MScCH-10

Vardhman Mahaveer Open University, Kota

Practical Chemistry II

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Vardhman Mahaveer Open University, Kota

Practical Chemistry II

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Preface

The present book entitled "Practical Chemistry II" has been designed so as to cover the unit-wise syllabus of MScCH-10 course for M.Sc. Chemistry (Final) students of Vardhman Mahaveer Open University, Kota. The basic principles and theory have been explained in simple, concise and lucid manner. Adequate examples, diagrammes , photographs and self-learning exercises have also been included to enable the students to grasp the subject easily. The unit writers have consulted various standard books and internet as their reference on the subject and they are thankful to the authors of these reference books.

Unit – 1

Preparations

Experiment 1

Object:

Preparation of sodium tetratnionate ($Na_2S_4O_6$).

Chemical Reaction:

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Sodium thiosulphate Sodium tetratnionate

Chemicals required:

(i) Iodine – 4 gm

(ii) Ethanol – 40 ml

(iii) Sodium thiosulphate – 4 gm

Apparatus required

100 ml Beaker, Buchner Funnel, Vacuum desiccator, Glass rod.

Method

Take 4gmot sodium thiosulphate and 4gm of iodine in a 100ml beaker and add 2ml water. Add Ethylalcohal (40ml) and leave the mixture for 15hrs at room temperature. Filter the sodium tetrathionate on a Buchner funnel and wash it will with Ethyl alcohol to remove the excess iodine. Dissolve the sodium tetrathionate in the minimum quantity of Hot water. Filter; dry it in a vaccumdesicater.

Yield = 4.0gm.

Experiment 2

Object

Preparation of Ferrocene ($(C_5H_5)_2$ Fe)

Chemical Reaction

Ferrocene can be prepared by reacting with $FeCl_2$ with potassium cyclopentadienide

$C_5H_6 + KOH \rightarrow C_5H_5K + H_2O$

$$2C_5H_5K + FeCl_2 \rightarrow (C_5H_5)_2Fe + 2KCl$$

Chemical Required:

(i) KOH = 45 gm.

(ii) Diethyl Ether = 110 ml.

(iii) Cyclopentadienyl = 10 ml

(iv) DMSO = 40 ml

(v) Ferrous chloride = 12 gm.

Apparatus required

Conical Flask, Dropping funnel, Beaker, Stirrer.

Method

Take 45gm KOH and 110 ml diethyl ether in a conical flask and stirred for 10-15 minutes and then 10 ml of cyclopentadiene is added to it, again whole mixture stirrer for 10-15 minutes, 12 gm of ferrous chloride powder dissolved in 40ml DMSO and taken in the dropping funnel. Then dropping funnel iron solution is added dropwise in to conical flask with stirring. The reaction is complete in about 30 to 40 minutes. At the end of the reaction, ether layer is separated and wasted with dil HCl. The ether layer is concentrated and cooled to obtain orange crystal of ferrocene.

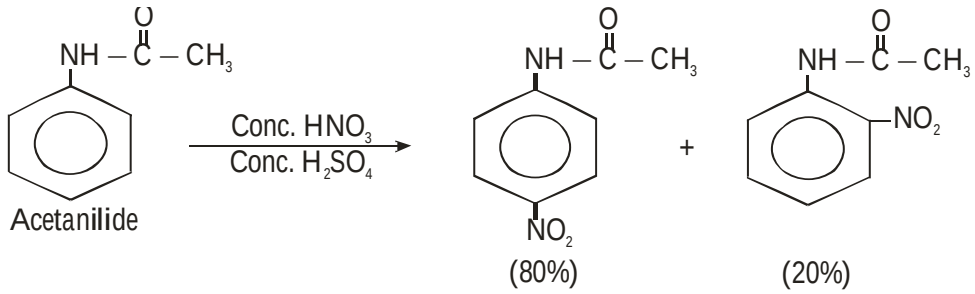
Yield = 15 gm.

Experiment 3

Object

Preparation of p-nitro acetanilide from acetanilide.

