

EMT 509: STRUCTURAL ELUCIDATION OF ORGANIC POLLUTANTS (3 UNITS)

Lecturers: Professor O. Bamgbose & Professor T.A. Arowolo

SYNOPSIS

Structural elucidation of organic pollutant, basic instrumentation and techniques. Application of *uv*, *ir*, *nmr* and *ms* in chemical analysis and structural elucidation of organic pollutants.

LECTURE CONTENT

ELECTROMAGNETIC SPECTRUM

The electromagnetic spectrum covers a wide range of wavelength. The spectrum consists of the following x-ray, ultraviolet, visible, infra-red, microwaves and radio-waves as shown in the table below.

These waves are usually described by 3 methods;

1. In terms of
- 2.
- 3.
4. wavelength λ which is the distance between the peaks of waves (in cm)
5. In terms of wave number this is the number of waves within a distance of 1cm and is abbreviated as V , measured in cm^{-1}
6. In terms of frequency this is the number of waves per second and the unit is referred to as hertz (Hz), A relationship exist between the 3 representations such that

$$1/\lambda = V = \nu/c$$

Units - \AA angstrom unit $10^{-10}\text{m} = 10^{-8}\text{cm}$
 $1\text{nm} = 10\text{\AA} = 10^{-7}\text{cm} = 10^{-9}\text{m}$
 $1\mu\text{m} = 10^4\text{\AA} = 10^{-4}\text{cm} = 10^{-6}\text{m}$
 $C = 3 \times 10^8 \text{ m/s} = 3 \times 10^{10} \text{ cm/s}$

Calculate for sodium D-line with a wavelength of 589nm, its wave number and frequency

$$V = 1/\lambda = 1/589 \times 10^{-7}\text{cm} \quad V = 16977.9\text{cm}^{-1}$$

$$\lambda = \text{wavelength} = 589\text{nm}$$

Taking a look at the diagram above we observe that the region to which the human eye is visible is very small and that radiation such as x-ray or radio waves differ from visible light only in terms of frequency and hence energy. Methods used in determining the structures of organic compounds include UV, IR, NMR and mass spectroscopy. All these four methods in order to be used for successful determination of organic compounds, electromagnetic radiation must be applied to the organic compound and as such energy transition must occur.

Spec method	Energy transition
UV	Electronic
IR	Vibration
NMR	Nuclear spin
Mass spec.	Low energy transition but fragmentation

INFRA-RED SPECTROSCOPY

In the IR region, we have interval of 4000 cm^{-1} to 500 cm^{-1} Initial unit of wavelength is cm^{-1} and this unit is also expressed as wave number but however in recent times when wavelength is used, the unit is referred to as μ and as such the corresponding region of IR is 2.5μ to 1.5μ and so we have far and near IR regions ($1/\mu \times 10^4$) stands for conversion from μ to cm^{-1}

Instrumentation – the instrument is the IR spectrometer, it consist basically of

1. The source – this emit the IR radiation and is usually in the form of Nerst filament or Globar. Both are heated at high temperature of about 1000 to 1800°C . The radiation produced is split in two so that one goes through the sample and the other beam passes through the monochromator
2. Detector – This detects any radiation by measuring its light energy in the form of radiant energy. A thermocouple detector is usually used. The radiant energy from the thermocouple is further amplified. The amplifier is coupled to an alternator drive; the alternator drive gives a null effect by balancing the wave which doesn't pass through the sample as well as that which comes out of the sample.

BASIC SCHEMATIC DIAGRAM OF IR SPECTROMETER

In IR the various functional groups and bonds within, an organic compound have specific wave length at which it absorbs. The whole stretch of IR absorption can be divided into four.

- | | | | | |
|-----|-----------------------|---|----------------------|---|
| (a) | 4000 cm ⁻¹ | - | 2300cm ⁻¹ | OH, NH, CH |
| (b) | 2300cm ⁻¹ | - | 1980cm ⁻¹ | C ≡ C, C ≡ N, |
| (c) | 1900cm ⁻¹ | - | 1450cm ⁻¹ | C = C, C = O C = N N = O |
| (d) | 1450cm ⁻¹ | - | 500cm ⁻¹ | Stretching, bending and combination bands.
(also known as finger print region) |

CHARACTERISTICS OF GROUP FREQUENCY OF ORGANIC MOLECULES – This actually indicate at what point these molecules absorb.

Alkanes

C

CH₃ CH₂ CH₂

C – H Vibration – This occur as stretching and bending vibration.

Stretching:- A stretching vibration can be either symmetrical or asymmetrical the C – H symmetrical stretching vibration occurs at 2872cm⁻¹



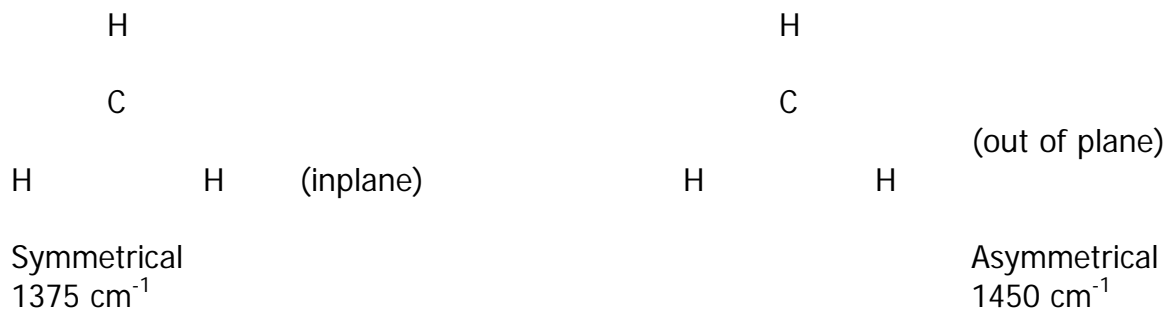
These two vibrational appear in all cases of hydrocarbons containing methyl group

