Unit 6.4 Spin resonance spectroscopy (Marks 10)

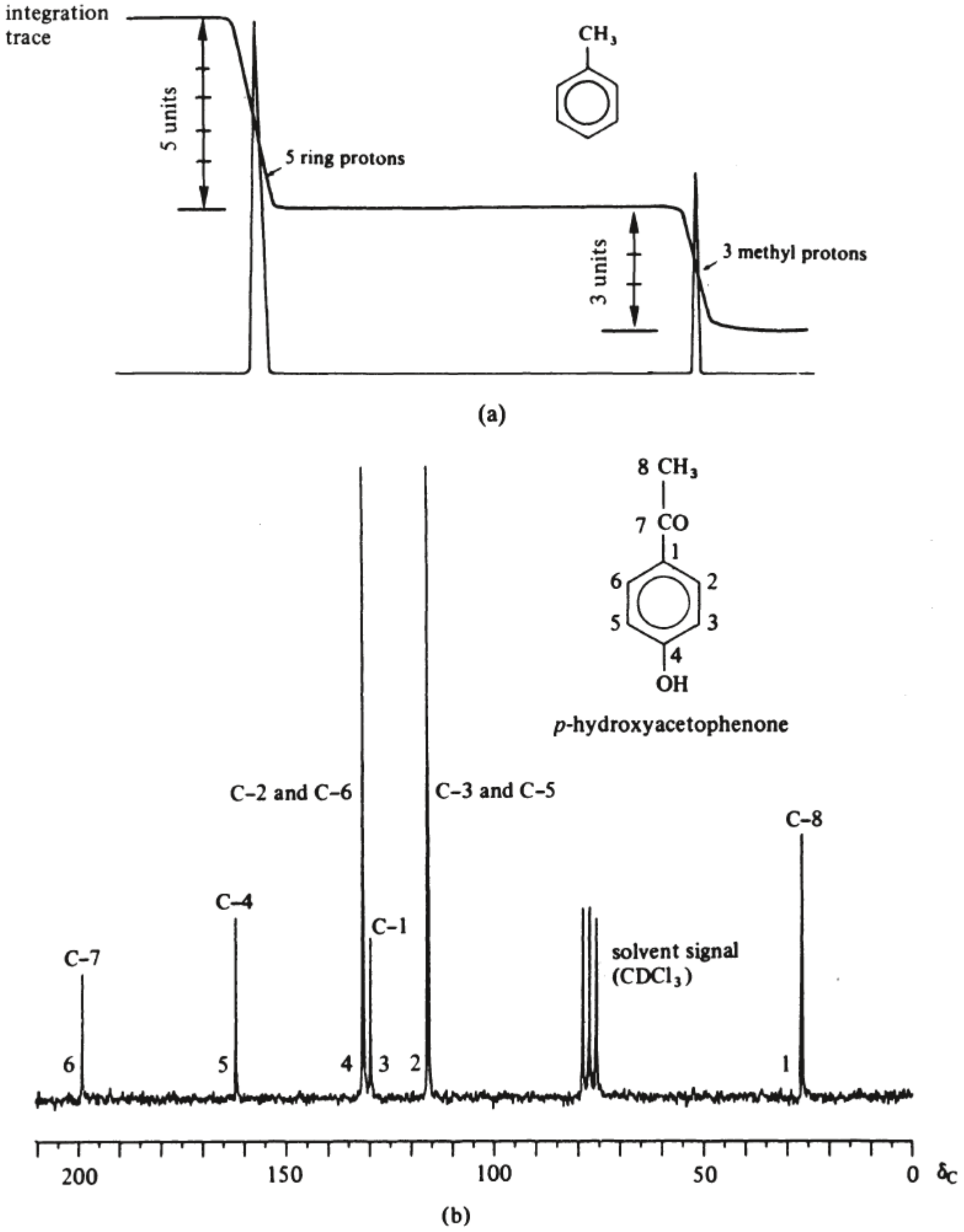
Interaction between spin and magnetic field – Nuclear spin – Nuclear magnetic resonance spectroscopy – 1H NMR – presentation of the spectrum - chemical shift and its unit – chemical shifts for simple organic molecules (alkane, alkene, alkyne, arenas, aldehydes, carboxylic acids and esters). Spin-spin coupling and high resolution 1H NMR spectra of ethanol, ethyl benzoate, 2-iodopropane, cyanohydrin.

Basic concept of electron spin resonance spectroscopy – presentation of the spectrum – hyperfine structure – esr of H- atom , deuterium atom.

What is NMR Spectroscopy ?

- Nuclear magnetic resonance (or NMR) is concerned with the magnetic properties of certain atomic nuclei , notably the nucleus of the hydrogen atom-the proton (1H) -and that of the carbon-13 (13C) isotope of carbon, 31P, 19F, 11B etc.
- NMR studies enable us to record differences in the magnetic properties of the various magnetic nuclei present, and to deduce in large measure what the positions of these nuclei are within the molecule.
- Deduce different kinds of environments there are in the molecule, and also which atoms are present in neighboring groups.
- Measure how many atoms are present in each of these environments.

NMR Spectrum



(a)

(b)

Figure 3.1 (a) *Diagrammatic* ^{1}H *NMR spectrum of toluene,* $C_6H_5CH_3$*, showing two signals in the intensity ratio 5:3.* (b) ^{13}C *NMR spectrum of p-hydroxyacetophenone, p-*$CH_3COC_6H_4OH$*, showing six signals corresponding to the six different carbon environments in the molecule.* (20 MHz, *in* $CDCl_3$.)

Interaction between Spin and Magnetic Field

- **THE SPINNING NUCLEUS**: The nucleus of the hydrogen atom (the proton) behaves as a tiny spinning bar magnet, and it does so because it possesses both electric charge and mechanical spin; any spinning charged body will generate a magnetic field, and the nucleus of hydrogen is no exception.
- **THE EFFECT OF AN EXTERNAL MAGNETIC FIELD:** Like all bar magnets, 'the proton will respond to the influence of an external magnetic field , and will tend to align itself with that field, in the manner of a compass needle in the earth's magnetic field. Because of quantum restrictions which apply to nuclei but not to compass needles, the proton can only adopt two orientations with respect to an external magnetic field-either *aligned with the field (the lower energy* state) or *opposed to the field (the higher energy state). We can also* describe these orientations as *parallel with or antiparallel with the applied* field.

Interaction between Spin and Magnetic Field

❖**PRECESSIONAL MOTION:** Because the proton is behaving as a *spinning magnet, not only can it align* itself with or oppose an external magnetic field, but also it will move in a characteristic way under the influence of the external magnet. Consider the behavior of a spinning top: as well as describing its spinning motion, the top will (unless absolutely vertical) also perform a slower waltz-like motion, in which the spinning axis of the top moves slowly around the vertical. This is *precessional motion, and the top is said to be precessing around the vertical axis of the earth's gravitational field. The* precession arises from the interaction of spin-that is, gyroscopic motion-with the earth's gravity acting vertically downward. Only a spinning top will precess ; a static top will merely fall over.

As the proton is a spinning magnet, it will, like the top , precess around the axis of an applied external magnetic field, and can do so in two principal orientations, either aligned with the field (low energy) or opposed to the field (high energy). This is represented in figure 3.2, where *Bo* is the external magnetic field.

Interaction between Spin and Magnetic Field

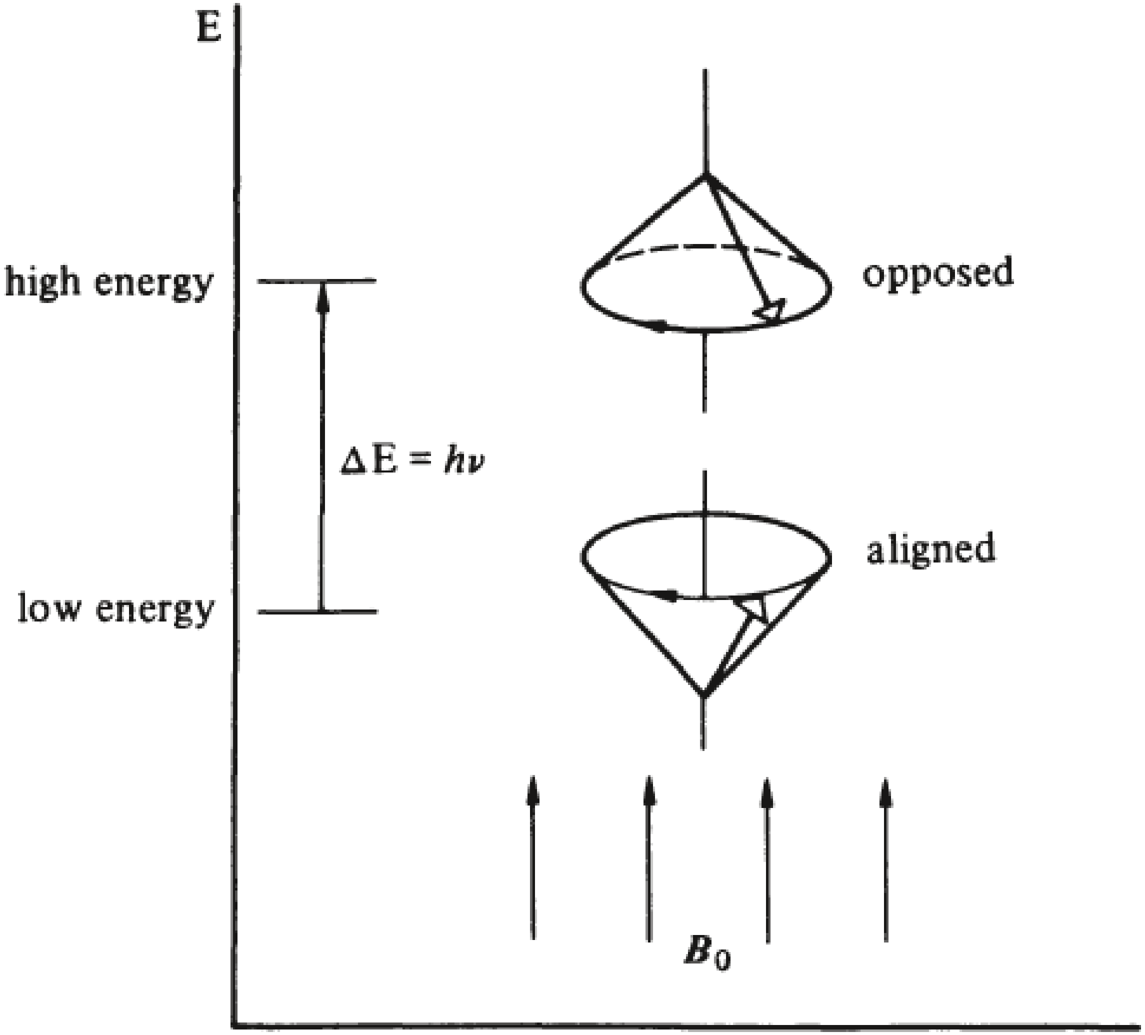


Figure 3.2 *Representation of precessing nuclei, and the ΔE transition between the aligned and opposed conditions.*

Interaction between Spin and Magnetic Field

- ❖**PRECESSIONAL FREQUENCY:** The spinning frequency of the nucleus does not change, but the speed of precession does . The *precessional frequency, v, is directly proportional to* the strength of the external field, *Bo*: that is,

$$\nu \propto B_0$$

- ❖**ENERGY TRANSITIONS:** If a proton is precessing in the *aligned orientation, it can absorb energy* and pass into the *opposed orientation; subsequently it can lose this extra* energy and relax back into the aligned position. If we irradiate the precessing nuclei with a beam of radiofrequency energy of the correct frequency , the low-energy nuclei may absorb this energy and move to a higher energy state. The precessing proton will only absorb energy from the radiofrequency source if the precessing frequency is the same as the frequency of the radiofrequency beam; when this occurs, the nucleus and the radiofrequency beam are said to be *in resonance; hence the term nuclear magnetic resonance.*

Interaction between Spin and Magnetic Field

The simplest NMR experiment consists in exposing the protons in an organic molecule to a powerful external magnetic field; the protons will precess, although they may not all precess at the same frequency. We irradiate these precessing protons with radiofrequency energy of the appropriate frequencies, and promote protons from the low-energy (aligned) state to the high-energy (opposed) state. We record this absorption of energy in the form of an NMR spectrum.