Chemical reaction:



Chemicals required:

(i) Acetanilide – 20 gm

(ii) Glacial acetic acid – 20 ml

(iii) Conc. H_2SO_4 – 40 ml

(iv) Conc. HNO_3 – 20 ml.

Apparatus required:

500ml beaker, Buchner funnel, Glass rod.

Method:

Mix 20 gm of dry acetanilide and 20 ml of glacial acetic acid in a 500ml beaker; introduced into the well stirred mixture 40ml of conc. sulphuric acid. The mixture becomes warm and a clear solution results. Surround the beaker with a freezing mixture of ice and salt, and stir the solution mechanically. Support a separatory funnel containing a cold mixture of 14 ml of conc. nitric acid and 10 ml of conc. H_2SO_4, over the beaker. When the temperature of the solution falls to 0-5^oC, run in the acid mixture gradually while the temperature is maintained below 10^oC.

After all the mixed acid has been added; remove the beaker from the freezing mixture and allow it to stand at room temperature for 1 hour. Pour the reaction mixture on to 400 ml of crushed ice water, where by the crude nitro acetanilide is at once precipitated. Allow to stand for 20 minutes, filter with suction on a Buchner funnel, wash it thoroughly with cold water until free from acids and drain well. Recrystallize the place yellow product from ethanol, filter at the pump, wash with a litter cold ethanol and dry in the air upon filter paper.

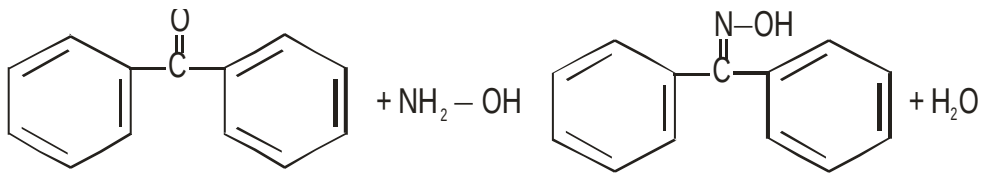
Yield: The yield p-nitro acetanilide is 15 gm.

Experiment 4

Object:

Preparation of benzophenone oxime from benzophenone.

Chemical Reaction:



Benzophenone Benzophenone oxime

Chemical required:

(i) Benzophenone – 20 gm.

(ii) Hydroxyl amine hydrochloride – 10 gm.

(iii) Rectified sprit – 40 ml

(iv) Sodium hydroxide – 25 gm.

(v) Conc. HCl – 70 ml

Apparatus required:

500ml round bottom flask, vaccum desiccator, beaker etc.

Method :

In a 500 ml round bottom flask 20 gm benzophenone, 10 gm hydroxylamine hydrochloride, 5 ml distilled water and 40ml rectified spirit. To this mixture add 25 gm of sodium hydroxide slowly in portion of about 0.5 gm. With constant shaking with cooling, it necessary, fit reflux condenser to the flask and reflux the contents for about 15 minutes cool and then pour the reaction, mixture in to a solution of 70ml conc. HCl in about 120ml water taken in a 500ml. beaker. The benzophenone oxime separates out as colorless crystals. Filter it, wash with water and dry by pressing between filter paper.

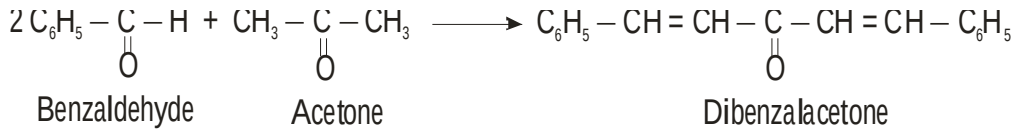
Yield: The yield of benzophenone oxime is 20gm and m.p. 142^{o}C.

Experiment 5

Object:

Preparation of dibenzalacetone from benzaldehyde.

Chemical reaction:



Chemical required:

(i) Sodium hydroxide – 20 gm

(ii) Ethanol – 150 ml

(iii) Benzaldehyde – 20 ml

(iv) Acetone – 10 ml

Apparatus required:

50 ml round bottom flask, flask.