CH₂ (methylene)

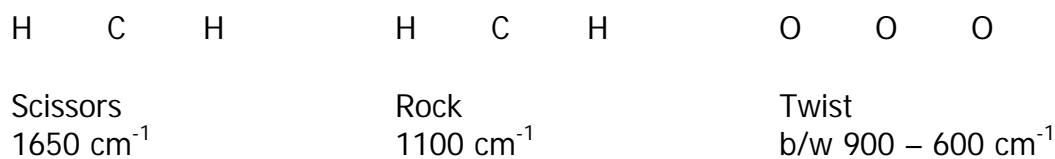


CH absorptions are usually at 2890 cm⁻¹ and usually very weak and as such of no use in identification purposes.

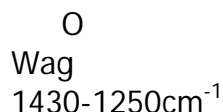
Bending (CH₃)



Bending vibrations are normally very prominent. For CH₂, the bending vibrations are of several types and are not prominent as stretching vibration



O O + here indicates that the vibration is perpendicular to the plane



Alkenes C = C C = C CH₂ CH

- (a) The CH stretching vibration is very weak and observed around 3000cm⁻¹
- (b) A C = C stretching vibration is the most important spectra in alkenes. C = Cstr. 1660 – 1640cm⁻¹ which is either strong or weak

It is usually weak for symmetrical compound e.g Ar – C = C – Ar having identical substituents at both sides of carbon atoms.

It is usually strong if the substituents are different i.e asymmetrical and this absorption is diagnostic of double bonds. This absorption is also the type found in aromatic compounds or in benzenoids and also very strong.

Bending vibration for Alkene – there are two types of bending vibration for alkenes

- (a) In plane between 1430cm⁻¹-1000cm⁻¹
- (b) Out of plane 1000-650cm⁻¹ and these are usually very strong.

For the C = C bond there is no bending vibration however the bending vibration for benzene ring is very important and is used to determine whether a compound is aromatic or not and found in the region btw 850- 650 cm^{-1}

No of adjacent H	ν	Types of substituents
6	675 cm^{-1}	None
5	721, 694	one
4	742	Di
3	767, 709	Tri
2	804	Tetra
1	810	Penta

The table above represents the CH bending in aromatic compounds which are usually strong and prominent and are usually useful in determining substituent around benzene ring.

ALCOHOLS AND PHENOLS (R –OH and Ar – OH)

The absorptions recognized are 3 types

1. OH stretching at $3700\text{cm}^{-1} - 3600\text{cm}^{-1}$. The absorption is very strong and diagnostic and it is only the free OH that absorbs at this wavelength
2. OH bending at $1470\text{cm}^{-1} - 1300\text{cm}^{-1}$. These are usually broad absorption and not particularly useful
3. C-O stretching. This is very important and its absorption is around $1260\text{cm}^{-1} - 1000\text{cm}^{-1}$ the OH stretching vibration sometimes vary due to the formation of hydrogen bonding and as such we have absorption range of 3400cm^{-1}

CARBONYL

For Carbonyl there are four classes

Aldehyde RCHO, ketone RCOR, carboxylic acid RCOOH and ethers

The strong absorption is due to double bond C = O stretch and it is found in the region of $1870 - 1540\text{cm}^{-1}$, no other group of compound absorb in this region

Around 1150cm^{-1} is observed for C-O(Stretch) and it is usually very strong

Aldehyde

Straight chain – $1740 - 1720\text{cm}^{-1}$

Aryl - $1710 - 1615\text{cm}^{-1}$

Ketone

Straight chain $1725 - 1705\text{cm}^{-1}$

Aryl – $1700 - 1680\text{cm}^{-1}$

Acid anhydride

RCOX X = (Cl) $1815 - 1790\text{cm}^{-1}$

$\equiv \text{C} - \text{H}$ str at 3320cm^{-1}

Fig 2.3

benzaldehyde

$\text{C} = \text{O}$ str 1700cm^{-1} $\text{C} - \text{H}$ str 2800cm^{-1}

Fig 2.4

$\text{C} = \text{O}$ str 1700cm^{-1}

CH str is absent in acetophenone

Fig 2.6

The dotted line insert around 3500cm^{-1} was recorded in dilute solution (about 1 percent in CCl_4) at low conc. a sharp band appears at 3650cm^{-1} in addition to the broad band at 3350cm^{-1} .

The sharp band is O-H str is free alcohol molecules, the broad band is O-H str in hydrogen bonded alcohol molecules. Alcohols and phenols in condensed phases are strongly hydrogen bonded, usually in the form of a dynamic polymeric association dimers, trimers and tetramers also exist and this leads to a wide envelope of absorptions and hence to broadening of the absorption band. In dilute solution, in inert soln (or in the vapor phase) the proportion of free molecules increases and these give rise to the 3650cm^{-1} band.

Fig 2.7

Broad band at $2500 - 3500\text{cm}^{-1}$ is hydrogen bonded O - H str O - H str bend for the carboxylic acid dimer structure. In condensed phases, all carboxylic acids exist in this stable dimeric association in which the H bonds are particularly strong.