Nuclear Spin and NMR Theory

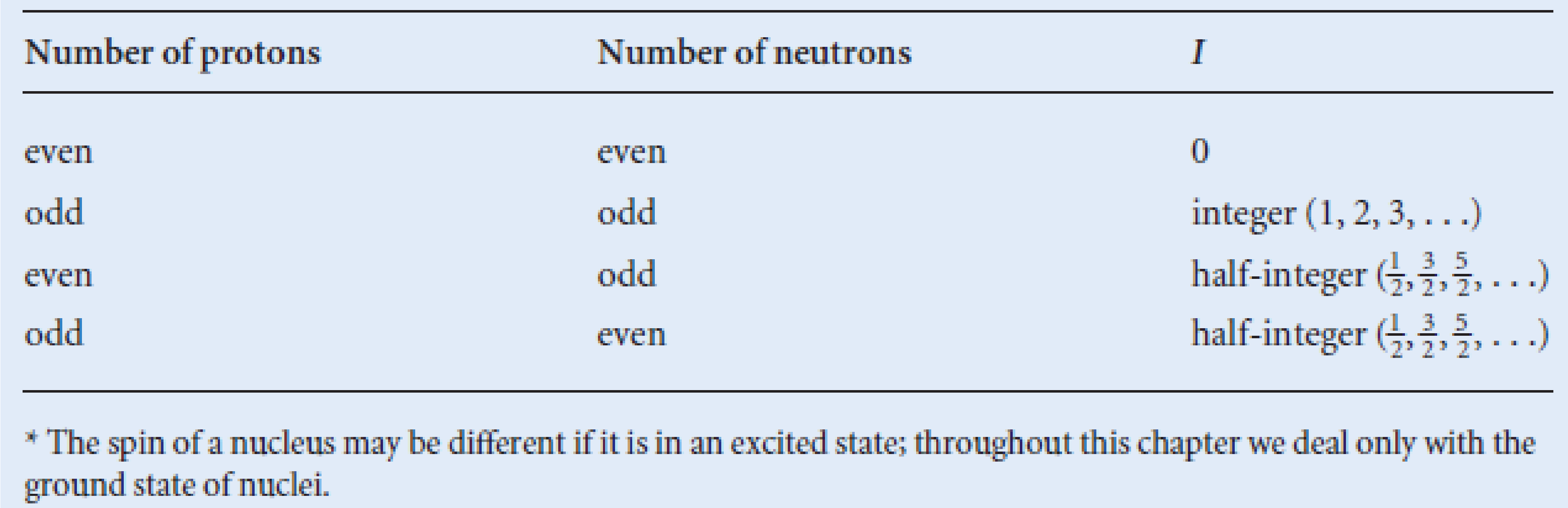
The spin quantum number, I*, of a nucleus is a fixed characteristic property of a* nucleus and is either an integer or a half-integer. A nucleus with spin quantum number *I has the following properties:*

1. An angular momentum of magnitude $\{I(I+1)\}^{1/2}\hbar$.
2. A component of angular momentum $m_I\hbar$ *on a specified axis ('the z-axis'),* where $m_I = I, I-1, \ldots, -I$.
3. If $I > 0$*, a magnetic moment with a constant magnitude and an orientation that* is determined by the value of m_I.

According to the second property, the spin, and hence the magnetic moment, of the nucleus may lie in $2I + 1$ *different orientations relative to an axis. A proton has* $I = ½$ and its spin may adopt either of two orientations; a 14N nucleus has $I = 1$ *and its spin* may adopt any of three orientations; both 12C and 16O have $I = 0$ *and hence zero magnetic* moment.

Nuclear Spin and NMR Theory

The only nuclei that exhibit the NMR phenomenon are those for which the spin quantum number *I is greater than 0: the spin quantum number I is* associated with the mass number and atomic number of the nuclei as follows:



Number of protons	Number of neutrons	I
even	even	0
odd	odd	integer (1, 2, 3, . . .)
even	odd	half-integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$)
odd	even	half-integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$)

* The spin of a nucleus may be different if it is in an excited state; throughout this chapter we deal only with the ground state of nuclei.

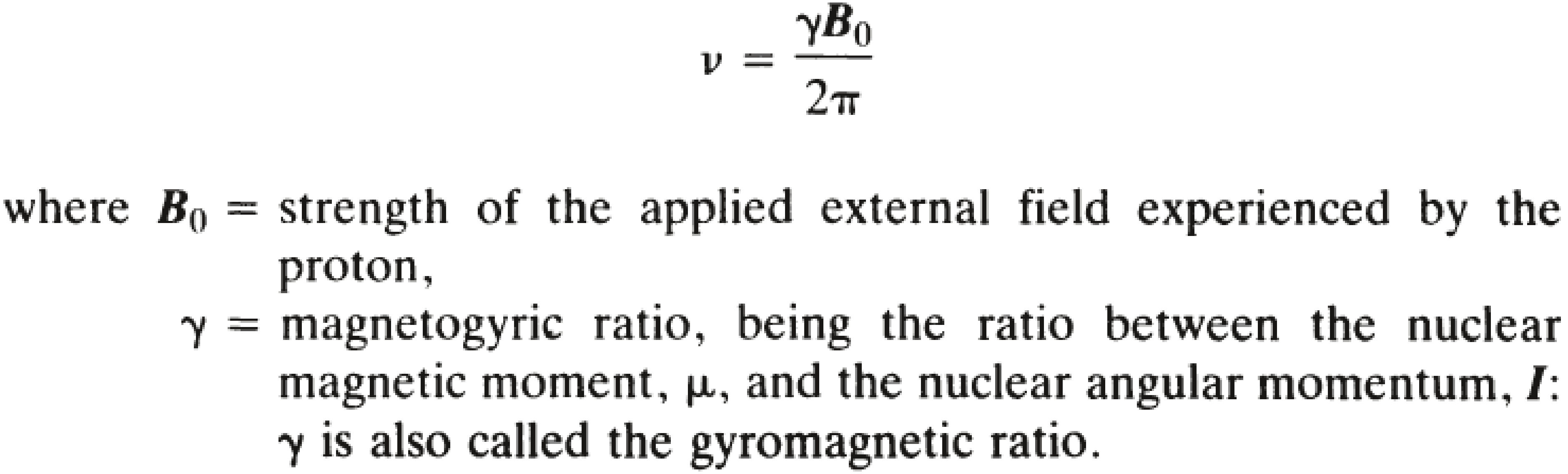
The nucleus of 1H, the proton, has *I = ½ , whereas I2C and 16O have I = 0 and are therefore nonmagnetic. If I2C and 16O had been magnetic,* the NMR spectra of organic molecules would have been much more complex.

Nuclear Spin and NMR Theory

Under the influence of an external magnetic field, a magnetic nucleus can take up different orientations with respect to that field ; the number of possible orientations is given by (2I + 1), so that for nuclei with spin ½ (1H, 13C, 19F, etc .) only two orientations are allowed. Deuterium and 14N have I = 1 and so can take .up three orientations: these nuclei do not simply possess magnetic *dipoles, but rather possess electric quadrupoles . Nuclei* possessing electric quadrupoles can interact with both magnetic and electric field gradients, the relative importance of the two effects being related to their magnetic moments and electric quadrupole moments, respectively .

Nuclear Spin and NMR Theory

In an applied magnetic field, magnetic nuclei like the proton precess at a frequency *v , which is proportional to the strength of the applied field. The* exact frequency is given by



$$\nu = \frac{\gamma B_0}{2\pi}$$

where B_0 = strength of the applied external field experienced by the proton,

γ = magnetogyric ratio, being the ratio between the nuclear magnetic moment, μ, and the nuclear angular momentum, I: γ is also called the gyromagnetic ratio.

Nuclear Spin and NMR Theory

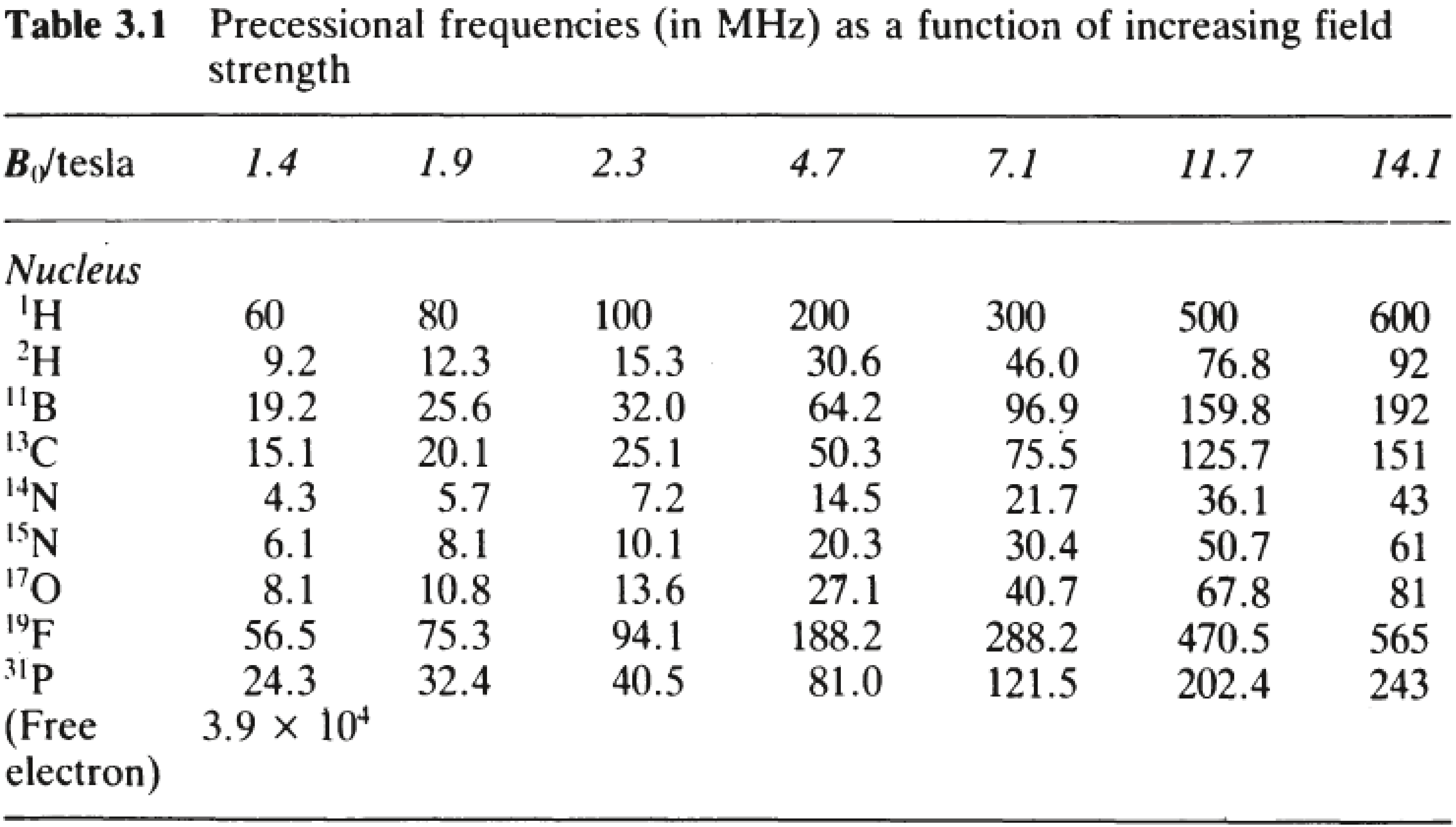


Table 3.1 Precessional frequencies (in MHz) as a function of increasing field strength

B_0/tesla	*1.4*	*1.9*	*2.3*	*4.7*	*7.1*	*11.7*	*14.1*
Nucleus							
^{1}H	60	80	100	200	300	500	600
^{2}H	9.2	12.3	15.3	30.6	46.0	76.8	92
^{11}B	19.2	25.6	32.0	64.2	96.9	159.8	192
^{13}C	15.1	20.1	25.1	50.3	75.5	125.7	151
^{14}N	4.3	5.7	7.2	14.5	21.7	36.1	43
^{15}N	6.1	8.1	10.1	20.3	30.4	50.7	61
^{17}O	8.1	10.8	13.6	27.1	40.7	67.8	81
^{19}F	56.5	75.3	94.1	188.2	288.2	470.5	565
^{31}P	24.3	32.4	40.5	81.0	121.5	202.4	243
(Free electron)	3.9×10^4						

Nuclear Spin and NMR Theory

The strength of the signal, and , hence, the sensitivity of the NMR experiment for a particular nucleus, are related to the magnitude of the magnetic moment, **μ**. The magnetic moments of ^1H and ^{19}F are relatively large, and detection of NMR with these nuclei is fairly sensitive . The magnetic moment for ^{13}C is about one-quarter that of ^1H, and that of ^2H is roughly one-third the moment of ^1H; these nuclei are less sensitively detected in NMR.

Chemical Shift

Nuclear magnetic moments interact with the *local magnetic field. The local field* may differ from the applied field because the latter induces electronic orbital angular momentum (that is, the circulation of electronic currents) which gives rise to a small additional magnetic field δB *at the nuclei. This additional field is proportional to the* applied field, and it is conventional to write

$$\delta B = -\sigma B_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(15.15)$$

where the dimensionless quantity σ is called the **shielding constant of the nucleus (σ** is usually positive but may be negative). The ability of the applied field to induce an electronic current in the molecule, and hence affect the strength of the resulting local magnetic field experienced by the nucleus, depends on the details of the electronic structure near the magnetic nucleus of interest, so nuclei in different chemical groups have different shielding constants. The calculation of reliable values of the shielding constant is very difficult, but trends in it are quite well understood and we concentrate on them.