Method:

Mix 20 gm of sodium hydroxide in 200 ml water and 150 ml ethanol in a 500 ml round bottom flask, equip the flask with a mechanical stirrer and surround it with a bath of water. Maintain the temperature of the solution at 20-25°C, stir vigorously and add one half of prepared mixture of 20 ml of benzaldehyde and 10 ml of acetone. A flocculent precipitate forms in 5 minute. After 20 minutes add the reaming of the benzaldehyde acetone mixture. Continue the stirring for a further 30 minutes. Filter at the pump and wash with cold water to eliminate the alkali as completely as possible. Dry the solid at room temperature upon filter paper to constant weight of crude dibenzalacetone are obtained.

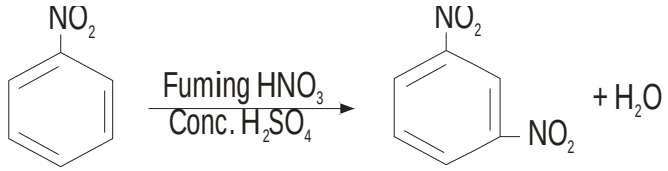
Yield: 10 gm; M.P. – 122°C.

Experiment 7

Object:

Preparation of m-dinitrobenzene from nitrobenzene.

Chemical reaction:



Nitrobnzene m-dinitrobenzene

Chemical required:

(i) Nitrobenzene – 10 ml

(ii) Fuming HNO_3 – 15 ml

(iii) Conc. H_2SO_4 – 20 ml

Apparatus required:

500ml round bottom flask, beaker.

Method:

mix 20ml. of conc. H_2SO_4 and 15 ml of for fuming HNO_3 in a 500ml round bottom flask and add a few fragments of unglazed in porcelain.

Attach a reflux condenser and place the apparatus in fume cupboard. Add slowly of nitrobenzene and shake the flask to ensure through mixing. Heat the mixture with frequent shaking on a boiling water bath for 30 minutes. Allow the mixture to cool somewhat and pour it cautiously with vigorous stirring into about 500 ml of cold water filter with suction, wash thoroughly with cold water and allow to drain as completely possible.

Transfer the crude dinitrobenzene to a 500ml flask fitted with a reflux condenser, mix 70 ml of rectified spirit and heat on a water bath until all the crystalline solid dissolves. Filter it through a filter paper.

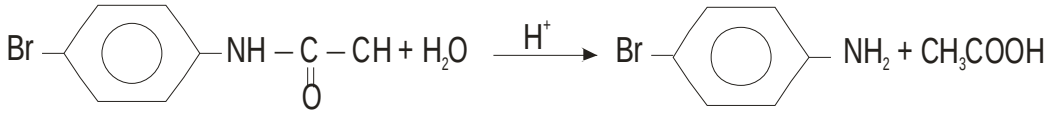
Yield: 10gm of colorless crystals of m-dinitrobenzene&M.P. – 90°C.

Experiment -8

Object:

Preparation of p-bromoaniline from p-bromoacetanilide.

Chemical reaction:



p-bromoacetanilide p-bromoaniline

Chemical required:

(i) p-bromoacetanilide – 15 gm.

(ii) Ethanol – 30 ml.

(iii) Conc. HCl – 15 ml.

(iv) 5% NaOH solution

Method:

Dissolve 15 gm of p-bromoacetanilide in 30 ml Ethanol contained in a 500 ml round bottom flask equipped with a reflux condenser. Add 15ml of conc. HCl in to the boiling solution. Reflux for 30-45 minutes. Dilute with 150 ml of water and fit the flask on air bath and collect about 100 ml of distillate, pour the residual solution of p-bromoaniline hydrochloride into 100 ml of ice water and add with vigorous stirring, 5% NaOH until just alkaline. The p-bromoaniline separates as an oil, which soon crystallize. Filter the crystals at the pump, wash with cold water and dry in the air upon pads of filter paper.

Yield: The yield of p-bromonaniline is 10 gm. M.P. – 60°C.