UV – SPECTROSCOPY

There are two types of EMR (electromagnetic spectrum) in this region viz; visible and ultraviolet lying between $190 - 800\text{nm}$. The UV is between $190-400$ and visible is between $400 - 800$. UV is also referred to as electronic spectroscopy because a spectrum is produced which is as a result of electronic transition. A molecule normally exists in two states, the ground and the excited states, with the ground state having a lower energy

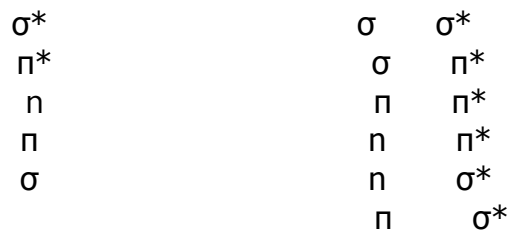
The energy supplied that will cause the promotion from ground to excited state comes from electromagnetic radiation of the UV – visible type

Types of Energy Levels & Transition

In an organic molecule, there are essentially two types of bonds

- (a) Single covalent bond (σ) sigma
- (b) Double covalent bond (π)

There is non-bonding orbital referred to as n so that we can have the following types of energy level with the following transitions



Compounds in which these types of bonds exist can therefore show UV absorption as in for example:-

Carbonyl compounds, Alkenes and Alkynes

Carbonyl strongly absorbs in UV due to these transitions

Strong $\sigma - \pi^*$

Weak $\pi - \pi^*$

Strong $n - \pi^*$

PRINCIPLE OF ELECTRONIC ABSORPTION SPECTROSCOPY

UV spectroscopy is also guided by the Beer lamberts law where $\log I_0/I = \epsilon Cl$

Where I_0 = Intensity of light incident upon sample cell, I = intensity of light leaving the sample cell (Transmitted light)

C = molar concn of solute in mol/L

L = length of sample cell (cm)

ϵ = molar absorptivity

$\log I_0/I$ = Absorbance (A) or optical density

ϵ is a property of a molecule undergoing electronic transition and it is not dependent on how the sample was prepared i.e It is a constant. The value is between $0 - 10^6$. Values exceeding 10^4 are high intensity absorption and below 10^3 are low intensity absorptions.

ϵ is also controlled by the size of the absorbent system and electronic transition taking place

ϵ changes as wavelength changes

Presentation of UV – spectra

SOLVENTS

Are very important in UV – spec since the choice of solvent is crucial to:

(1) the type of spectrum obtained. A good solvent should not absorb in the same region as the solute.

(2) A solvent should not contain conjugated systems or carbonyl entity as this interferes with the UV absorption of the solute. Some useful solvents and their useful absorption spectra are given below.

Water – 190nm, Normal hexane – 201nm, ethanol – 205 nm, acetonitrile – 190nm, 1,4 dioxane – 215nm, methanol – 205nm, iso – octane – 195nm.

The first three are the most important solvents.

DEFINITION OF TERMS

Chromophore- This is characteristic energy of a transition and the wavelength of the radiation absorbed are properties of a group of atoms rather than electrons. The group of atoms producing such an absorption is called a chromophore.

Types of chromophore include alkenes and functionalized alkenes. Also the position of intensity of absorption can be modified by attachment of a substituent group, this change of position is referred to as shifts. This makes the λ_{max} to be shifted to a new value

- (a) Bathochromic shift (red shift) – This is a shift to lower frequency or longer wavelength
- (b) Hypsochromic shift (Blue shift) – This is a shift to a higher frequency or shorter wavelength
- (c) Hyper chromic effect – This is an increase in intensity
- (d) Hypochromic effect – This is a decrease in intensity

Isosbestic point – This is a point where the UV-spectrum of a particular substance determined at various pH values meet i.e it is a point common to all curves produced in a spectrum of a compound taken at several pH values.

Auxochrome – is a substituent on a chromophore which leads to a red shift, for example in – C = C – N. The lone pair of the electrons on N interact with the electron of the double bond - C = C – H 190nm
- C = C – N 230nm

In this case the Nitrogen Substituent is the auxochrome, therefore an auxochrome extends a chromophore to give a new chromophore.

Some simple organic chromophore and the approximate wavelength at which they absorb are shown in the table below

Chromophore	λ_{nm}	Intensity ϵ_{max}
-C = C-	175	14,000
-C = C -	170, 195, 223	10,000, 21,000, 150

C = O	160, 180, 280	18,000, 900, 15
RNO ₂	200, 274	500, 15
- C = C – C = C (diene)	217	20,000
- C = C – C = O (ketone)	220, 315	10,000
	184, 204, 225	10,000, 7400, 204

The one with the highest intensity is the best representation of the absorption spectrum (λ)

Application of UV – Spectroscopy

Conjugated diene

Conjugated triene

Conjugated tetradiene

Homoannular

Heteroannular

unconjugated triene

Exocyclic (bond touching tips of 2 rings)

It is sometimes useful to carry out theoretical calculation of the absorption of these compounds as such it's quite easy to correlate the point at which they absorb along with the substrate in the compound. Woodward has put forward a set of rules that is used for this theoretical expression.

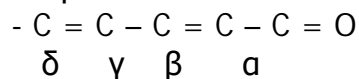
Woodward rules for dienes and trienes

	λ_{max}
Acyclic & Heteroannular dienes	214nm
Homoannular dienes	253nm
Acyclic diene	245nm
Addition for each substituent	
R – alkyl (including part of a carbon/ring)	5nm
OR	6nm
SR	30nm
Cl, Br	5nm
CH = CH additional conjugation	30nm

Double bond exocyclic to ring 5nm
 - OCOR O

Wood ward rules for α - β unsaturated carbonyls

α - β unsaturated carbonyls

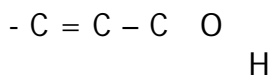


delta gamma beta alpha

The wood – ward rules also operate for these types of compounds

(a) Ketones, α - β acyclic or 6 member ring 215nm, or 5 –member ring 202nm

(b) Aldehyde 207



(c) Acid and esters



Additional conjugation is 30 while second bond homoannular to the first ring is 39

	α	β	γ	δ
R-akyl	10	12	17	17
-OR	35	30	17	31
-OH	35	30	30	50
-SR	0	80	0	0
-Cl	15	12	12	12
-Br	25	30	25	25
-OCOR 6	6	6	6	
NHR, -NR ₂ NH ₂	0	95	0	0

Double bond exocyclic to a ring is 5

In case of α - β unsaturated carbonyl, there is solvent shift effect particularly if the solvent is specific

Solvent	shifts
Water	+8nm
Methanol, ethanol	0
Chloroform	-1
Dioxane	-5
Diethylether	-7
Hexane	-11
Cyclohexane	-11

Note – if the question says that the compound is run in a certain solvent you either add or subtract the above number from the table values.