Chemical Shift

Because the total local field is

$$\mathcal{B}_{\text{loc}} = \mathcal{B}_0 + \delta\mathcal{B} = (1-\sigma)\mathcal{B}_0 \qquad (15.16)$$

the nuclear Larmor frequency is

$$\nu_{\text{L}} = \frac{\gamma\mathcal{B}_{\text{loc}}}{2\pi} = (1-\sigma)\frac{\gamma\mathcal{B}_0}{2\pi} \qquad (15.17)$$

This frequency is different for nuclei in different environments. Hence, different nuclei, even of the same element, come into resonance at different frequencies. It is conventional to express the resonance frequencies in terms of an empirical quantity called the **chemical shift, which is related to the difference between the resonance** frequency, *ν*, of the nucleus in question and that of a reference standard, *ν* °:

$$\delta = \frac{\nu - \nu^{\circ}}{\nu^{\circ}} \times 10^6 \qquad [15.18]$$

Chemical Shift

The standard for protons is the proton resonance in tetramethylsilane (Si(CH3)4, commonly referred to as TMS), which bristles with protons and dissolves without reaction in many liquids. Other references are used for other nuclei. For 13C, the reference frequency is the 13C resonance in TMS; for 31P it is the 31P resonance in 85 per cent H3PO4(aq). The advantage of the δ -scale is that shifts reported on it are independent of the applied field (because both numerator and denominator are proportional to the applied field). The relation between δ andσ is obtained by substituting eqn 15.17 into eqn 15.18:

$$\delta = \frac{(1-\sigma)\mathcal{B}_0 - (1-\sigma^{\circ})\mathcal{B}_0}{(1-\sigma^{\circ})\mathcal{B}_0} \times 10^6 = \frac{\sigma^{\circ} - \sigma}{1-\sigma^{\circ}} \times 10^6 \approx (\sigma^{\circ} - \sigma) \times 10^6 \qquad (15.19)$$

Chemical Shift

As the shielding, σ, gets smaller, δ *increases. Therefore, we speak of nuclei with large* chemical shift as being strongly **deshielded. Some typical chemical shifts are given in** Fig. 15.5. As can be seen from the illustration, the nuclei of different elements have very different ranges of chemical shifts. The ranges exhibit the variety of electronic environments of the nuclei in molecules: the heavier the element, the greater the number of electrons around the nucleus and hence the greater the range of shieldings. By convention, NMR spectra are plotted with δ increasing from right to left. Consequently, in a given applied magnetic field the Larmor frequency also increases from right to left. In the original continuous wave (CW) spectrometers, in which the radiofrequency was held constant and the magnetic field varied (a 'field sweep experiment'), the spectrum was displayed with the applied magnetic field increasing from left to right: a nucleus with a small chemical shift experiences a relatively low local magnetic field, so it needs a higher applied magnetic field to bring it into resonance with the radiofrequency field. Consequently, the right-hand (low chemical shift) end of the spectrum became known as the 'high field end' of the spectrum.

Chemical Shift

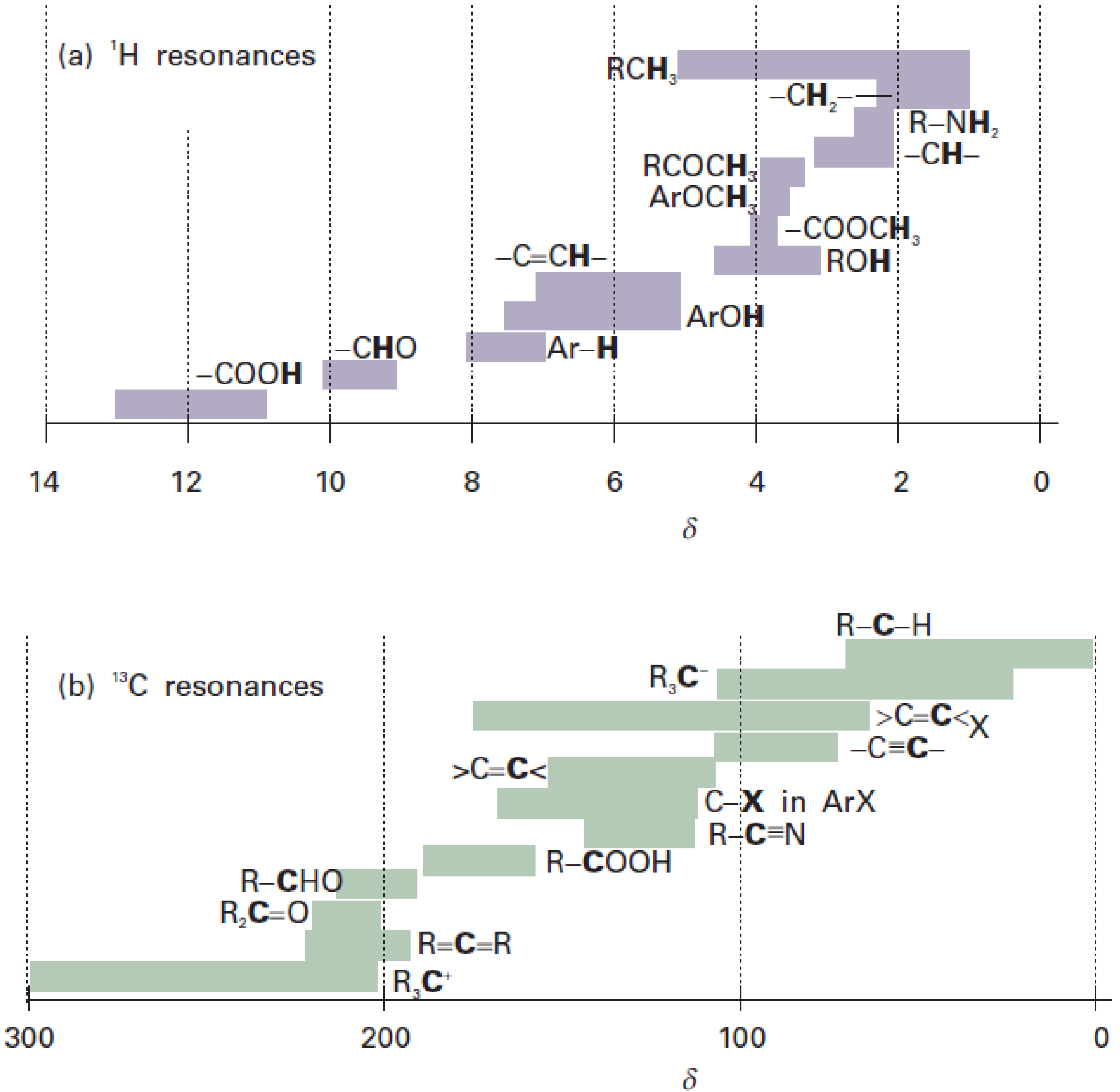


Fig. 15.5 The range of typical chemical shifts for (a) ^{1}H resonances and (b) ^{13}C resonances.

Resonance of Different Nuclei

The existence of a chemical shift explains the general features of the spectrum of ethanol shown in Fig.15.6. The CH3 protons form one group of nuclei with δ ≈ 1. The two CH2 protons are in a different part of the molecule, experience a different local magnetic field, and resonate at δ ≈ 3. Finally, the OH proton is in another environment, and has a chemical shift of δ ≈ 4. The increasing value of δ (that is, the decrease in shielding) is consistent with the electron-withdrawing power of the O atom: it reduces the electron density of the OH proton most, and that proton is strongly deshielded. It reduces the electron density of the distant methyl protons least, and those nuclei are least deshielded. The relative intensities of the signals (the areas under the absorption lines) can be used to help distinguish which group of lines corresponds to which chemical group. The determination of the area under an absorption line is referred to as the **integration** of the signal (just as any area under a curve may be determined by mathematical integration). Spectrometers can integrate the absorption automatically (as indicated in Fig. 15.6).

Resonance of Different Nuclei

In ethanol the group intensities are in the ratio 3:2:1 because there are three CH3 protons, two CH2 protons, and one OH proton in each molecule. Counting the number of magnetic nuclei as well as noting their chemical shifts helps to identify a compound present in a sample.

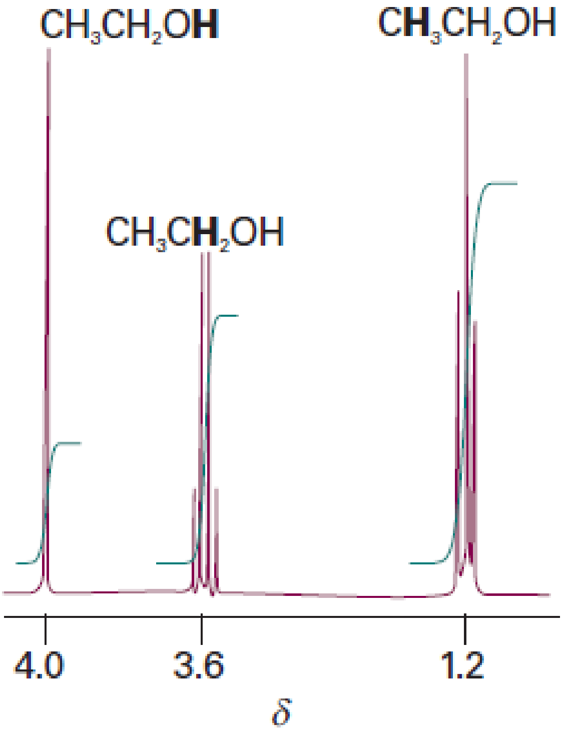


Fig. 15.6 The ^{1}H-NMR spectrum of ethanol. The bold letters denote the protons giving rise to the resonance peak, and the step-like curve is the integrated signal.

Factors Influencing Chemical Shift

1. ELECTRONEGATIVITY-SHIELDING AND DESHIELDING:

Table 3.2 shows the chemical shift positions for CH3 protons when a methyl group is attached to functions of increasing electronegativity. As the electronegativity of the function is increased , the CH3 protons come to resonance at higher δ) values.

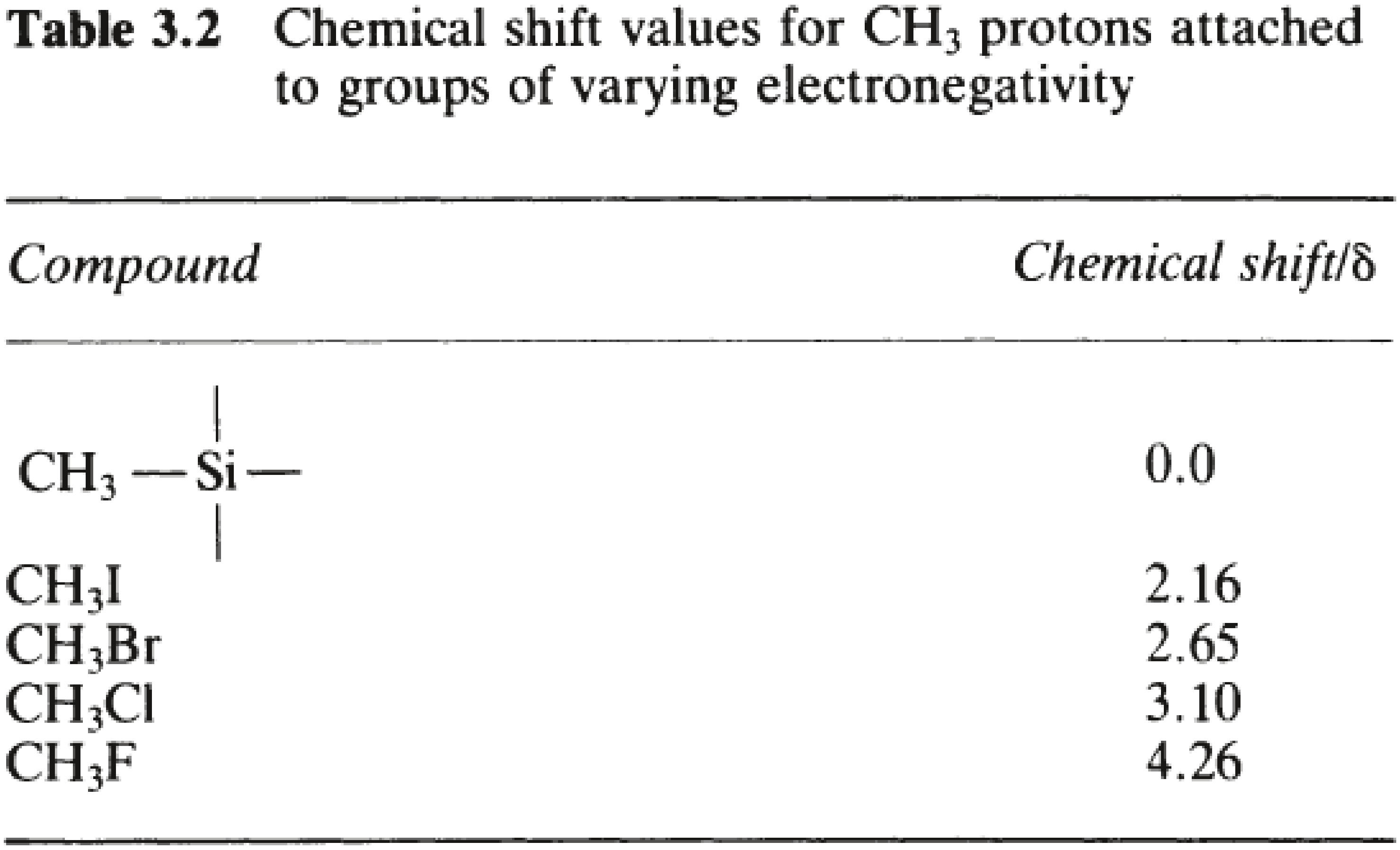


Table 3.2 Chemical shift values for CH_3 protons attached to groups of varying electronegativity

Compound	*Chemical shift/δ*
$CH_3-\overset{\vert}{\underset{\vert}{Si}}-$	0.0
CH_3I	2.16
CH_3Br	2.65
CH_3Cl	3.10
CH_3F	4.26

Factors Influencing Chemical Shift

Why do the protons of the CH3 group in CH3F come to resonance at higher frequency than those of CH3Cl, etc.? The explanation relates to the electron density around the 1H nuclei.