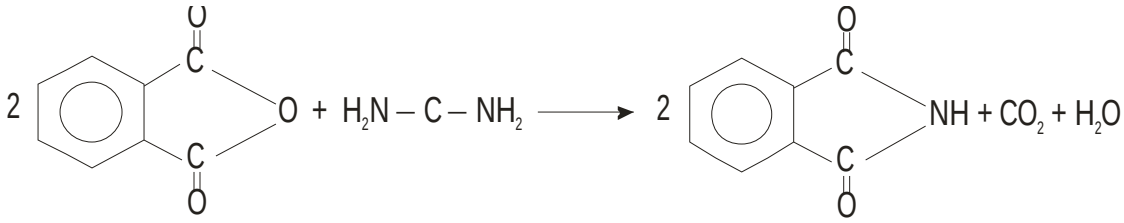
Experiment -9

Object:

Preparation of anthranilic acid from phthalic anhydride.

(A)First step: Phthalimide from phthalic anhydride.

Chemical reaction:



Phthalic angydride Phthalimide

Apparatus required:

250 ml round bottom flask, and both, Buchner funnel.

Chemical required:

(i) Phathalic anhydride – 15 gm.

(ii) Urea – 5 gm.

Method:

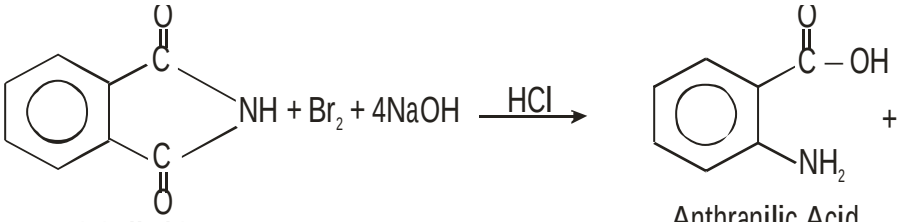
Mix 15 gm of phthalic anhydride and 5gm of urea in 250 ml round bottom flask and heat it on a sand bath. A thermometer is immersed in the reaction mixture and maintained temperature between 125 – 135°C. The reaction begins with frothing of the mass and the temperature rise to 160°C. When the frothing subsides, stop heating and cold water to the spongy solid.

Filter the phthalimide in a Buchner funnel with suction. Wash it with water drain well and dry by pressing between filter papers.

Yield: 10 gm. & M.P. – 235°C.

(B) Second step: Anthranilic acid from phthalimide.

Chemical reactions:



Phthalimide

Anthranilic Acid
+ 2NaBr + Na_2CO_3 + H_2O

Chemical required:

(i) Sodium hydroxide – 15 gm.

(ii) Conc. HCl – 20 ml.

(iii) Bromine – 2.5 ml.

(iv) Glacial acetic acid – 7.5 ml.

(v) Phthalimide – 8 gm.

Apparatus required:

250 ml conical flask, Glass rod.

Method:

Sodium hypobromite solution prepared by dissolving 15 gm of NaOH in 50 ml water in a 250 ml conical flask, cooling the solution to $0^{o}C$ in an ice bath and then add 2.5 ml bromine to it with stirring. To this solution add 8 gm phthalimide in cold with continuous. Stirring and then pour a solution of 6.5 gm of sodium hydroxide in 25 ml water. On addition of sodium the solid phthalimide dissolve and the flask become hot. Warm the reaction mixture in a water bath of $75^{o}C$ for 10 minutes and if any solid residue is left, filter it off. Cool the filtrate taken in 500 ml beaker in an ice bath and add about 20 ml conc. HCl slowly and with stirring until the solution is just neutral. Then add 7.5 ml glacial acetic acid; when anthranilic acid separates out. Filter it. Wash with cold water. Recrystallize the crude acid from hot water; filter pure anthranilic acid separates out.

Yield : The yield of anthranilic acid is 6.5 gm and M.P. is $145^{o}C$.