NUCLEAR MAGNETIC RESONANCE (NMR)

This is the absorption of EMR (electromagnetic radiation in the radio frequency region in the spectrum, resulting in changes of orientation of spinning nuclei in a magnetic field. The magnetic properties of nuclei can be explained by the assumption that nuclei charge is spinning around an axis. Such nucleus, possesses what is referred to as ANGULAR MOMENTUM, represented in terms of spin number I and it is assigned $\frac{1}{2}$ integral values such that we can have a range of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, 2 etc i.e etc i.e depending on a particular nucleus.

For nuclei having odd proton or odd number of neutrons (i.e. both the proton and neutrons are not odd at the same time). Such nuclei exhibit $\frac{1}{2}$ integral spin quantum number e.g.

${}^1_1\text{H}$	${}^{11}_5\text{B}$	${}^{19}_9\text{F}$
P1	5	9
N0	6	10

$I = \frac{1}{2}$ (both the neutron and proton are not odd at the same time)

If both neutrons and protons are odd, $I = 1$.

${}^2_1\text{H}$	${}^{14}_7\text{N}$	${}^{17}_9\text{H}$
P1	7	9
N1	7	10

When both protons and neutrons are even numbers, such nuclei have no angular momentum i.e. $I = 0$ and therefore exhibit no magnetic property i.e. they are magnetically inert and are not detected in NMR experiment.

	${}^{12}_6\text{C}$	${}^{16}_8\text{O}$	${}^{32}_{16}\text{S}$	${}^{40}_{20}\text{Ca}$
P	6	8	16	20
N	6	8	16	20

NMR PROCESS

Proton NMR

The magnetic nuclei ($I = \frac{1}{2}$) interact with an external magnetic field by assuming discrete orientation with corresponding energy levels. The numbers of quantized energy levels depend on I and it is given by $I, I-1, I-2, \dots, I-I$.

For protons where $I = \frac{1}{2}$, there are only 2 orientations corresponding to alignment with applied field (lower energy) or alignment against the applied field (higher energy).

This shows that absorption frequency, μ is in proportion to the strength of the applied magnetic field. Practically, absorption of energy may be detected by subjecting the sample to radiation of varying λ at a fixed value of the applied field or vice versa until the condition requested by the equation is met. At this point, the system is in resonance and both upward and downward transition occur and a net absorption of energy is observed because of the small excess of nuclei from the lower level.

NMR INSTRUMENTATION

The NMR spectrometer contains six major parts;

1. A magnet with a strong, stable and homogenous field.
2. A sweep generator, which supplies a variable direct current to a secondary magnetic field so that the total applied magnetic field can be varied (swept) over a limited range.
3. A radio frequency oscillator (transmitter) connected to a coil which transmits energy to the sample in a direction perpendicular to the magnetic field.
4. A radio frequency receiver connected to a coil encircling the sample. The two coils are perpendicular to each other and to the magnetic field.
5. A read out system consisting of the amplifier and a recorder.
6. A sample container, usually a glass tube spun by an air driven turbine to average the magnetic field over the sample direction.

SCHEMATIC DIAGRAM OF NMR SPECTROMETER

HANDLING OF SAMPLES

A dilute solution of the sample of about 2-10% concentration is used. It is also very important that the solvent used must not contain any additional proton which will interfere with the sample determination. Therefore, solvents such as CCl_4 or Deuterated solvents of chloroform (CDCl_3) and Benzene (C_6D_6) are used. Other common solvents used are: CS_2 , $(\text{CD}_3)_2\text{SO}$ (Hexa-deuterio dimethyl sulfoxide), $(\text{CD}_3)_2\text{CO}$ (Hexa-

deuterioacetone) and $(\text{CCl}_3)_2\text{CO}$ (Hexa chloro acetone) and D_2O (Heavy water/deuterium oxide).

D_2O is used for samples that are soluble in aqueous solution. A 5mm outer diameter (OD) glass serves as a sample container. It is held by a propeller arrangement so that it can be spun by a jet of compressed air.

FACTORS AFFECTING NMR

CHEMICAL SHIFT

Normally, at a given frequency, all protons will absorb energy at the same value of the magnetic field (H_0). However, the field experienced by a particular nuclei differs in magnitude from that of the applied field because of shielding effect by neighbouring electrons. It is because of varied degree of shielding that protons in different chemical environment absorb at different values of the applied field. Differences between such absorptions are referred to as "Chemical shift" e.g. The chemical shift values for methyl protons attached to groups of varied electronegativity are given below:

- | | | | | |
|----|------------------------|---|---------------|-------------------------------------|
| | CH_3 | | | |
| 1. | CH_3 | - | Si | - |
| | | | CH_3 | $\text{Si}(\text{CH}_3)_4 \text{O}$ |
| | CH_3 | | | |
| 2. | CH_3I | | | 2.16 |
| 3. | CH_3Br | | | 2.65 2.65 |
| 4. | CH_3Cl | | | 3.10 |
| 5. | CH_3F | | | 4.26 |

As the electronegativity of a functional group is increased, the CH_3 protons come to resonance at higher σ values. This is due to the e- density around the H nuclei. H nuclei are surrounded by electronic charge which to some extent shields the nucleus from the influence of the applied field and in order to bring a proton to resonance, the magnetic flux must overcome this shielding effect.