Hydrogen nuclei are surrounded by electron density, which to some extent *shields the nucleus from the influence of the applied field Bo, and* the extent of this shielding will influence the precessional frequency of the nucleus-the greater the *shielding effect, the lower the precessional* frequency. In a magnetic field the electrons around the proton are induced to circulate, and in so doing they generate a small secondary magnetic field, which acts in opposition (that is, diamagnetically) to the applied field (see figure 3.5(a)). The greater the electron density circulating around the proton, the greater the induced diamagnetic shielding effect and the lower the precessional frequency of the proton. Electronegative groups, such as fluorine in CH3F, withdraw electron density from the methyl group (inductive effect) and this *deshielding effect means that the methyl protons* experience a greater nett magnetic field, and, hence, precess with higher frequency.

Factors Influencing Chemical Shift

Since fluorine is more electronegative than chlorine, its deshielding influence is greater and, hence, the attached protons have higher precessional frequencies (higher δ values).

Silicon is electropositive, and the opposite effect operates in, for example, TMS; silicon pushes electrons into the methyl groups of TMS by a +I inductive effect, and this powerful *shielding effect means that the TMS* protons come to resonance at low frequency (low δ value, defined as zero) .

The effect of charged species on chemical shift values is very marked; protons adjacent to N+ (as in quaternary ammonium ions, R4N+) are very strongly deshielded (high δ values) , while carbanionic centers act as powerful shielding influences (low δ values) .

Factors Influencing Chemical Shift

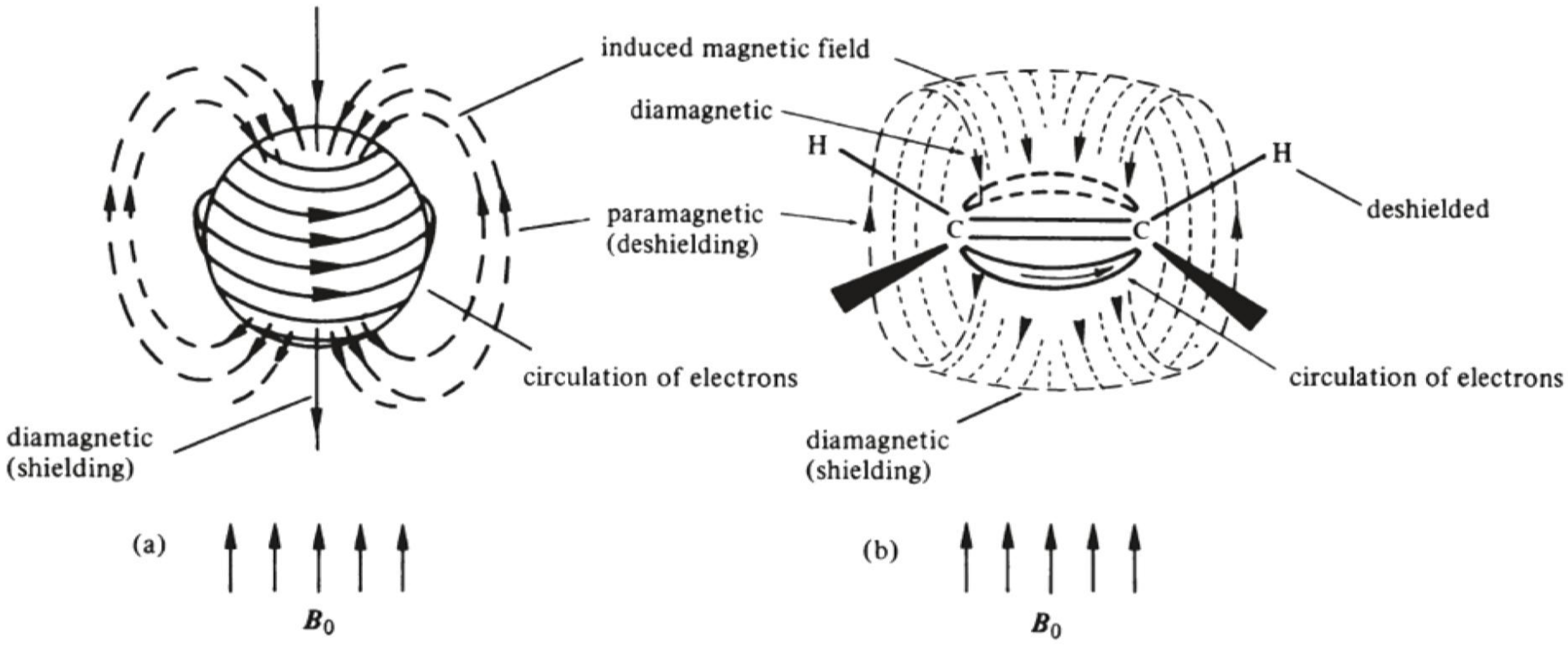


Figure 3.5 *Induced anisotropic magnetic field around* (a) *a hydrogen atom and* (b) *an alkene group.*

Factors Influencing Chemical Shift

2. VAN DER WAALS DESHIELDING:

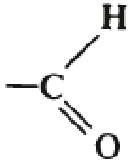
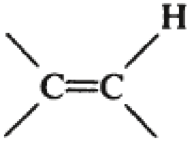
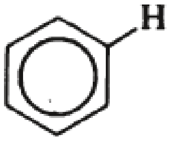
In a rigid molecule it is possible for a proton to occupy a sterically hindered position, and in consequence the electron cloud of the hindering group will tend to repel, by electrostatic repulsion, the electron cloud surrounding the proton. The proton will be deshielded and appear at higher δ values than would be predicted in the absence of the effect. Although this influence is small (usually less than 1 ppm), it must be borne in mind when predicting the chemical shift positions in overcrowded molecules such as highly substituted steroids or alkaloids.

Factors Influencing Chemical Shift

3. ANISOTROPIC EFFECTS:

The chemical shift positions (δ) for protons attached to C=C in alkenes is higher than can be accounted for by electronegativity effects alone. The same is true of aldehydic protons and aromatic protons, whereas alkyne protons appear at relatively low δ. Table 3.3 lists approximate δ values for these protons.

Table 3.3 Approximate chemical shift ranges for protons attached to anisotropic groups

Structure	*Approximate chemical shift range/δ*
	9.5–10.0
	4–8
	6–9
$-C\equiv C-H$	1.5–3.5

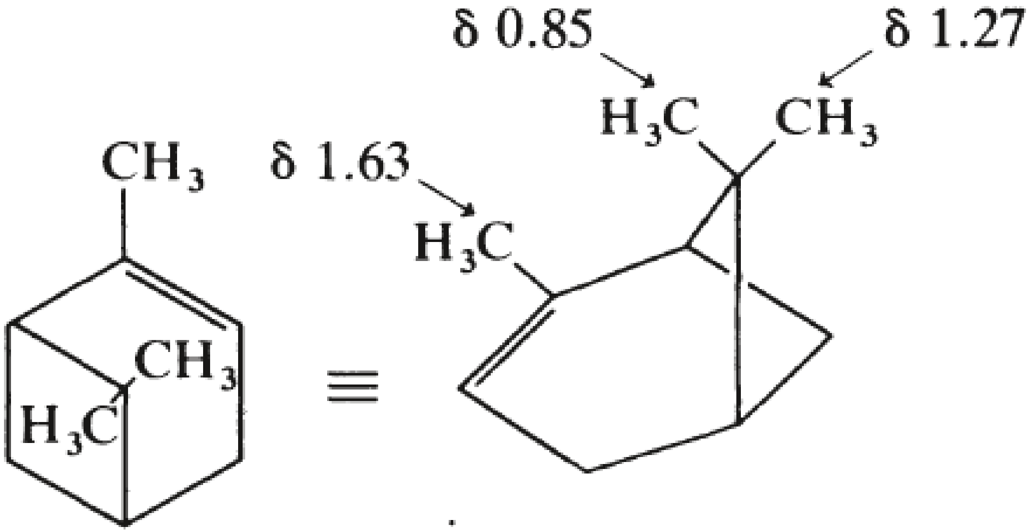
Factors Influencing Chemical Shift

The explanation is again collated with the manner in which electrons, in this case ***π*** electrons, circulate under the influence of the applied field . The effect is complex, and can lead to shifts to higher frequency (downfield shifts , or paramagnetic shifts) or to lower frequency (upfield shifts, or diamagnetic shifts). In addition, the effects are paramagnetic in certain directions around the ***π*** clouds, and diamagnetic in others, so that these effects are described as *anisotropic, as opposed to isotropic (operating* equally through space) .

Alkenes**: When an alkene group is so oriented that the plane of the double* bond is at 90° to the direction of the applied field (as in figure 3.5(b)), induced circulation of the ***π electrons generates a secondary magnetic field, which is diamagnetic around the carbon atoms, but paramagnetic (that is, it augments *Bo) in the region of the alkene protons.* Where the direction of the induced magnetic field is parallel to the applied field, *Bo, the net field is greater than Bo. Protons in these zones* come to resonance therefore at higher δ values than expected.

Factors Influencing Chemical Shift

Any group held above or below the plane of the double bond will experience a shielding effect , since in these areas the induced field opposes Bo. In ex-pinene one of the geminal methyl groups is held in just such a shielded position, and comes to resonance at significantly lower δ (frequency) than its twin . The third methyl group appears at higher δ (frequency), since it lies in the plane of the double bond and is thus deshielded .



α-pinene

Factors Influencing Chemical Shift

In summary, we can divide the space around a double bond into two categories, as shown in figure 3.6(a). Deshielding occurs in the cone shaped zones, and in these zones δ values will tend to be higher. Shielding is found outside the cones and protons in these zones are shielded (lower δ values) .

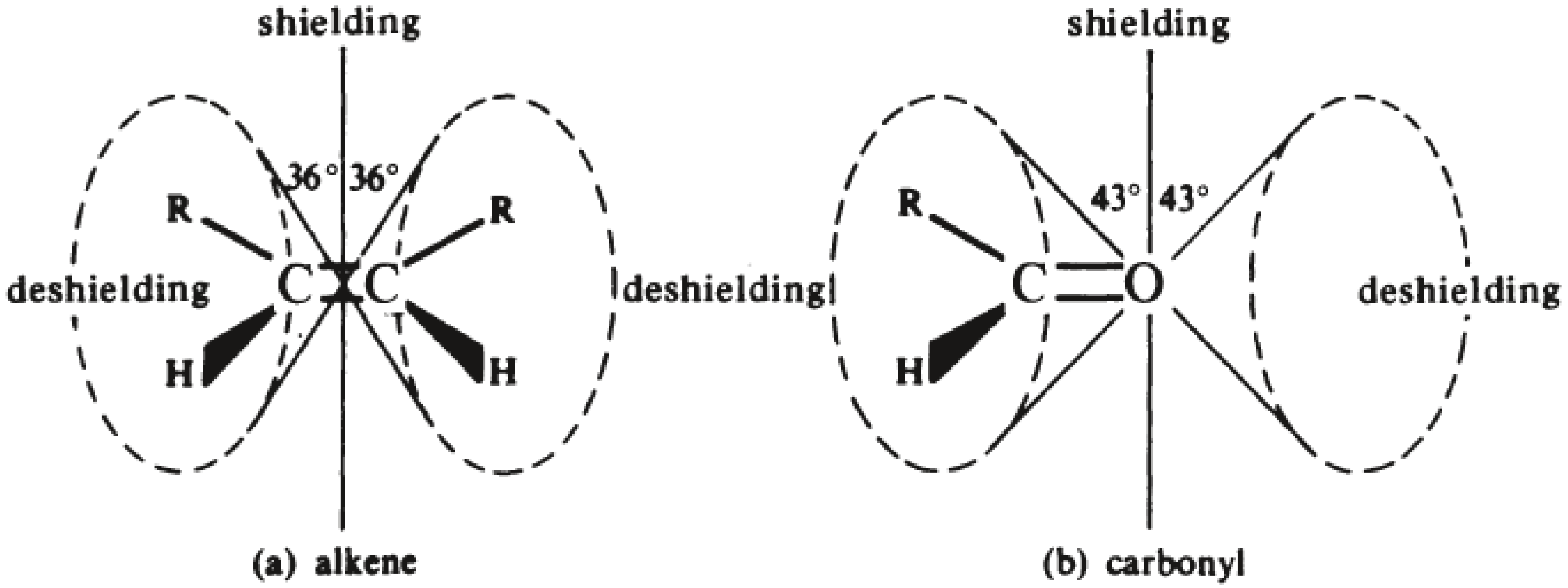


Figure 3.6 *Anisotropic shielding and deshielding around* (a) *alkene groups,* (b) *carbonyl groups. Protons inside the cones are deshielded (have higher* δ *values).*

Factors Influencing Chemical Shift

***Carbonyl compounds**. For the carbonyl group a similar situation arises,* although the best representation of shielding and deshielding zones is slightly different from the alkene pattern; see figure 3.6(b) Two cone shaped volumes, centered on the oxygen atom, lie parallel to the axis of the C=O bond; protons within these cones experience deshielding, so that aldehydic protons, and the formyl protons of formate esters, appear at high δ values . Protons held above or below these cones will come to resonance at lower δ values .