Experiment -10

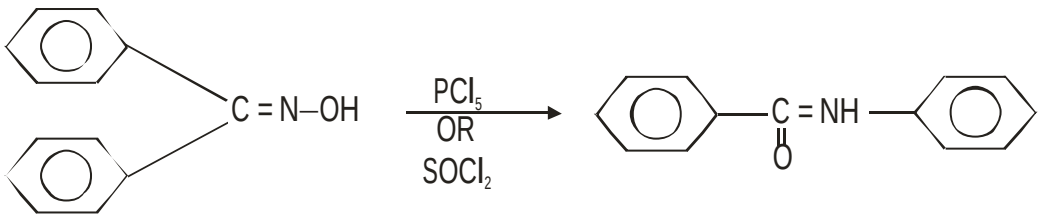
Object:

Preparation of Benzanilide from Benzophenone.

(A) First step: Benzophenone oxime from benzophenone(follow experiment 9)

(B) Second step: Benzanilide from benzophenone oxime.

Chemical reaction:



Benzophenone oxime Benzanilide

Chemical required:

(i) Benzophenone oxime – 5 gm.

(ii) Dry Ether – 25 ml.

(iii) Phosphorus pentachloride – 6 gm.

Apparatus required:

Conical flask, round bottom flask, water bath.

Method:

mix 5 gm of benzophenone oxime in 25 ml of dry ether in a 100 ml round bottom flask and add 6 gm of phosphorous pentachloride with shaking. After 15 minutes distill off the solvent on a water bath and 30 ml water to the residue. Warm the mixture for few minutes, cool and filter. Recrystallize the product from rectified spirit.

Yield: Colorless benzanilide – 6 gm. &M.P. – 163^{0}C.

Unit- 2

Isolations & Separations

Experiment -1

Object:

Isolation of casein from milk.

Chemical required:

(i) Glacial acetic acid

(ii) 0.1% NaOH

(iii) Magnesium carbonate

(iv) Fresh buffalo milk – 250 ml

Apparatus required:

2 liter beaker, Glass rod.

Method:

Mix one liter distilled water in to 250 ml milk in a 2-liter beaker and add 1 ml glacial acetic acid, due to this precipitate settles down. Decant off the aqueous layer and wash the precipitate several times with water by decantation. Transfer the precipitate to a mortar and grind it with minimum amount of 0.1% NaOH solution. Test the resultant solution with litmus paper to check that amount of NaOH solution added is just sufficient to neutralize it. Filter the resultant, suspension through cloth by pressing it hard until the liquid coming out is turbid. Acidify the filtrate again by adding glacial acetic acid so that the solution about 0.1% of it, wash the precipitate obtained by decantation with water neutralize it with just 0.1% NaOH solution and filter through muslin cloth. Repeat the method of precipitation and washing finally drain off as much water as possible from the precipitate and make a paste of it with rectified spirit again filter it, wash it first with alcohol and then with ether. Dry it in air, case in is obtained as white powder.

Yield: 7.5 gm.

Experiment -2

Object:

Isolation of nicotine dipicrate from tobacco

Materials required:

(i) Tobacco – 8 gm

(ii) Ether – 50 ml

(iii) 25% NaOH solution – 80 ml

Method:

Mix the 8 gm. of tobacco and 80 ml of 25% NaOH solution in 200 ml beaker. After 15 minutes filter the solution. Transfer the dark brown filtrate to a separating funnel and add 50 ml ether to it shake the flask thoroughly and leave it for 10 minute and allow the layers to separate. Remove the ether layer. Repeat the extraction process again using 50 ml ether. Combine the two organic layers and distill off the ether on steam bath. Transfer the residual oily portion in a porcelain dish and evaporate off the residual ether. The oily residue in the porcelain dish is nicotine dipicrate.

$Na_2S_2O_3$

Experiment -3

Object:

Isolation of piperine from black papper materials required.

Materials required:

(i) Dichloromethane – 25 ml.

(ii) Diethyl ether – 5 ml

(iii) Acetone

(iv) Hexane

(v) Black pepper – 15 gm.

Method:

Mix 15 gm of black pepper and 20 ml of dichloromethane in a 100ml round bottom flask. Attach a water condenser to the flask and allow water to run through it to condense the dichloromethane vapours while refluxing the

solution for 25 minutes. After the cooling the flask, use vaccum filtration with a buchner tunnel.