In a magnetic field, the e⁻ around the protons are induced to circulate and in so doing; they generate a small 2^o magnetic field that acts in opposition (i.e. diamagnetically) to the applied field. The greater the e⁻ density circulating around the proton, the greater the induced diamagnetic effect and the greater the external field required to overcome the shielding effect. Electro-ve groups like fluorine in CH₃F withdraws e⁻ density from the CH₃ group (-inductive effect), resulting in de-shielding meaning that a lower value of an applied magnetic field is needed to bring the methyl proton to resonance. Since fluorine is more electro-ve than Cl, then the proton in CH₃F will appear at a higher δ values than those in CH₃Cl.

Mathematically, the nucleus finds itself in an effective field which is somewhat smaller than the applied field i.e. $H_{eff} = H_o - \delta H_o$.

Where δ represents the shielding parameters. The value of δ depends on e⁻ density around the proton. For instance, comparing the shielding parameters in methanol (CH₃OH), the shielding parameter δ CH₃ is less than δ OH. Therefore, at any given applied field H_o, H_{eff} for CH₃ protons would be lower than the H_{eff} of the OH proton.

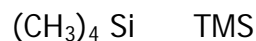
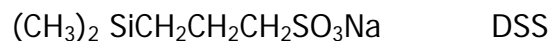
For example, the relative absorption for protons attached to Carbon, Silicon, Nitrogen and Oxygen shows that the trend of shielding is such that Si>C>N>O which depends on the e⁻ density around each of the atoms.

Measurement of chemical shift.

Quantitative chemical shift are measured in frequency (Hertz) relative to a standard, Tetra methyl silane (TMS).

TMS has twelve (12) highly shielded protons with identical chemical and magnetic environment thereby producing a single sharp resonance peak at a higher field than most organic proton. It is usually chemically inert soluble in organic solvent and boils

at inert; soluble in organic solvent and boils at 27°C. For aqueous samples, Sodium 2,2 dimethyl 2-silapentane-5 Sulphate is used.



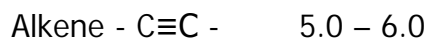
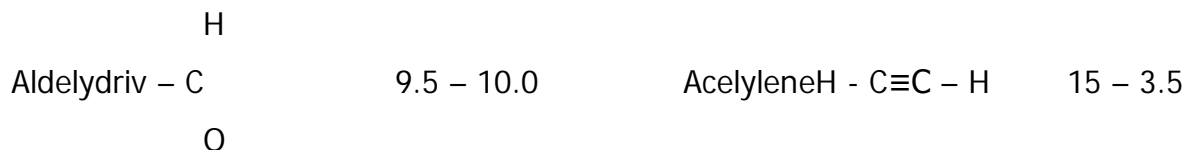
Chemical shifts are expressed in dimensionless units δ which is obtained by dividing the operating frequency of the sample minus that of the standard divided by that of the instrument.

$$\delta = \frac{\delta_{\text{Sample}} - \delta_{\text{TMS}}}{\delta_{\text{Instrument}}}$$

Alternatively, the tau (τ) scale in which the TMS peak is assigned in values of 10 is used such that $\tau = 10 - \delta$. Diagrammatically shielding can be represented on a δ scale for the following compounds.

2. MAGNETIC ANISOTROPY (ANISOTROPIC EFFECT)

The chemical shift positions for protons attached to C=C in alkenes is higher than that can be accounted for by electronegative effect alone. The same is true of aldehydic protons and aromatic protons. For example alkene and aromatic protons appear at high δ values while alkyne C≡C protons appear at a relatively low δ value.



It would have been expected that acetylinic proton being more acidic would have experienced less magnetic shielding (i.e. δ would be very high). This and other anomalous effects in any unsaturated molecules is explained in terms of shielding and deshielding zones in space caused by the circulation of π electrons.

INDUCED ANISOTROPIC MAGNETIC FIELD AROUND AN ALKENE GROUP

When an alkene group is so orientated such that the plane of the double bond is at 90° (perpendicular) to the direction of the applied field, the induced circulation of the π e- generates a 2° magnetic field which is diamagnetic around the carbon atoms but paramagnetic in the region of the alkene group. Where the direction of the induced magnetic field is parallel to the applied field, the net field is greater than the applied field. Protons in this zone would therefore require a lower value of applied field to come to resonance and will appear at a lower field (higher δ value) than expected. Any group held above/below the plane of the double bond will experience a shielding effect since in these areas; the induced field opposes the applied field. In summary, the space around the double bond can be divided into two in which (i) Deshielding occurs in the cone-shaped zone and the δ values will tend to be higher than expected. and (ii) Shielding is indicated by the positive Sign and protons in this zone would have lower δ values.

CARBONYL COMPOUNDS

A similar situation arises in which π e- also circulates around the double bond between carbon and oxygen. However, shielding and deshielding zones differ slightly from the alkene pattern

In this case, two cone shaped volumes centred on the oxygen atom lie parallel to the axis of the C = O bond. Protons within this zone experience deshielding so that

aldehydic protons and formal protons appear at high δ values. Protons held above or below these cones will come to resonance at lower δ values.

Anisotropic shielding of a proton in an alkyne group

Whereas alkenes and aldehydic protons appear at high δ values, alkyne protons appear around 1.5-3.5 δ value. Electron circulation around the triple bond occur in such a way that the protons experience a diamagnetic shielding effect. From the diagram, when the axis of an alkyne group lies parallel to the direction of applied field the cylindrical sheath of π e⁻ is induced to circulate around the axis and the resultant annulus-shaped magnetic field acts in a direction that opposes the applied field in the vicinity of the protons and as such, higher applied field values are needed to bring the protons to resonance. Therefore acetylenic protons appear at low δ value in the spectrum.

