NMR spectrum of monoethyl fumarate (AB system)

When the difference in chemical shift between the A and the B signal in frequency units ($\nu_A - \nu_B$) is comparable in magnitude to the coupling constant J_{AB} , the two lines of the doublets are not equal in intensity. As an example, we can look at **Fig. 24** showing the alkene signals from the mono-ethyl ester **44** of fumaric acid. The two protons, H_α and H_β , are in slightly different chemical environments, and as a result, they have slightly different chemical shifts (δ 6.97 and 6.87). The difference in chemical shift in this 400 MHz spectrum is 40 Hz and the coupling constant of 17 Hz is not very different. In consequence, the 'inside' lines of the AB system are more intense, and the 'outside' lines less intense. The comparison is with a simple, first-order AX system, where the lines in the A and the X signals are essentially equal in intensity (**Fig. 16**).

Thus, the closer the signals are in chemical shift, the greater the perturbation, as we can see by comparing the AB systems in **Fig. 26** given by the protons on the double bonds in three α, β -unsaturated carbonyl compounds. The protons in methyl 3-methoxyacrylate **46** have very different chemical shifts, because the β -proton is adjacent to a σ -withdrawing substituent, conjugated, and *cis* to a π -withdrawing substituent; in contrast, the α -proton is conjugated to a π -donor substituent (see **Table 4**).