Transfer the filtrate to a 50ml round bottom flask and using a sand bath to remove the dichloromethane until dark brown oil is left. Cool the oil in an ice bath and add 5 ml of Ether. After stirring for 10 minutes, remove the solvent again via sand bath heating. Cool the oil in an ice bath and add 5 ml of ether again. Allow the flask for 15 minutes in an ice bath with occasional stirring. Using the filtration the yellow piperine crystals obtained.

Experiment -4

Object:

Isolation of carotene from carrots.

Meterial required:

(i) Carrot – 500 gm.

(ii) Methyl alcohol – 10 ml.

(iii) Benzene – 20 ml.

(iv) CCl_4 – 750 ml.

(v) Anhydrous sodium sulphate

Method:

Almost 500 gm of carrot cut into thin strips and then leave for two days. Due to this water remove fromit. Powder the dried carrot strips in a pastel mortare and then transfer it in a 2 liter round bottom flask. Add 750 ml CCl_4 and shake the flask vigorously. Heat the flask on water bath for 5 minutes. Filter the yellow filtrate and store separately.

Repeat the extraction process twice each time using 750 ml of CCl_4. mix the three organic layers and pour in separatory funnel containing 600 ml water. Mix the flask and remove the lower CCl_4 layer and dry over anhydrous sodium sulphate. Filter the solution and transfer it in a round bottom flask and distill off the solvent on steam bath. Transfer the dark oily residue to porcelain dish, now add 5ml benzene to it and evaporate it on water bath. Due to this CCl_4 Completely removed. Now add almost 15 ml of benzene and heat on water bath to get clear solution. Cool the solution and add 5 ml methyl alcohol. Now collect the crystal of carotene.

Experiment -5

Object:

Isolation of lycopene from tomatoes.

Material required:

(i) Methyl alcohol – 1200 ml

(ii) CCl_4 - 400ml

(iii) Anhydrous sodium sulphate

(iv) Tomato paste – 600 gm.

Method:

Mix 600gm of tomato paste and 750 ml of methyl alcohol in a 2 liter conical flask. Shake the mixture vigorously and then filter the thick suspension on a Buchner funnel. Transfer the dark red lake to the 2 liter round bottom flask while discarding the yellow filtrate. The dark red lake is returned to the flask and shaken with a mixture of 400ml of methyl alcohol and 400ml CCl_4. The stopper of the flask must fit well and should be lifted for moment after mixing in order to release any pressure. Heat the flask on water bath for 5 minutes and then cooled to room temperature. The suspension is shaken for 20 minutes and separated by filtration on a large Buchner funnel. The filtrate consists of a lower, very dark red, carbon tetrachloride phase and an orange aqueous methyl alcohol layer. Repeat the extraction process twice each time with 450ml of CCl_4 and 300 ml of methyl alcohol as described and the suspension is filtered. The filtrates are combined. The methyl alcohol layer is transferred to a separatory funnel. Add the 500 ml water due to this in upper phase white emulsion appeared. If the emulsion is reddish, it is stirred with a glass rod. Until the droplets of CCl_4 join the lower layer. The phases are separated. The lower CCl_4 layer is separated and dried over anhydrous sodium sulphate. The extract is then poured through a folded filter paper into a round bottom flask. The solution is transferred to 100 ml capacity using a few ml CCl_4 to rinse the larger flask. The solvent is then removed completely, leaving a dark oily residue which is diluted with benzene and evaporated again in order to remove the CCl_4 completely. The partly crystalline, dark residue is transferred quantitatively with benzene in erlen meyer flask. A clear solution is obtained by immersing the flask in a hot water bath. Boiling methyl alcohol is added using droper. Crystal of crude lycopene begins to appear immediately.

Experiment - 6

Separation of Solid –Solid Organic Mixture

The mixtures of organic solids may contain two or more components although the former type i.e. those containing only two organic solids are the most common ones. The separation of these mixtures, as of course of any other type of mixture also, cannot be always achieved by following a set of procedures without modifications. Hence, the first step in separation of these mixtures is the preliminary investigation of the mixtures itself which provides useful clue regarding the ideal method for separation.