AROMATIC COMPOUNDS

In the case of a benzene ring, the circulating π e⁻ setup a ring current with the e⁻ cloud below and above the molecule. This therefore makes the protons to be deshielded such that the protons of benzene resonate at a high δ value between 7-8 in contrast to a value of between 2 and 4 that would have been expected in the absence of the anisotropic effect.

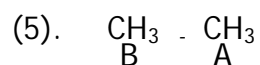
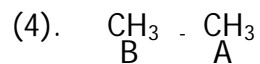
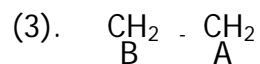
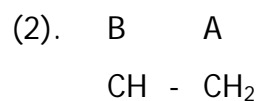
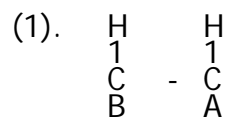
Appearance of NMR spectrum (Spectra)

1. Spin- Spin coupling (splitting)

Absorption bands arising from adjacent protons are split into multiplet peaks by mutual interactions of the spins. The effect is due to the small variations in the effective field experienced by a proton when neighboring nuclei can occupy two or more energy levels / spin states. This effect is transmitted through the intervening bonds by a tendency for electrons and nuclear spins to be paired.

Consider two protons A and B on neighbouring carbon atoms. The effective field at A is either decreased or enhanced by the local field generated by B, depending on whether

B is orientated with or against the applied field. A proton with n equivalent protons on the neighbouring carbon atom will be split by the n protons into (n+1) lines multiplet with relative sub area given by the coefficient of the binomial expression $(n+1)^n$ where n is equal to the number of protons on the neighbouring carbon atoms. E.g.



Ethanol. ($\text{CH}_3\text{CH}_2\text{OH}$).

Identify the splitting patterns.

TABLE OF NMR

Values for the protons CH_3 , CH_2 and CH groups attached to groups nX , where $\text{R} = \text{alkyl}$ and $\text{Ar} = \text{aryl}$.

X	CH_3X	$\text{R}^1\text{CH}_2\text{X}$	$\text{R}^1\text{R}^{11}\text{CHX}$	d values for the protons OH, NH and SH and Benzene
-R	0.9	1.3	1.5	ROH 0.5- 4.0

-COOR	2.0	2.1	2.2	Ar OH	4.5(Raised
-COOAr		2.0	2.1		by H-bonding
-CN		2.0	2.5		to 9.0
-CONH ₂ , -CONR ₂	2.0	2.0	2.1	RCOOH	10 -13.0
-COOH	2.1	2.3	2.6	RNH ₂ , RNHR ¹	5.0- 8.0
-COR	2.1	2.4	2.5	ArNH ₂ , ArNHR ¹	3.5- 6.0
-SH, - SR	2.1	2.4	2.5	RCONH ₂ , RCONHR ¹	5.0 8.5
-NH ₂ , NR ₂	2.1	2.5	2.9	RCONHCOR ¹	9 -12.0
-I	2.2	3.1	4.2	RSH	1.0 -2.0
-CHO	2.2	2.2	2.4	ArSH	3.0- 4.0
-Ph	2.3	2.6	2.9	= NOH	10.0-
12.0					
-Br		2.6	3.3		
-NHCOR, - NRCOR	2.9	3.3	4.1		7.2- 8.0
-Cl	3.0	3.4	4.0		
-OR	3.3	3.3	3.8		
-Nr ₃	3.3	3.4	3.5		X - 8.5
-OH	3.4	3.6	3.8		B - 7.0
-OCOR	3.6	4.1	5.0		X - 7.4
-OAr	3.7	3.9	4.0	C = C-H	5.3
-OCOAr	3.9	4.2	5.1	C ≡ C - H	1.8
-NO ₂	4.3	4.4	4.6		

INTERPRETATION OF NMR SPECTRA

The basic information gathered from NMR spectra are: -

1. Chemical shift: - This identifies the type of proton based on their electronic environment.
2. Spin-Spin splitting patterns: - This identifies neighbouring protons.
3. Peak Area: - This is proportional to the number of protons giving a particular resonance line.

Other identification parameters of note are.

- The observation of a triplet and a quartet spin state confirming usually the presence of an ethyl group (CH₃CH₂).
- The observation of δ values between 7.2-8.0 indicates that the structure contains a benzene ring (benzyl proton)

INTEGRATION OF PEAK AREAS

The NMR signal is directly proportional to the number of H nuclei that are responsible for the resonance i.e. the spectrometer counts. Most recorders are equipped with automatic integrator, which gives peak area directly. The integrator trace is superimposed on the spectrum and the height of a step on the integrator trace represents the area in arbitrary units. The number of hydrogen atoms in each peak can be determined by two methods as shown below by using the spectral of ethanol (C₂H₅OH) as example

1). RATIO METHOD

The steps corresponding to each peak is measured and arranged from the smallest to the highest and calculated as a simple ratio to each of them (dividing by the smallest).

$$6 : 12.4 : 17.8$$

$$1 : 2 : 3$$

Meaning 1 Proton, 2 Protons, 3 Protons.

s(2). METHOD TWO

This assumes the knowledge of the total number of protons in the compound and the ratio of each of the height to the total height is found as a ratio of the total number of protons.

$$6 + 12.4 + 17.8 \longrightarrow 36.2$$

$$\frac{6}{36.2} \times 6,$$

$$\frac{12.4}{36.2} \times 6,$$

$$\frac{17.8}{36.2} \times 6$$

36.2

1,

36.2

2,

32.2

3.