Alkynes.** Whereas alkene and aldehydic protons appear at high & values,* alkyne protons appear around δ 1.5-3.5. Electron circulation around the triple bond occurs in such a way that the protons experience a *diamagnetic shielding effect. Figure 3.7 shows how this arises, when the axis of the* alkyne group lies parallel to the direction of *Bo. The cylindrical sheath of* ***π electrons is induced to circulate around the axis, and the resultant annulus-shaped magnetic field acts in a direction that opposes *Bo in the* vicinity of the protons'. These protons experience lower values of field; therefore, acetylenic protons appear at low δ values in the spectrum .

Factors Influencing Chemical Shift

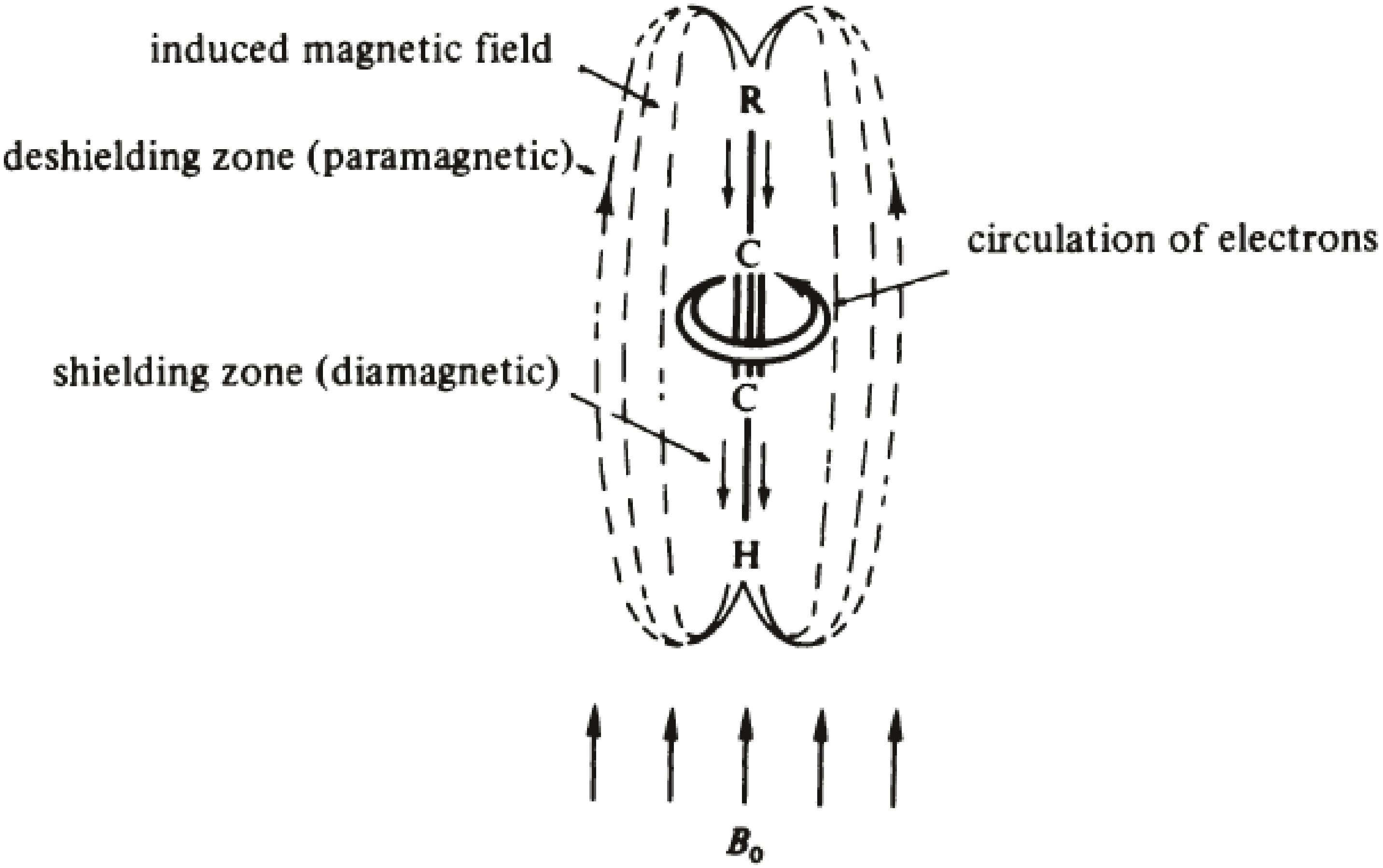


Figure 3.7 *Anisotropic shielding of a proton in an alkyne group.*

Factors Influencing Chemical Shift

Aromatic compounds. *In the molecule of benzene (and aromatic compounds* in general) ***π*** electrons are delocalized cyclically over the aromatic ring . These loops of electrons are induced to circulate in the presence of the applied field, *Bo, producing a substantial electric current, called the ring current. The magnetic field associated with this electric field has the* geometry and direction shown in figure 3.8 . (An analogy in the macr-oworld is a ring of copper wire moved into a magnetic field : electric current flows in the wire, and sets up a magnetic field similar in geometry and direction to that shown for benzene in figure 3.8.)

Factors Influencing Chemical Shift

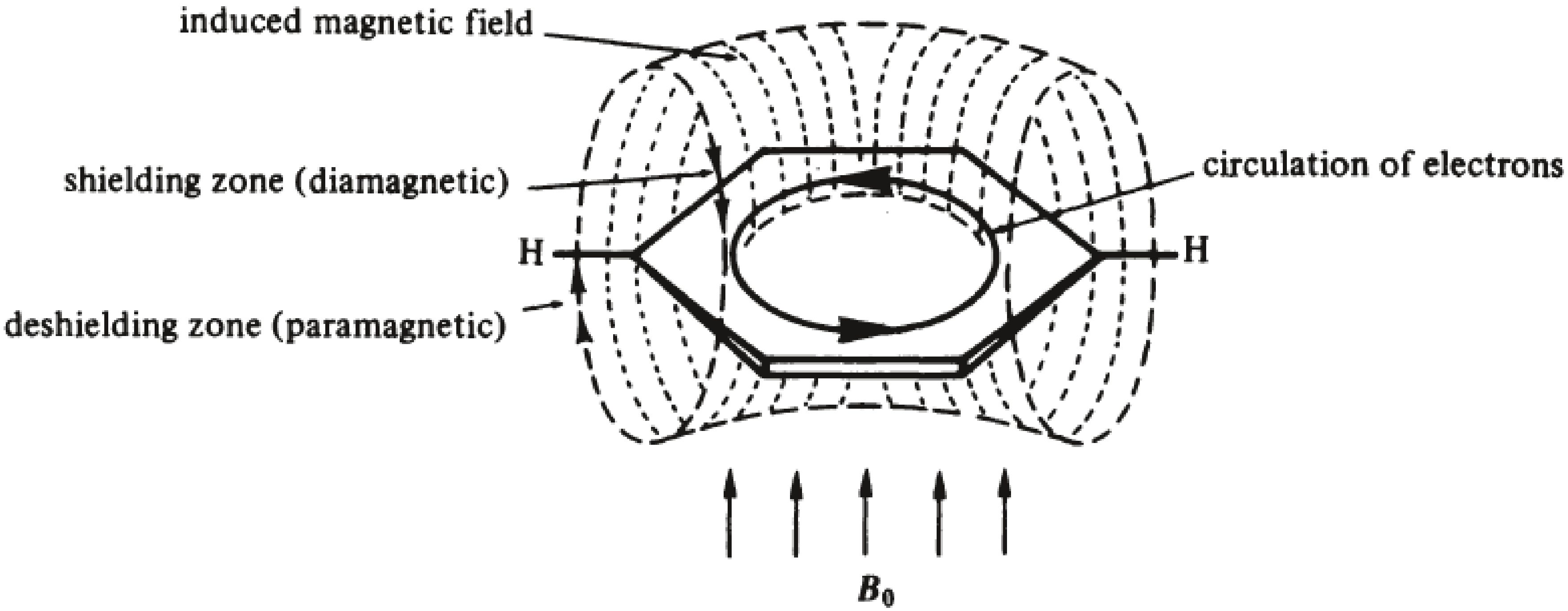


Figure 3.8 *Anisotropic shielding and deshielding associated with the aromatic ring current. The molecules are constantly tumbling, but a nett effect is still present. Protons attached to the ring have high δ values.*

Factors Influencing Chemical Shift

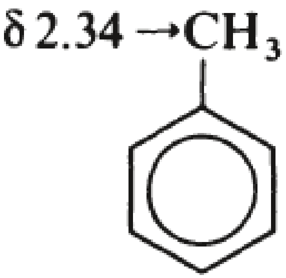
The induced field is diamagnetic (opposing *Bo) in the center of the ring ,* but the returning flux outside the ring is paramagnetic (augmenting *Bo).* Protons around the periphery of the ring experience an augmented magnetic field , and consequently come to resonance at higher δ) values than would otherwise be so. Protons held above or below the plane of the ring resonate at low δ) values. Two examples will illustrate the magnitude of these effects.

In the molecule of toluene the methyl protons resonate at δ 2.34, whereas a methyl group attached to an acyclic conjugated alkene appears at δ 1.95. This is some measure of the greater deshielding influence of the ring current in aromatic compounds (cyclically delocalized π electrons) compared with the deshielding of conjugated alkene groups (having no cyclic delocalization). Indeed, so important is this observation that NMR has become one of the principal criteria used in deciding whether an organic compound has substantial aromatic character (at least in so far as aromatic character relates to cyclic delocalization of *(4n + 2)*π *electrons).*

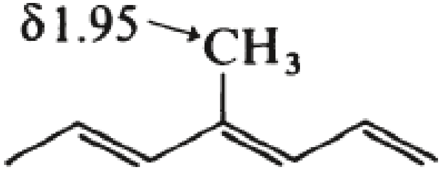
Factors Influencing Chemical Shift

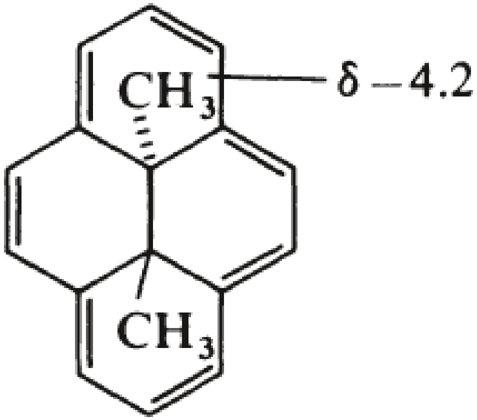
The method has been applied successfully to heterocyclic systems and to the annulenes; for example, [18]annulene sustains a ring current , so that the twelve peripheral protons are deshielded and the six internal protons shielded. The outer protons appear at δ 8 8.9, while the inner protons are at a *lower frequency than TMS at* δ *- 1.8. (This is true only around 20°C;* molecular motion makes the spectrum change with variable temperature.) One of the most dramatic observations in NMR work on aromatic systems involves the dimethyl derivative of pyrene (I), in which the methyl groups appear at δ -4.2, *lower in frequency than TMS. This shows that the* cyclic ***π*** electron system around the periphery of the molecule sustains a substantial ring current, and therefore indicates aromatic character in a nonbenzenoid ring system. The methyl groups are deep in the shielding zone of this ring current, and it is for this reason that they appear at such an extraordinary δ value .