(a) Preliminary Investigations

(i) **Physical properties.** Observes the colour, smell and if possible the crystalline form.

(ii) **Test for elements,**

(iii) **Ignition test.** Place a small amount of substance on nicket spatula or in the porcelain dish. Heat gently and then strongly. Observe the inflammability i.e., whether it burns with a smoky or non-smoky flame; and whether it melts or decomposes; and whether a metallic residue is left or not.

(iv) **Solubility tests,** Observe the solution of the mixture in water both cold and hot and see if the components are soluble or in-soluble. Whether one of them is soluble or not.

Besides water observe the solubility of the mixture in (a) $NaHCO_3$ solution, (b) NaOH solution, (c) HCl solution, and (d) Organic solvents.

As most of the separations of organic mixtures are based on the differences in the solubilities of individual components, these solubility determinations must be done carefully. If one of the components is soluble or insoluble in one of the above solvents, then some inference to its possible class be made in consultaion with in which separation of organic compounds into various solubility groups has been presented.

(v) Functional group tests. Perform the test for various functional groups including unsaturation. Also tests for additional functional groups if N, S or halogen is prsent in the mixture.

A close scrutiny of the results of these preliminary investigations will provide useful clue to the suitable method or its modification which may be used for the separation of organic mixture.

(b) Separation of Mixtures containing Two Organic Solids

Depending on the solubilities in water of the organic compounds present in the mixture one of the three methods described below must be used.

(i) If both the components are insoluble in water then chemical method may be used.

(ii) If both the components are soluble in water then the solvent extraction method using organic solvents may be used.

(iii) In case one of the components is soluble in water (cold or hot) then separation may be achieved by shaking the mixture with excess.

Table – 1

Classification of organic compounds on the basis of solubility

1.	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**
Soluble in both ether and water	**Soluble in water but insoluble in ether**	**Soluble in 5% sodium hydroxide solution**	**Soluble in 5% hydrochloric acid**	**Not containing N or S. Soluble only in concentrated sulphuric acid**	**Not containing N or S. Insoluble in concentrated sulphuric acid**	**Neutral compounds containing N or S**
The lower member	Polybasic acid and hydroxy	Acids, Phenols, Imides.	Primary amines. Second	Unsaturated hydroca	Saturated aliphati	Nitro compounds

s of the homologous series of: Alcohols; Aldehydes; Ketones; Acids; Esters; Phenols; Anhydrides; Amines: Nitriles; Polyhydroxy-phenols.	acids. Glycols, polyhydric alcohols, polyhydroxyaldenhydes and hetones(sugars). Some amides, amino acids, di-and polyamino compounds, amino alcohols, Sulphonic acids, Sulphinic acids, Salts.	Some primary and secondary nitro compounds; oximes, Thiols and thiophenol. Sulphonic acids, Sulphinic acids, aminosulphonic acids and sulphonamides, Some diketones and β – ketoexters.	ary aliphatic and aryl-alkyl amines. Aliphatic and some aryl-alky tertiary amines. Hydrazines.	bons. Some polyalkylated aromatic hydrocarbons. Alcohols. Aldehydes, Ketones. Esters, Anhydries. Ethers and acetals. Lactones. Acyl halides.	c hydrocarbons. Cycloalkanes. Aromatic hydrocarbons. Halogen derivatives of the above hydrocarbons. Diary ethers.	(tertiary). Amides and derivatives of aldehydes and ketones. Nitriles. Negatively substituted amines. Nitroso, azo, hydrozo and other intermediate reduction products of nitro compounds. Sulphnes, sulphonamids of secondary amines,

						sulphides, sulphates and other sulphur compounds.

Water (cold or hot). On filtration, the insoluble component is recovered as residue while the soluble component passes into the filtrate. The filtrate is evaporated on a water bath when solid component is obtained as residue.

When trying to arrive at a suitable method for separation only small amounts of mixture should be used. Once the method of separation becomes known then the entire mixture can be separated following the most suitable method.