Double Bond Equivalent

In the interpretation of spectroscopic data, the best place to begin is with the molecular ion in the mass spectrum from which a molecular formula may be deduced. In the absence of a molecular ion, a combustion analysis can also give this information (i.e. C = 70%, H = 11%, N = 9.5% O = 9.5%).

To therefore get an idea of the complexity in the structure it is best to work out the number of double bonds and rings in the structure. This is done by inspecting the molecular formula. If the molecule contains only C, H, and O, then the number of double bonds and rings (double bond equivalents, DBE) is given by Eq. 5.1.

$$\text{C}_a\text{H}_b\text{O}_c \quad \text{DBE} = \frac{(2a + 2) - b}{2}$$

The $(2a + 2)$ term is the number of hydrogens in a saturated hydrocarbon having a carbon atoms. Since every ring or double bond means two fewer hydrogen atoms (cyclohexane is C_6H_{12} and ethylene, C_2H_4), subtracting b , the actual number of hydrogen atoms present, from $(2a + 2)$ and dividing by two gives the total number of double bonds and rings in the molecule. It is useful to remember that a benzene ring has a total of four double bond equivalents: three 'double bonds' and one ring. The number of divalent atoms (O, S, etc.) present makes no difference to this sum, but mono- and trivalent atoms do. Count mono-valent atoms (Cl, Br, etc.) as hydrogens and add them to b . When trivalent atoms (N, trivalent P, etc.) are present, use Eq. 5.2, i.e. subtract one from b for each trivalent atom present.

$$\text{C}_a\text{H}_b\text{O}_c\text{N}_d \quad \text{DBE} = \frac{(2a + 2) - (b - d)}{2}$$

Thus the formula $\text{C}_5\text{H}_{11}\text{N}$ has one double bond equivalent (often written: F1); it might be the I-propylamine or acetaldehyde (one double bond) or cyclopentylamine (one ring).

Examples of DBE calculations

TUTORIAL QUESTIONS

1. With a schematic diagram briefly describe the instrumentation of a typical nmr spectrometer.
Explain the term spin-spin coupling using the carbon chains CH-CH, CH-CH₂, CH₂-CH₂, CH₂-CH₃ and CH₃CHCH₃ to illustrate your understanding.
2. Explain in details the term chemical shift.
3. Explain the term spin-spin coupling using the carbon chains CH-CH, CH-CH₂, CH₂-CH₂, CH₂-CH₃ and CH₃CHCH₃ to illustrate your understanding.
4. Explain the phenomenon of diamagnetic Anisotropic
5. Explain the pattern and intensities of the isopropyl group in isopropyl iodide.
6. What arrangement of protons would give two triplets of equal area.
7. Predict the appearance of the H n.m.r spectrum of n-propyl bromide.
8. An organic compound has the following percentage composition C. 52.17, H. 13.05 and O.34.78 and a H n.m.r spectra as follows: 3H(t) • 1.5, 2H(q) • 3.0, 1H (s) • •6.0 from this information deduce the structure of the organic compound.
9. Deduce the structure of the following compounds from the n.m.r spectra.
C₉H₁₀O:- • 1.2 (3H,t), • 3.0 (2H,q), • 7.4 - • 8.0 (5H,m)
C₉H₁₀O₂:- • 1.4 (3H,t), • 4.0 (2H,q), • 7.4 - ••8.0 (5H,m)
C₉H₁₀O₃:- • 1.4 (3H,t), • 4.0 (2H,q), ••7.4 - ••8.0 (5H,m)
C₇H₆O₂:- • 6.5 (1H,s) and • 7.4 - ••8.0 (5H,m).
10. An organic compound with the % composition C=50.85, H = 8.47 and O = 40.68 has a molecular weight of 118. Given that its n.m.r spectra is as follows 2H(q) ••4.0 and 3H(t) •1.4. deduce the structure of this compound.
11. An organic compound with the % composition C 48.65% H 8.1% and O 43.24% has a molar mass of 74 and a n.m.r spectra as follows 1H(s)• 8.4, 2H(q) •4.2 and 3H (t) •1.2 from this information deduce its structure.
12. Predict the n.m.r spectra along with the intensities for the compounds.

- (g) 1,1,2 trichloro ethane (h) 2-Chloropropanoic acid (i) 1, Nitropropane
13. An organic compound has the following % composition C= 68.4, H = 7.772, N=7.2 O=16.50% and its empirical formula tallies with its molecular formula. Deduce the structure of this compound if its nmr spectra is as follows
 • 4.0 (2H,q), • 1.5 (3H,t), • 7.4 (1H,d) • 7.6 (1Hd), • 2.2 (6H,s).
14. An aromatic compound with a molecular mass of 164 gave on micro analysis 73.17%C, 7.31%H and 19.513%O. the Hnmr spectra revealed the following 3H(s, • 2.1) 4H (d, • 7.6-• 8.0), 2H (q, • 4.2) and 3H (t, • 1.4) • max determined by application of woodward rules is 325nm. Compound also gave two strong IR absorption bands at 5.917 and 13.477, with this information deduce the structure of the compound.
15. An aromatic unsaturated ketone has the following % composition. 68.4%C, 7.772%H, 7.2%N. given that its empirical formula tallies with its molecular formula, deduce the structure of this compound from its Hnmr spectra below (fig 1)
17. An aromatic unsaturated diketone, compound A with the percentage composition C=72.48, A= 6.04 was subjected to spectroscopic analysis as shown in figs 2 and 3. From this data deduce the structure of the compound.