Factors Influencing Chemical Shift



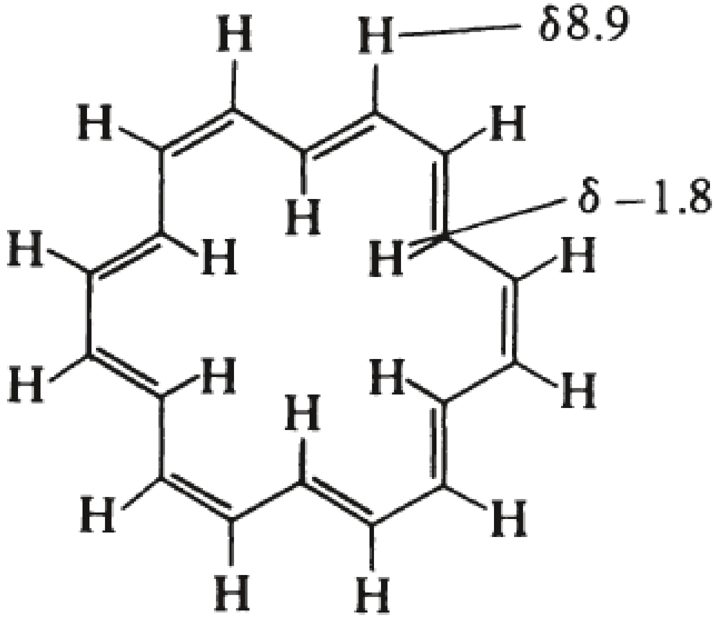
toluene



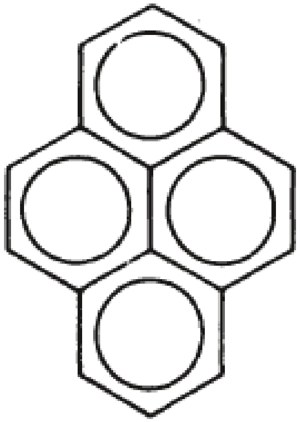


I

dihydrodimethylpyrene



[18]annulene



pyrene

Factors Influencing Chemical Shift

Alkanes. *The equatorial protons in cyclohexane rings come to resonance* about 0.5 ppm higher than axial protons, and this is attributed to anisotropic deshielding by the σ electrons in the **β**γ bonds, as shown in figure 3.9. The effect is small compared with the anisotropic influence of circulating ***π*** electrons, but is readily observed in rigid systems and also in mobile systems at low temperature. Simple electronegative (inductive) effects operate only along a chain of atoms, the effect weakening with distance, but magnetic anisotropy operates through space irrespective of whether the influenced group is directly joined to the anisotropic group. For this reason the stereochemistry of molecules must be carefully studied to predict whether magnetically anisotropic groups are likely to have an influence on the chemical shift of apparently distant protons.

Factors Influencing Chemical Shift

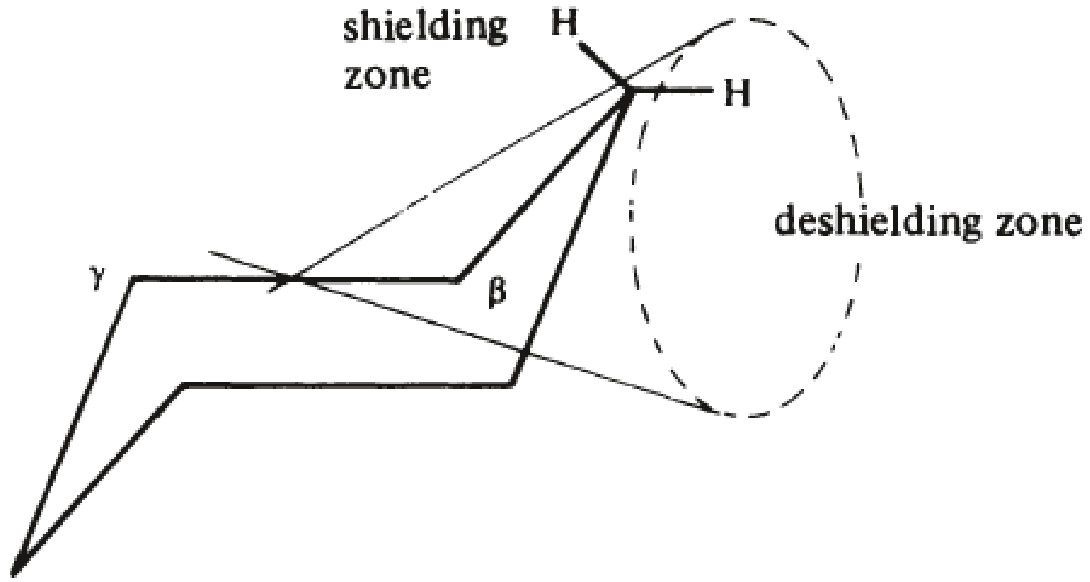


Figure 3.9 *Anisotropic shielding and deshielding in cyclohexanes.*

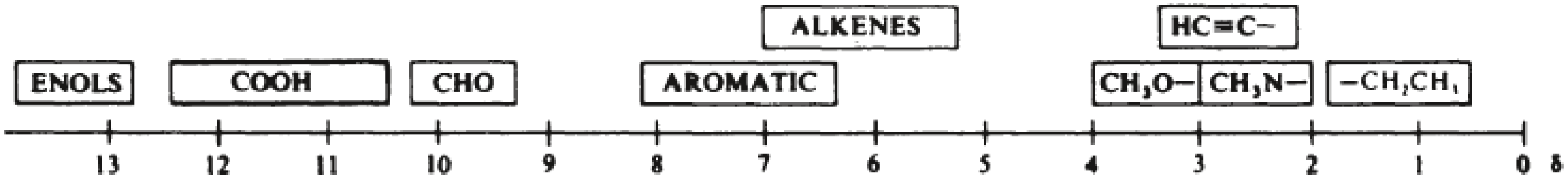
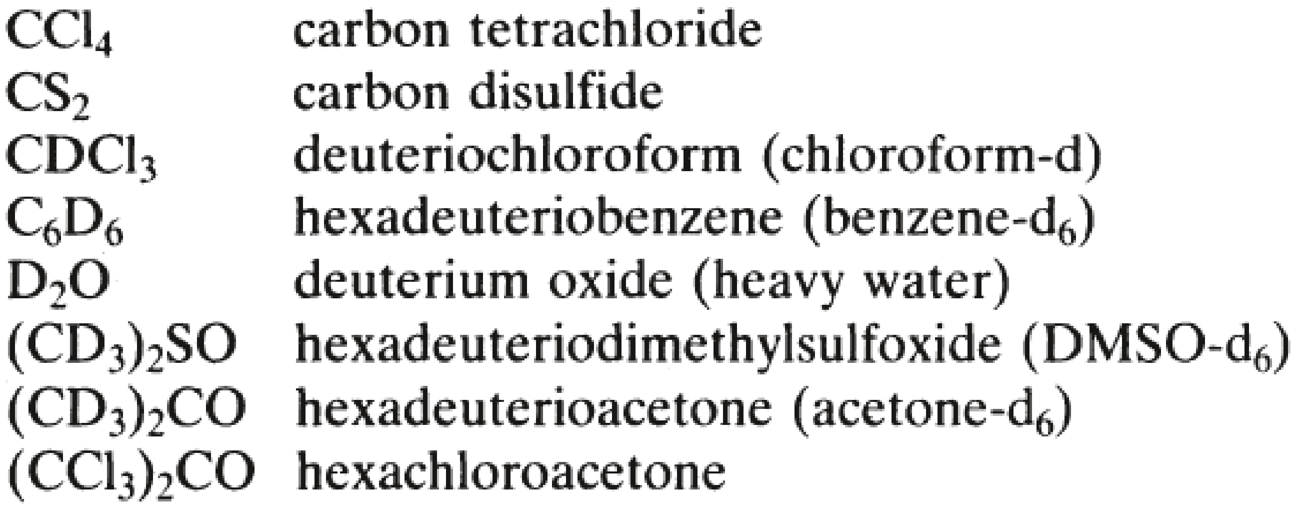


Figure 3.10 *Approximate chemical shift positions for protons in organic molecules.*

SOLVENTS USED IN NMR



CCl_4	carbon tetrachloride
CS_2	carbon disulfide
$CDCl_3$	deuteriochloroform (chloroform-d)
C_6D_6	hexadeuteriobenzene (benzene-d_6)
D_2O	deuterium oxide (heavy water)
$(CD_3)_2SO$	hexadeuteriodimethylsulfoxide (DMSO-d_6)
$(CD_3)_2CO$	hexadeuterioacetone (acetone-d_6)
$(CCl_3)_2CO$	hexachloroacetone

For deuteriated solvents the isotopic purity should ideally be as high as possible, but since greater isotopic purity means greater cost, most users compromise their ideals. Isotopic purity approaching 100 per cent can often be obtained, but, for example, a small CHCl3 peak at δ 7.3 in 99 percent CDCl3 will cause no difficulty or ambiguity unless accurate integrals for aromatic protons (also around δ 7.3) are demanded.

Spin-Spin Coupling

The 1H NMR spectrum of *trans-cinnamic acid is reproduced in figure 3.11.*

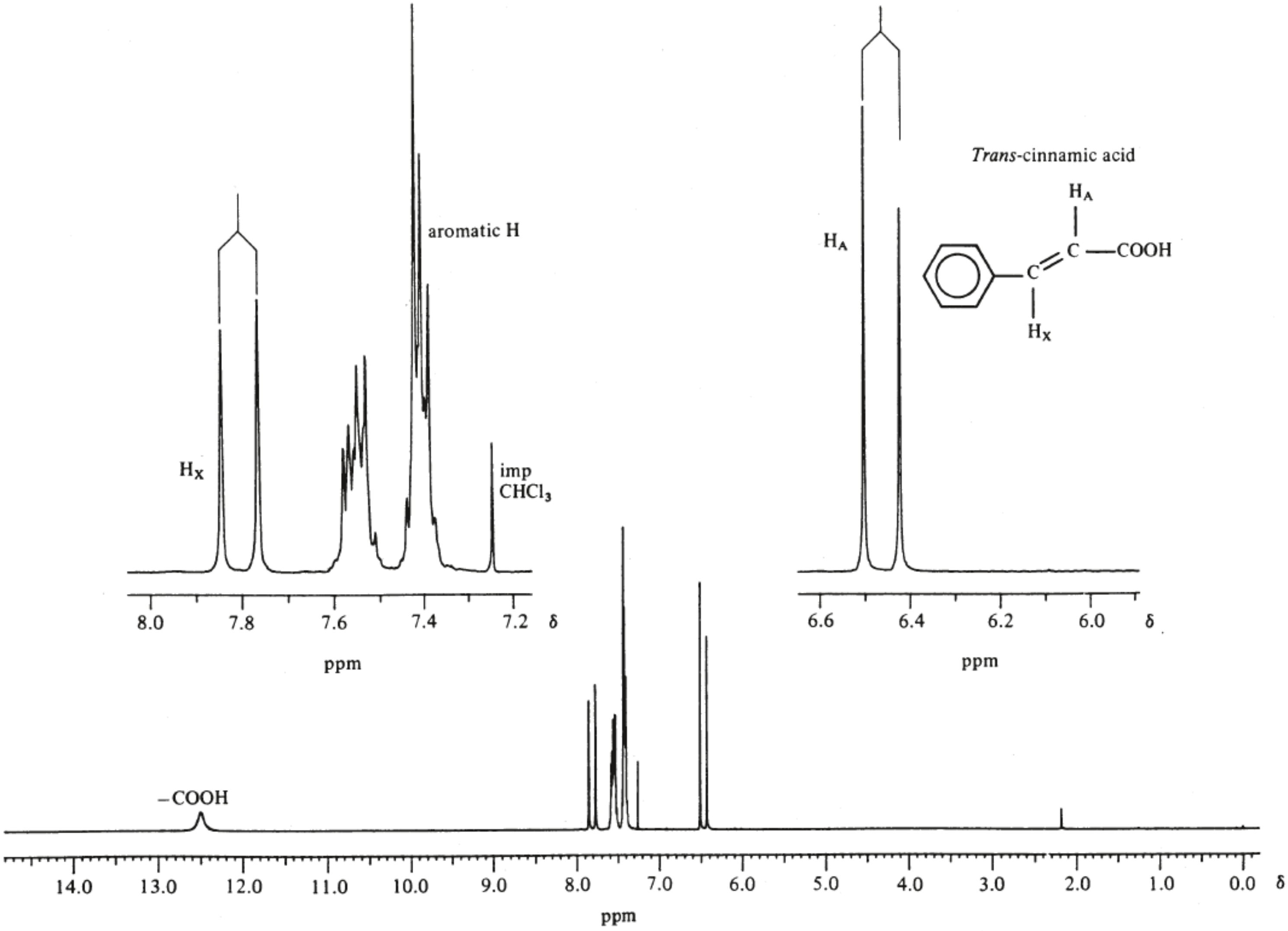


Figure 3.11 ^{1}H *NMR spectrum of trans-cinnamic acid (200* MHz *in* $CDCl_3$*). Lower trace, full spectrum; upper traces, expanded* × *6.*

Spin-Spin Coupling

The aromatic protons , five in number, give rise to the peaks at δ 7.4 and δ 7.55, and the carboxyl proton is at δ 12.5. Proton HA appears as *two lines on the spectrum (centered on* δ *6.45), and* proton Hx appears as *two lines (centered on* δ *7.8). We say that each signal* is split into a doublet. *Note that the separation between the two HA lines is* the same as the separation between the two HX lines.