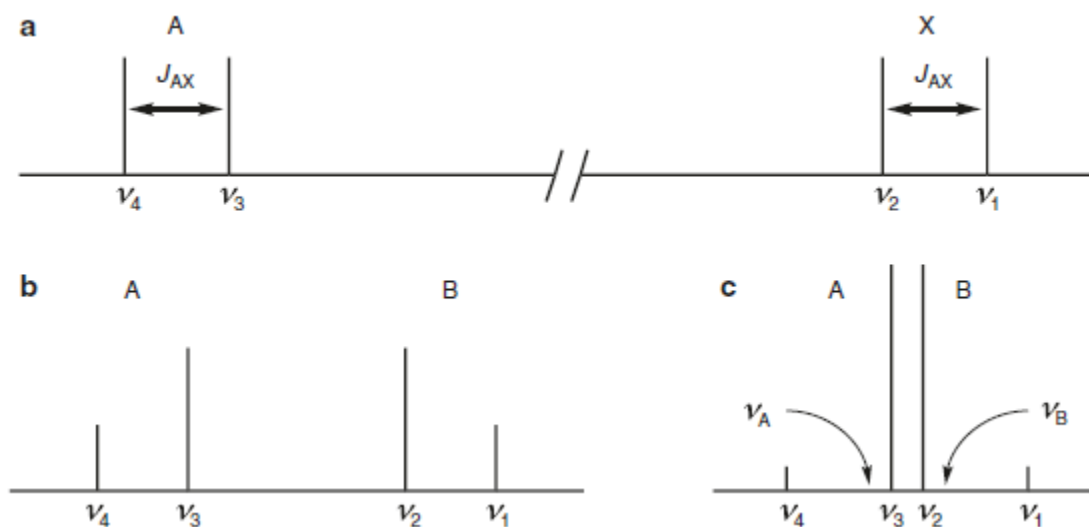


Fig 25: Geometry of AB systems

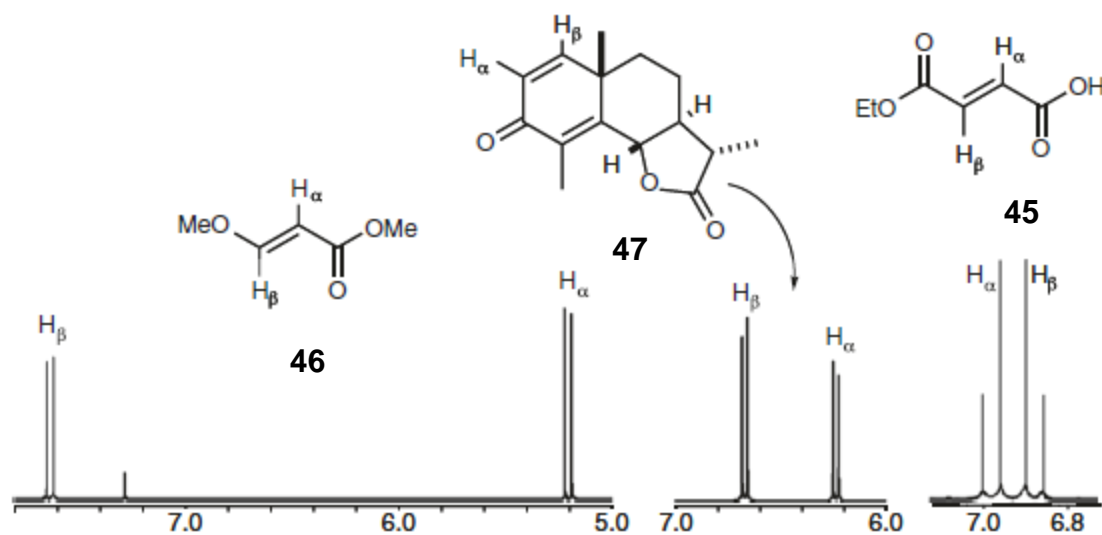


Fig 26: Three AB systems with different separations of the A and B signals

The values are δ 7.65 and 5.21, respectively, more or less at the extreme range for olefinic protons. At 400 MHz, this is a difference of 976 Hz, and the coupling constant, 13 Hz, is much smaller. As a result, the signals are only slightly perturbed from those of an AX system. Santonin **47** has the two signals separated by a much smaller amount, 172 Hz at 400 MHz, with a somewhat smaller coupling constant, 10 Hz, and the perturbation is more obvious. The ester **45** that we have already seen has a separation in chemical shift of only 40 Hz in the 400 MHz spectrum with a large coupling constant of 17 Hz, and the perturbation is considerable.

These patterns are helpful in identifying AB systems: a strongly perturbed doublet must be coupling to a proton close in chemical shift and a less perturbed doublet to one further away.

Nevertheless, it is always wise when you are assigning signals to measure up the doublets, in order to make sure that both halves of what you think are an AB system have matching coupling constants.

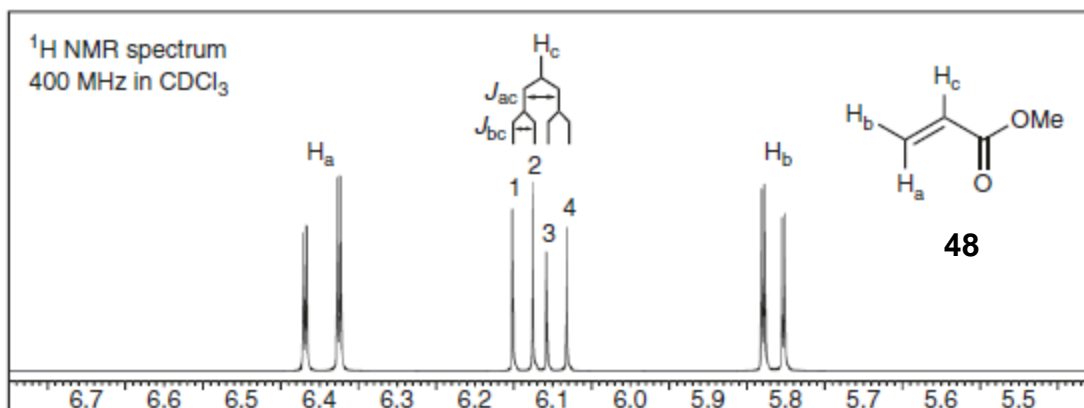


Fig 27: Part of the ¹H NMR spectrum of methyl acrylate

A complex pattern, such as that from the three olefinic protons in methyl acrylate **48** shown in **Fig. 27**. We can expect all three protons to be downfield, and the *cis*- β -proton Ha to be the most downfield of all. Judging by methyl vinyl ketone (**Compound 18**) (**See Table 4**), the α -proton Hc will be in between the two β -protons, as indeed it is. This assignment is reinforced by looking at the signal from the α -proton, which is a straightforward double doublet with coupling constants of 17.2 and 10.8 Hz. The larger separation of the lines 1 and 3, and the equally large separation of the lines 2 and 4, gives the coupling constant J_{ac} .

In turn, the doublets given by Ha and Hb point back to the central signal given by Hc. Of course, the same assignments can be made simply by looking at the coupling constants, but the roofing is a great help in quickly making sense of the appearance of the signal from Hc.

The spectrum in **Fig. 27** we note that the signals from both Ha and Hb are actually double doublets with fine coupling of each to the other. This is the first example of ²J_{HH} coupling (**geminal coupling**) that we have seen.