MASS SPECTROMETRY

In mass spectrometry, electronic transition is not involved. Rather. Organic molecules are bombarded with any and converted to highly energetic tvely charged ions (molecular/parent ion), which can then break up into smaller ions (fragment/daughter ions). Loss of an any from a molecule leads to the formation of a radical cation represented as $\overline{M} \rightarrow M^+$. A molecular ion (m^+) commonly decomposes to a pair of fragments which can either be a radical and an ion or a small.

$M^+ = M_1^+ + M_2$ Molecule and a radical atom.

The most abundant ion is called base peak and the mass to charge irrelative abundance (M/Z to RA) given as 86/15 represents the molecular ion which is always equivalent to the molecular mass of the compound e.g. 2 methyl pentane $C_6H_{14}=86$.

The tendency of cleavage for organic compounds is usually $3^0 > 2^0 > 1^0$. e.g. C-C-C-C-C.

Therefore, the most abundant ion is 43 because in breaking up of the molecule, there is M^+ peak of 43 on both sides of the cleavage. Other cleavages can be accounted for as follows.

The important peaks can be accounted for by looking at the fragmentation patterns. Over the years, by considering several thousands of organic molecules has led to Comprehensive/Semi-emperical rules about the preferred fragmentation modes for every kind of organic molecule. The molecular weight i.e. a molecular ion peak is normally determined by looking towards the end of the spectrum. A series of peaks can be seen and the last major ion peak represents the molecular ion and therefore, the molecular weight.

M/Z	Assignment
86	M^+
87	$M^+ + 1$
87	$M^+ + 2$

FRAGMENTATIONS ASSOCIATED WITH FUNCTIONAL GROUPS.

It is always easier to rationalize the mass spectrum of a known structure than to deduce the structure of an unknown compound from its mass spectrum. Other spectroscopic evidence for the presence of functional groups should ideally be available.

ALKANES

In general, for alkanes, the predominant peaks are the C_nH_{2n+1} peak. Associated with each of these C_nH_{2n+1} ions are lesser amounts of the corresponding alkenyl ions which is C_nH_{2n-1} , formed by loss of two hydrogen atoms. They therefore appear at m/e of 27,

41, 55, and 69. metastable ions of very low intensities can be detected for the fragmentation in which the alkyl ions extrude a smaller molecule, thus, $C_2H_5^+$ and $C_3H_7^+$ can extrude H_2 while $C_4H_9^+$ can extrude CH_4 , $C_5H_{11}^+$ and $C_6H_{13}^+$ extrude C_2H_4 and $C_7H_{15}^+$ extrude C_3H_6 .

Branched chain alkanes rupture predominantly at the branching point and the largest group attached to the branching point is often preferentially expelled as a radical. Preference is for the formation of 3^0 over 2^0 and 2^0 over 1^0 cations. For example,

ALKENES

The commonest fragmentation in alkene group involves rupture of the allylic bond (B to the double bond). Since the allylic radical is also stabilized, the fragmentation may give rise to peaks corresponding to charge retention by either of the fragments

A Maclafferty's rearrangement may occur if the carbon atom (position of C atom to the double bond) has hydrogen atoms on it

ALKYNES

No single pattern emerges for the fragmentation of alkynes that can be applied to the complex molecules. Loss of alkyl radicals gives prominent peaks in many cases at $M-15$, $M-29$ and extrusion of alkenes may give $M-28$ and $M-42$ peaks.

AROMATIC HYDROCARBONS

Molecular ions of aromatic hydrocarbon are always abundant and the M^+ is commonly the base peak while M^{+1} and M^{+2} M^{+2} are easily observed. Alkyl benzenes are the commonest HC's in this class. The dominant fragmentation in the group is at the benzylic bond.

The stable benzene cation (III) certainly explains the abundant m/e 91 peak observed in the mass spec of compound of this type.

McLafferty's rearrangement is also observed in alkyl benzenes provided the side chain has H on the X C-atom giving rise to an ion a m/e of 92.

The phenyl cation ($C_6H_5^+$) at m/e of 77 is produced by many aromatics by rupture of the bond X to the ring and this ion extrude C_2H_2 to give m/e of 51.

ALCOHOLS

The number of fragmentation for alcohols and their relative importance depend on 1^0 , 2^0 and 3^0 aliphatic or aromatic nature of the alcohol. The most importance fragmentation is rupture of the bond B to O_2 . For 1^0 alcohols, M-18 peak is observed which corresponds to loss of water. Also, for alcohols with more than 4 C atoms is simultaneous loss of water and alkene to give M-18- C_nH_{2n} .

2^0 and 3^0 alcohols fragment by loss of alkyl radicals. The case of elimination increasing with increased size and branching in the alcohol. Aromatic alcohols fragment so as to favour charge retention by the aryl group e.g. in 1-phenyl ethanol the base peak correspond to elimination of CH_3 . Also, peak corresponding to CO^+ and Ar^+ are also observed. The peak observed at m/e of 107 by these alcohols (base peak in the case of 1-phenyl ethanol) is best represented as hydroxyl tropylium ion loss of CO form this ion gives rise to m/e of 79 followed by loss of H giving rise to the phenyl cation at m/e 77 which then goes further to lose C_2H_2 giving rose to m/e of 51.

PHENOLS

Simple phenols give strong molecular ion peaks. The commonest fragmentation is loss of CO (M-28) and CHO (M-29). Those with alkyl side chains form the hydroxyl tropylium ion.

CARBONYL COMPOUNDS

For aryl carbonyl compounds, they have general this type of fragmentation.

1° amines fragment by loss of H ($M^+ - 1$) and loss of HCN ($M^+ - 27$) e.g. aniline NH_3 gives rise to a peak $93 - 27$. For 2° and 3° amines, base peak is given by $\text{CH}_2 = \text{NH}_2^+$ m/e 30 and is formed by the expulsion of the radical from M^+ .