Spectrum of 1,1,2-trichloroetha ne (figure 3.12). The signal from proton HA appear s as a *triplet, while that from protons HX is a doublet.*

Spin-Spin Coupling

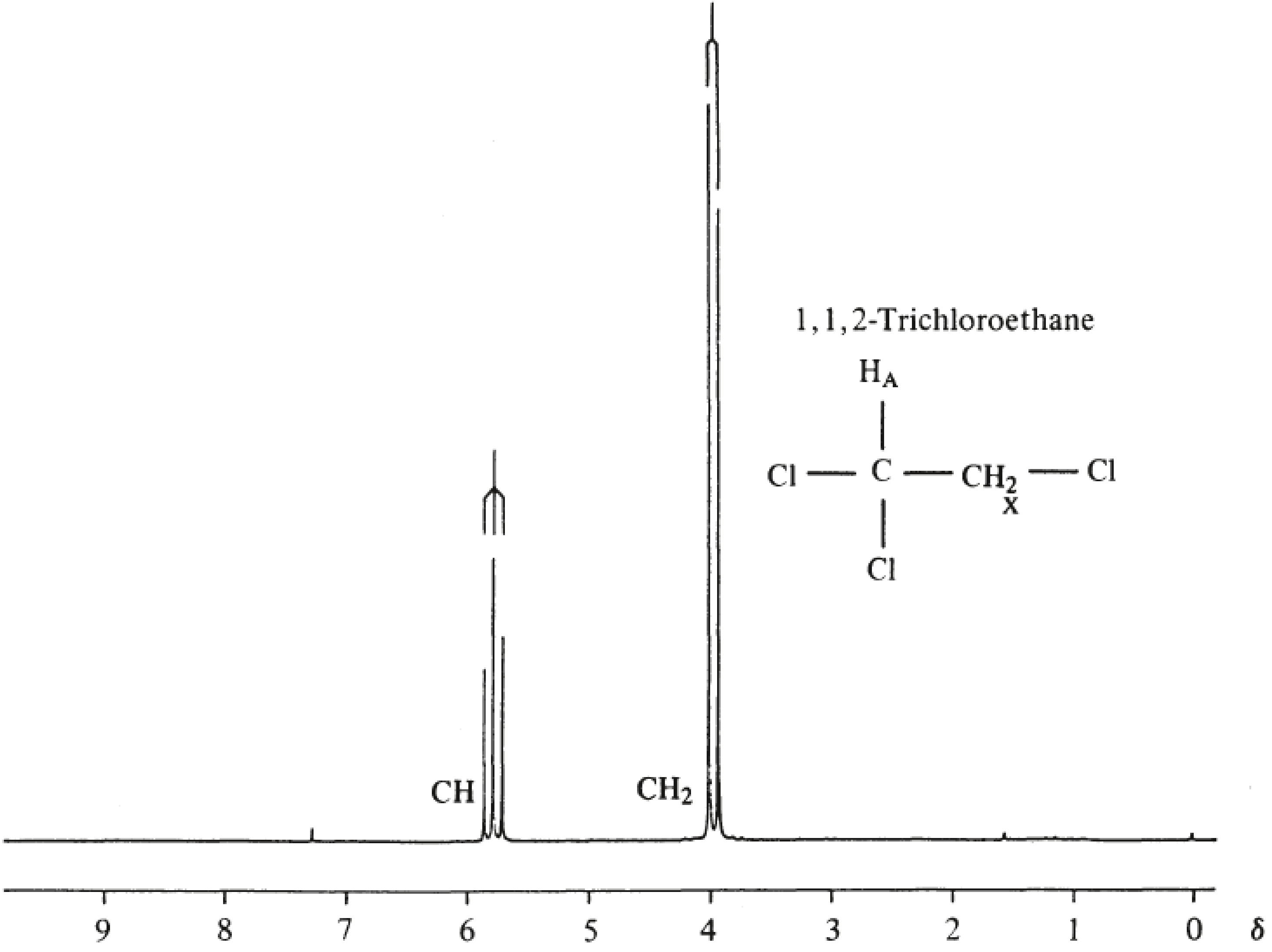


Figure 3.12 ^{1}H *NMR spectrum of 1,1,2-trichloroethane.* (80 MHz *in* $CDCl_3$.)

Spin-Spin Coupling

The number of lines (multiplicity) observed in the NMR signal for a group of protons is not related to the number ofprotons in that group; the multiplicity of lines is related to the number of protons in neighboring groups.

For example, protons HX in figure 3.12 have only *one neighboring* proton, and HX appears as a two-line signal (doublet); proton HA has *two* neighbors and the signal is split into three lines (triplet).

(n + 1) rule. *The simple rule is: to find the multiplicity of the signal from a group of protons, count the number of neighbors (n) and add 1.*

Splitting of the spectral lines arises because of a *coupling interaction* between neighbor protons, and is related to the number of possible spin orientations that these neighbors can adopt. The phenomenon is called either *spin-spin splitting or spin-spin coupling.*

Equivalent Nuclei

A group of nuclei are **chemically equivalent if they are related by a symmetry operation** of the molecule and have the same chemical shifts. Chemically equivalent nuclei are nuclei that would be regarded as ‘equivalent’ according to ordinary chemical criteria. Nuclei are **magnetically equivalent if, as well as being chemically equivalent,** they also have identical spin–spin interactions with any other magnetic nuclei in the molecule.

The difference between chemical and magnetic equivalence is illustrated by CH2F2 and H2C*=CF2. In each of these molecules the protons are chemically equivalent: they* are related by symmetry and undergo the same chemical reactions. However, although the protons in CH2F2 are magnetically equivalent, those in CH2*=CF2 are not. One*
proton in the latter has a *cis spin-coupling interaction with a given F nucleus whereas* the other proton has a *trans interaction with it. In constrast, in CH2F2 both protons* are connected to a given F nucleus by identical bonds, so there is no distinction between them. Strictly speaking, the CH3 protons in ethanol (and other compounds) are

Equivalent Nuclei

magnetically inequivalent on account of their different interactions with the CH2 protons in the next group. However, they are in practice made magnetically equivalent by the rapid rotation of the CH3 group, which averages out any differences. Magnetically, inequivalent species can give very complicated spectra (for instance, the proton and 19F spectra of H2C*=CF2 each consist of 12 lines), and we shall not consider them* further.

Theory of Spin-Spin Coupling

The diagram in figure 3.13 represents two vicinal protons similar to the alkene protons in cinnamic acid, HA and Hx. These protons, having different magnetic environments, come to resonance at different positions in the NMR spectrum; they do not give rise to single peaks (singlets) but doublets. The separation between the lines of each doublet is equal : this spacing is called the *coupling constant, J.*

Why is the signal for proton A split into a doublet? A simplistic explanation is that the resonance position for A depends on its total magnetic environment; part of its magnetic environment is the nearby proton X, which is itself magnetic, and proton X can have its nuclear magnet either *aligned with proton A or opposed to proton A. Thus, proton* A can either *increase the net magnetic field experienced by A (X aligned)* or *decrease it (X opposed); in fact, it does both. The two spin orientations* of X create two different magnetic fields around proton A: in roughly half of the molecules the spin orientation of X creates a shielding field around proton A, and in the other half a deshielding field. Therefore, proton A comes to resonance, not once , but twice, and proton A gives rise to a doublet.

Theory of Spin-Spin Coupling

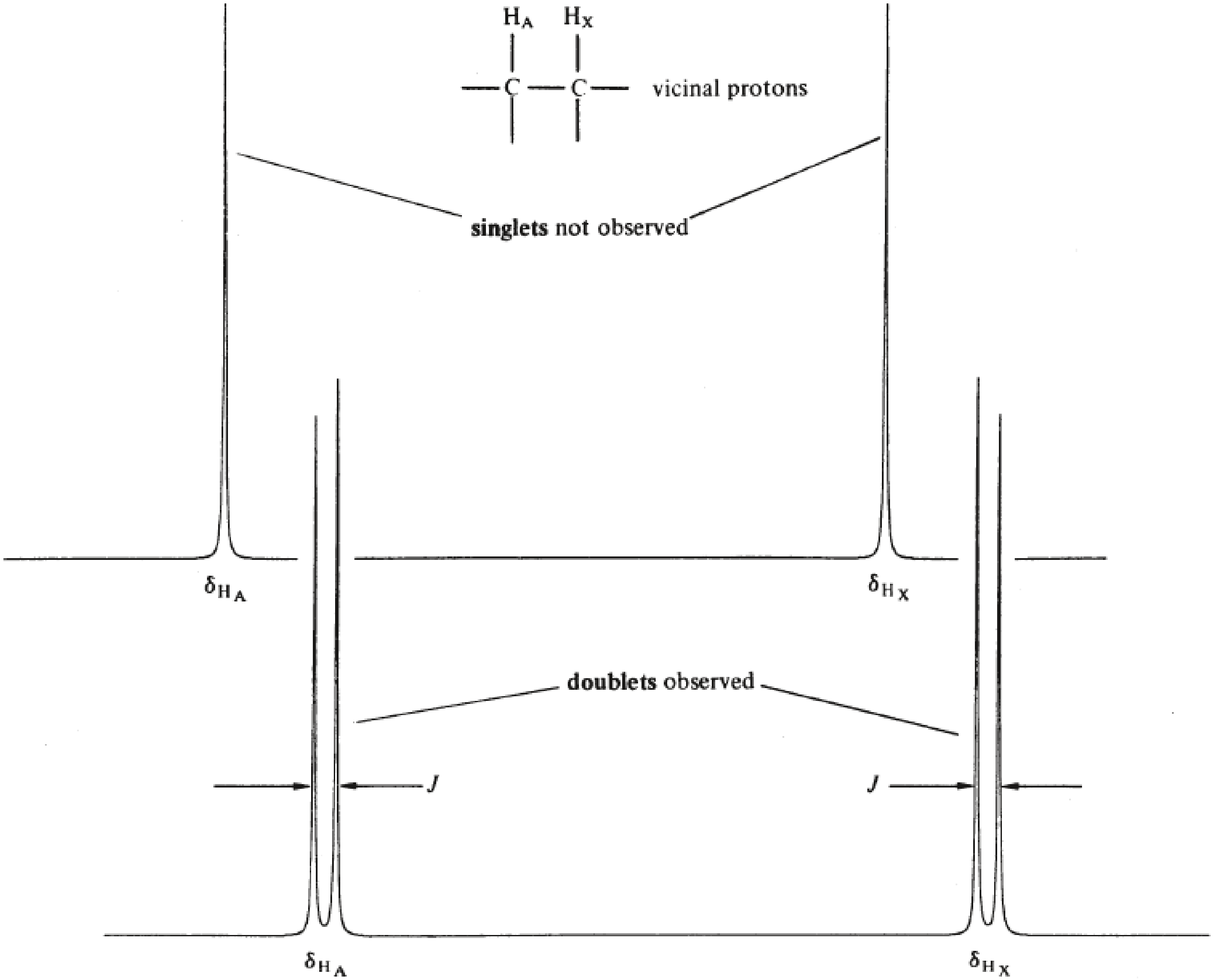


Figure 3.13 *Splitting in the signals of two vicinal protons.*

Theory of Spin-Spin Coupling

Similarly, proton A is a magnet having two spin orientations with respect to X, and A creates two magnetic fields around X. Proton X comes to resonance twice in the NMR spectrum. This mutual magnetic influence between protons A and X is not transmitted through space, but via the electrons in the intervening bonds . The nuclear spin of A couples with the electron spin of the C-HA bonding electrons; these, in turn, couple with the C-C bonding electrons and then with the C-Hx bonding electrons. The coupling is eventually transmitted to the spin of the Hx nucleus. This *electron-coupled spin* interaction operates strongly through one bond or two bonds, less strongly through three bonds, and, except in unusual cases, rather weakly through four or more bonds .

Theory of Spin-Spin Coupling

We can represent the possible spin orientations of coupling protons as in figure 3.14. Proton A can 'see' proton X as aligned (parallel ↑) or opposed antiparallel ↓): these two spin orientations correspond effectively to two different magnetic fields. Therefore, proton A comes to resonance twice. The same argument explains why proton X appears as a doublet.

The A and X protons of cinnamic acid give rise to this characteristic pair of doublets, caused by two protons undergoing spin coupling: such a spectrum is called an AX spectrum. Since the probability of the two spin orientations of A and X arising is equal in molecules throughout the sample, the two lines in each doublet are of equal intensity. Figure 3.15 represents the coupling that arises in the triplet signal in the NMR spectrum of 1,1,2-trichloroethane.