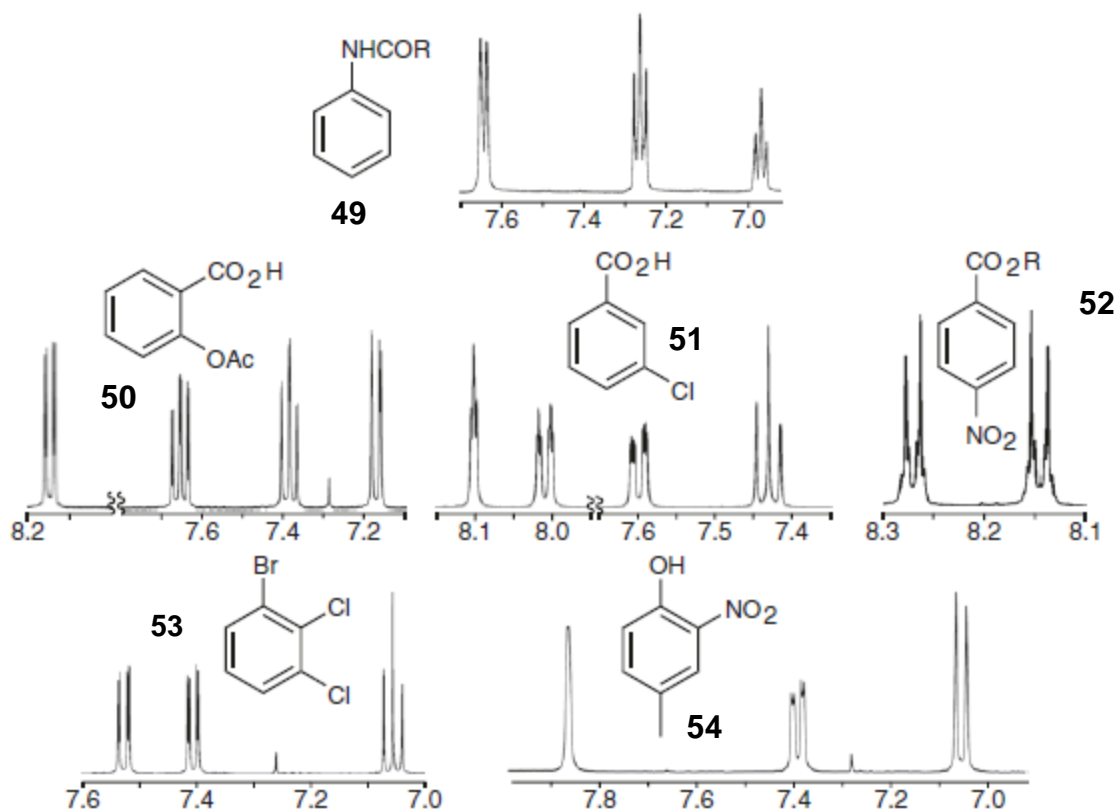
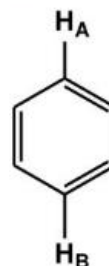
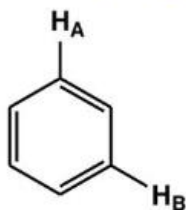
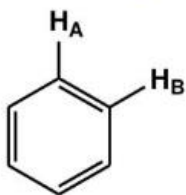


Fig 28: Some coupling patterns for mono-, di- and tri-substituted benzene rings

Looking only at the couplings with the larger coupling constants, the two-proton doublet, two-proton triplet and one-proton triplet make a characteristic pattern for a monosubstituted benzene ring (**Fig. 28: Compound 49**).

As with mono-substituted rings, the signals can appear in any order of chemical shift, depending upon the effects that the various substituents have in their different arrangements around the ring, as are two doublets and two triplets for an *ortho*-disubstituted ring (**Compound 50**), two doublets, a triplet and a singlet for a *meta*-disubstituted ring (**Compound 51**), two doublets for a *para*-disubstituted ring (**Compound 52**), two doublets and a triplet for a 1,2,3-trisubstituted ring (**Compound 53**), and two doublets and a singlet for a 1,2,4-trisubstituted ring (**Compound 54**), with, in this case, the meta coupling identifying which doublet is which.