Theory of Spin-Spin Coupling

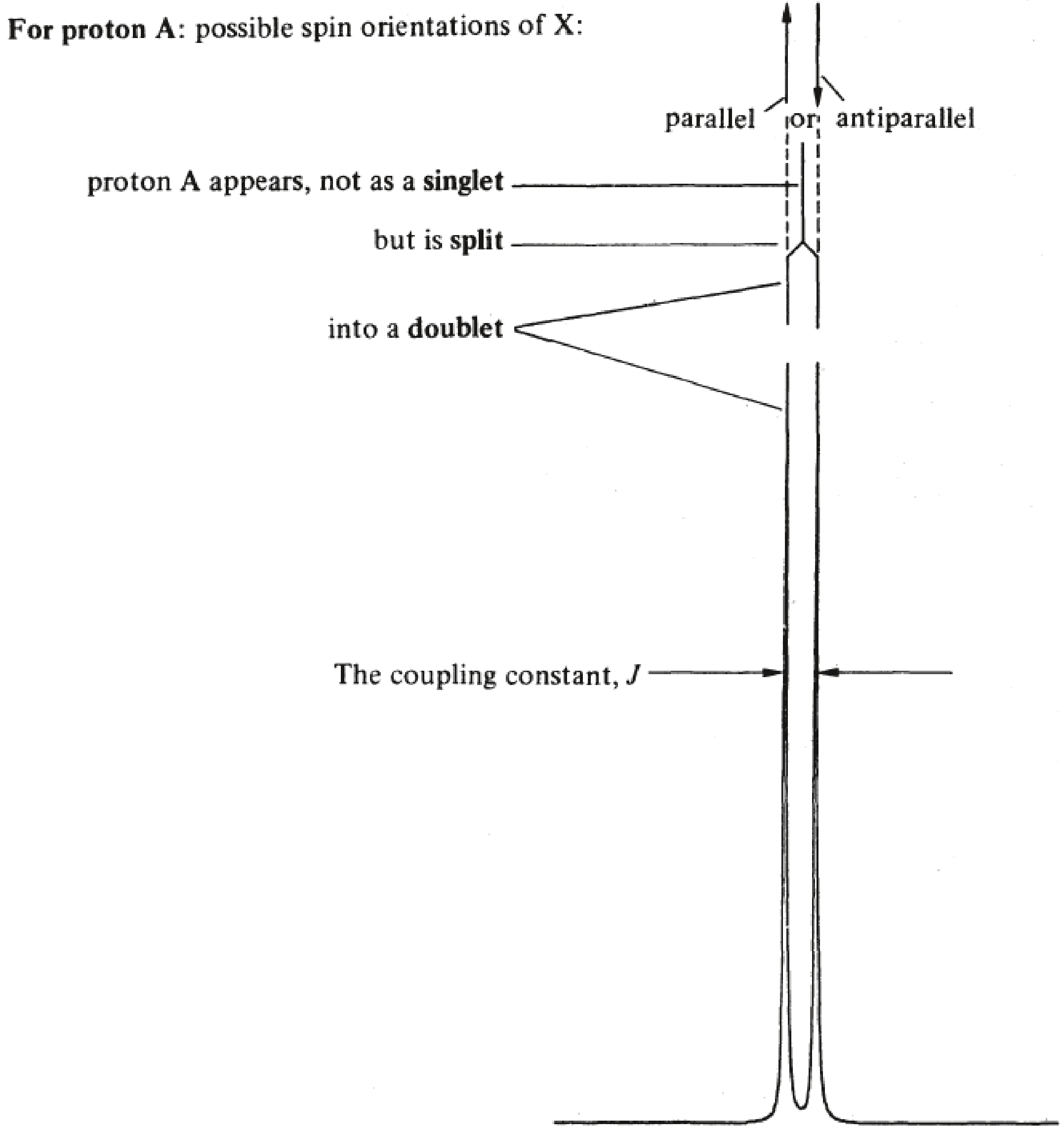


Figure 3.14 *Simulation of spin coupling between a proton A and one neighboring proton X.*

Theory of Spin-Spin Coupling

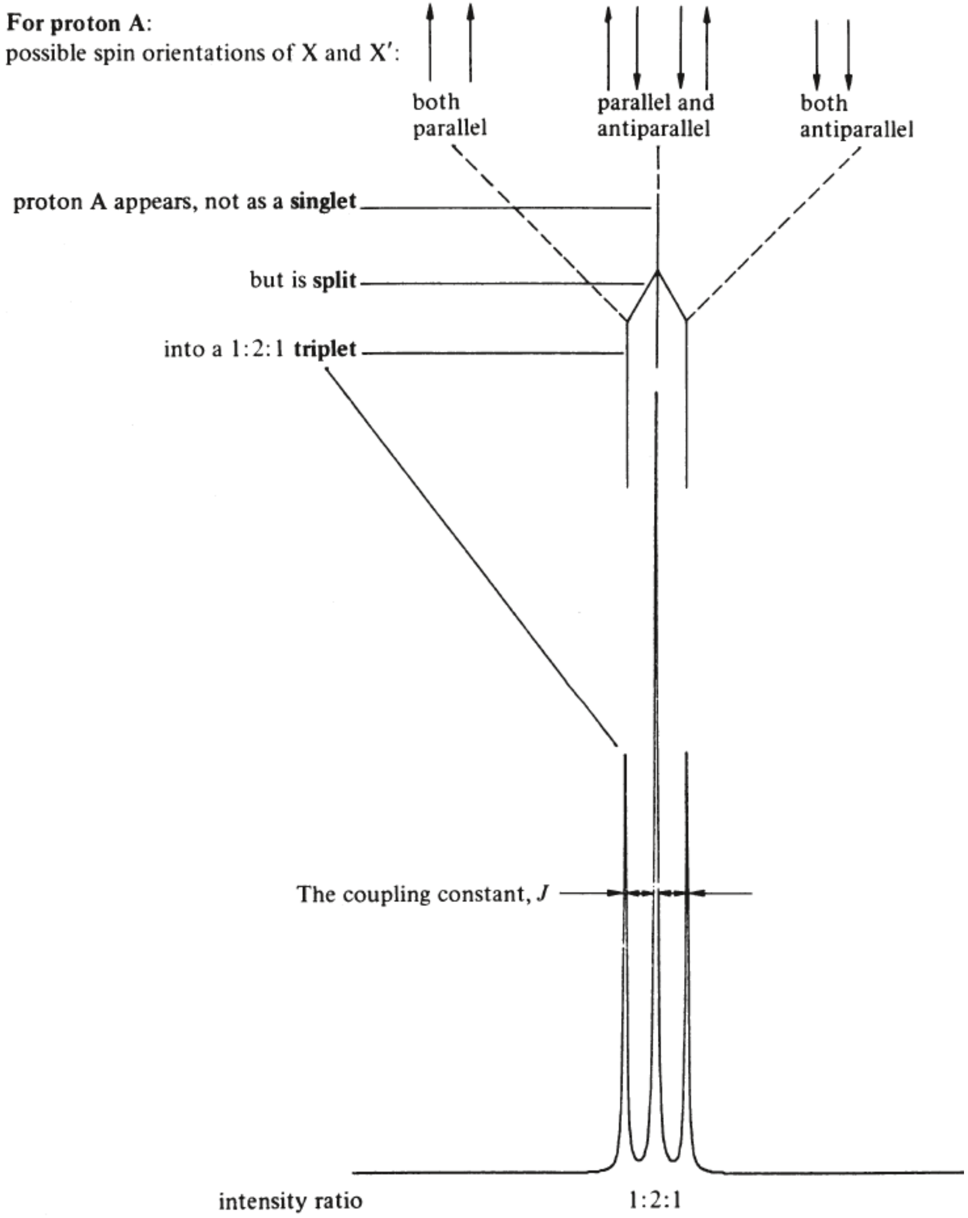


Figure 3.15 *Simulation of spin coupling between a proton* A *and two neighbor protons* X *and* X′.

Theory of Spin-Spin Coupling

When proton A 'sees ' the two neighboring protons X and X' , A can see *three different possible combinations of spin:*

(1) the nuclear spins of X and X' can both be parallel to A (↑ ↑);

(2) both can be antiparallel to A(↓ ↓)

(3) one can be parallel and the other antiparallel, and this can arise in two ways-X parallel with X' antiparallel (↑ ↓) or X antiparallel with X' parallel (↓ ↑). Three distinct energy situations, (1), (2) and (3), are created, and therefore proton A gives rise to a triplet. The probability of the first two energy states arising is equal, but since the third state can arise in two different ways, it is twice as likely to arise; the intensity of the signal associated with this state is twice that of the lines associated with the first two states, and we see in the spectrum of 1,1,2-trichloroethane that the relative line intensities in the triplet are 1:2:1.

Magnitude of Coupling-Coupling Constant J

The coupling constant , J, is a measure of the interaction between nuclei, and we have stated earlier that the interaction is transmitted through the intervening electrons: for two nuclei, there are four energy levels involved in the NMR transitions, and their relative positions are governed by the internuclear spin coupling as shown in figure 3.16. When there is zero coupling between A and X, both X transitions are equal, as are both A transitions: each nucleus gives rise to one line absorption. When coupling takes place, we can suppose that the energy levels are altered by ±E, the energy of interaction-then the transitions no longer remain equal: the X transition splits into an X' line (transition energy *X + 2E) and an X“ line (X – 2E). The A transition is likewise split into A’ (A + 2E) and A" (A – 2E)* . The spacings between *X' and X" and A' and* A" are equal, and have magnitude 4E: the coupling constant, *J, is therefore* equal to 4E, and is a measure of nuclear interaction, *which is wholly independent of any external magnetic field. The units of J are energy units,* usually Hz; and it is easy to see that *J can have sign as well as magnitude.* The sign of *J is hardly ever of importance to organic*

Magnitude of Coupling-Coupling Constant J

chemical applications of NMR; in practical terms, it is simpler to interpret signal multiplicity in more extensive coupling systems by utilizing the *(n + 1) rule and the* concept of *x nuclei 'seeing' y neighboring nuclei, etc.*

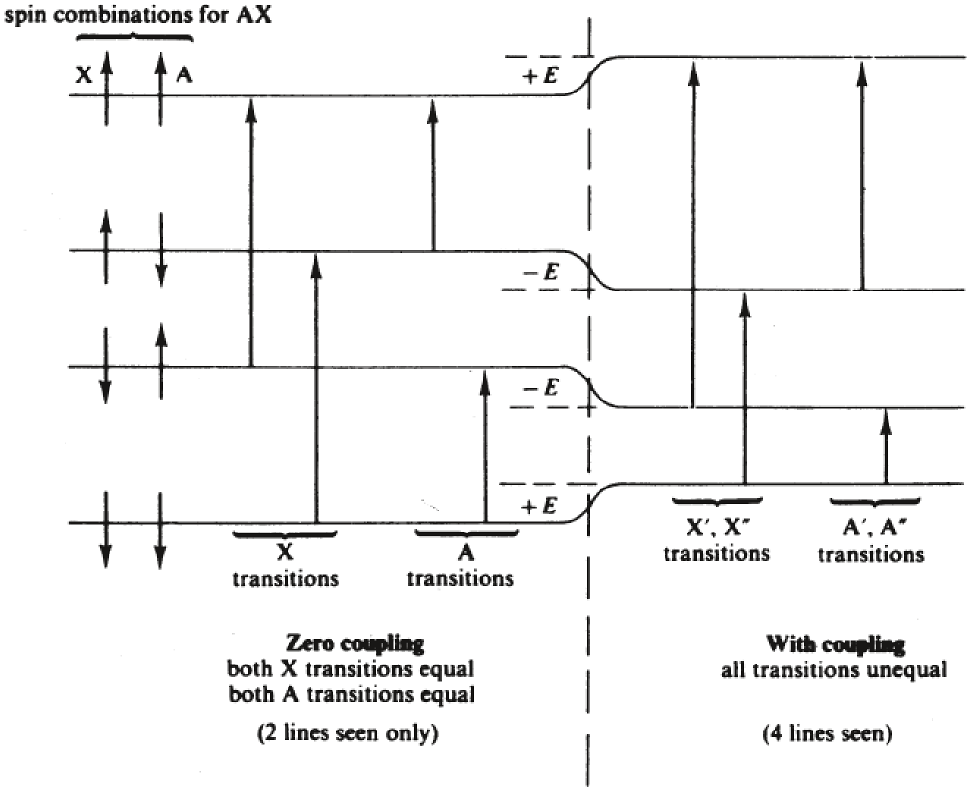
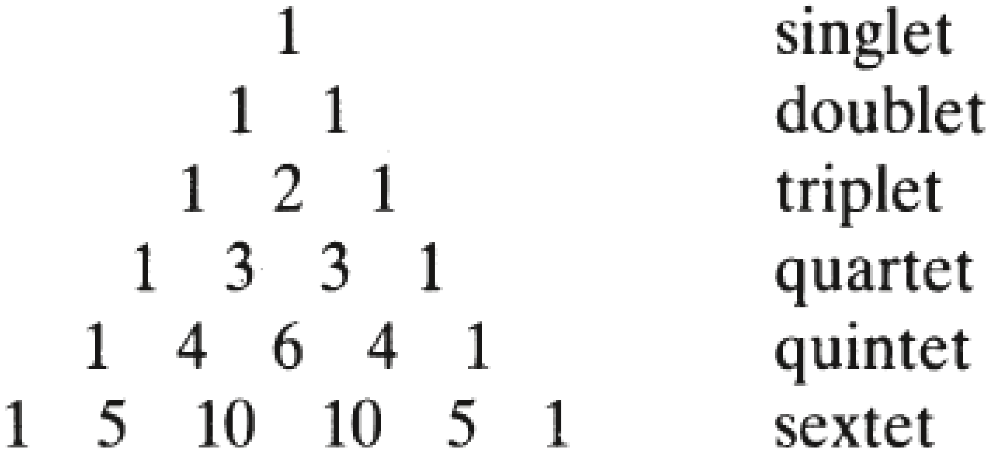


Figure 3.16 *Spin coupling as the energy of nuclear interaction. Only those transitions are allowed which involve one (and only one) change in nuclear spin; thus ↓ ↑→↑ ↑ is allowed, but ↓ ↑→↑ ↓ is forbidden. Example shown is for J positive (antiparallel spins of lower E): for negative J the ±E changes in energy levels are reversed (parallel spins of lower E).*

Spin-Spin Slitting of Higher Systems and Pascal’s Triangle

One can go further and predict the theoretical line intensities for quintets, sextets, etc ., and find that the ratios are the same as the coefficients in the binomial expansion. Pascal's famous triangle serves to remind:



1	singlet
1 1	doublet
1 2 1	triplet
1 3 3 1	quartet
1 4 6 4 1	quintet
1 5 10 10 5 1	sextet

The outer lines in substantial multiplets are of such low intensity that they may be all but unobservable , unless that part of the spectrum is rerun at increased intensity.