Magnitudes of coupling constants



$${}^3J_{AB(ortho)} = 6 - 10 \text{ Hz} \quad {}^4J_{AB(meta)} = 1 - 3 \text{ Hz} \quad {}^5J_{AB(para)} = 0 - 1.5 \text{ Hz}$$

- in aromatic systems, protons *ortho* to one another show a large coupling (typically 8 Hz)
- *meta*-couplings are much smaller (1 – 3 Hz) and thus may or may not appear in the ${}^1\text{H}$ NMR spectrum (signals may simply be broadened)
- *para*-couplings are very small (0 – 1 Hz) and normally do not appear in the ${}^1\text{H}$ NMR spectrum

In Fig. 29, shows the downfield double-doublet from H-o with both coupling constants appearing to be large, even though one was from ortho coupling and the other from meta coupling. This problem arose because the coupling partners H-*m* and H-*p* were close in chemical shift, only 7.0 Hz apart in the 200 MHz spectrometer, and H-*m* was coupled to H-o with a coupling constant of 7.75 Hz, similar in magnitude to the separation in chemical shift. In a higher-field spectrometer, the separation of the H-*m* and H-*p* signals is effectively greater, 21.0 Hz at 600 MHz, while the coupling constant remains the same at 7.75 Hz, making the value of $|(v_A - v_B)|/J_{AX} = 2.7$, safely above the value that leads to second-order spectra. The signals for these three protons become essentially first-order in appearance at 600 MHz.

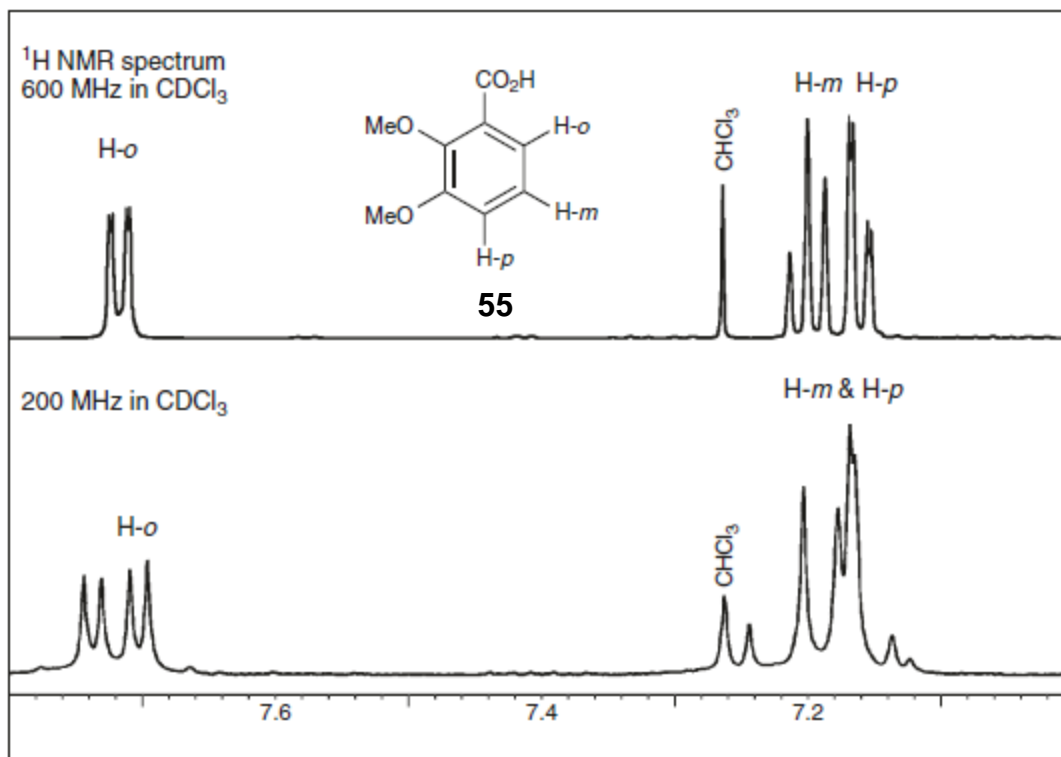


Fig 29: Details of the ^1H NMR spectra of 2,3-dimethoxybenzoic acid at 200 and 600 MHz

Note: Second-order effects decrease as the frequency difference between multiplets increases, so that high-field (i.e. high-frequency) NMR spectra display less distortion than lower frequency spectra. Early spectra at 60 MHz were more prone to distortion than spectra from later machines typically operating at frequencies at 200 MHz or above.