By following one of these schemes it is generally possible to separate mixtures containing two solid components but if the separation cannot be achieved by either of them, then a suitable modification of these schemes may be adopted.

While separating the mixture into individual components care must be taken to ensure that the separation is complete. Otherwise, the identifications of separated compounds will become impossible due to interferences from other components which may be present in smaller or larger amounts.

It has been observed that sometimes both the components are sparingly soluble in a particular solvent. Therefore on treatment of the mixture with that solvent, it may appear that one of the component has dissolved whereas only a part of the mixture dissolves and consequently on evaporation of the filtrate instead of pure compound only the mixture is obtained. In such cases the preliminary investigations of the mixture are very useful as they help in knowing, besides other things, the types of functional groups present in the mixture. It is unlikely in most cases that all these functional group test will be shown by both the components obtained on separation as would be the case if separation is only partial or incomplete. In such cases, it is desirable that separation be done by using some other solvent which may effect complete separation. Another criterion of the purity of separated component is usual, i.e., all pure substances possess sharp and well- defined m.p's. Hence determination of the m.p. of the

separated components may also give an idea regarding the efficiency of separation.

A few examples of separation of mixtures containing two components are given here to illustrate the application of the principles of separation.

Example 1

Separation of a mixture of anthracene and p- bromobenzoic acid. On preliminary investigations, it will be observed that mixture is almost insoluble in water, that bromine is present and a —COOH group is also present.

As the mixture contains carboxylic group, hence is separation is likely to occur with $NaHCO_3$ solution (Chemical method). Hence, first take a portion of mixture in a test – tube and to this add sufficient $NaHCO_3$ solution when the NaHCO3 and the acidic component will go into solution.

Filter it and wash the residue with $NaHCO_3$ solution to dissolve any remaining acidic component. Finally, wash with water and dry when anthracene is obtained as component 'A'.

Acidify the filtrate with dilute HCl adding only small amounts of HCl at a time. When the effervescences cease to occur a white precipitate of p-bromobenzoic acid will be obtained . Filter it, wash with cold water and dry when p-bromobenzoic acid is obtained as component 'B'.

Once it is established above scheme is successful for separation of the mixture, then, the entire mixture can be separated using excess $NaHCO_3$.

Example 2

Separation of a mixture of diphenyl and phenylacetic acid. Preliminary investigations of the mixture will reveal that mixture is partly soluble in hot water and contains a carboxylic group.

Boil a small portion of the mixture with water and filter while hot. As both the components are low melting on boiling with water an oily residue will be obtained. Wash the residue with hot water and then with cold water when it solidifies. Dry it and test for diphenyl. Allow the filtrate to cool when phenylacetic acid being insoluble in water separates out. Filter it, wash without cold water, dry and test for phenylacetic acid.

Another method that can be employed successfully for the separation of this mixture is a chemical method. To a solution of $NaHCO_3$ in water, add a small portion of mixture when phenylacetic acid dissolves with effervescences. Filter

and wash the residue first the $NaHCO_3$ solution and, then, with water when pure diphenyl is obtained as component 'A'. To the filtrate add dilute HCl in small portions when phenylacetic acid predipitates out. Filter, wash with portions when phenylacetic acid phenylacetic acid.

Example 3

Separation of a mixture of phenanthrene and p-anisidine. Preliminary investigation of the mixture will show that it is insoluble in water, contains nitrogen and a primary amino group.

It will be observed that it is not possible to separate the mixture by using water, $NaHCO_3$ solution or NaOH solution. Hence, treat a small portion of mixture with sufficient dilute HCl, shake and warm slightly. Filter and wash the residue first with dilute HCl and then with water when phenanthrene is obtained as insoluble when p-anisidine separates out as precipitate, filter it, wash with water and dry.

Experiment -7

Separation of Liquid –liquid organic mixture

(a) If the liquids are immiscible they will form separate layers and therefore can be easily separated with help of a separating funnel.

(b) If the liquids are miscible with each other, then, they can be separated either by fractional distillation or by a chemical method.

In fractional distillation, the liquid with lower boiling point will distil over first leaving behind the liquid with higher boiling point. The distillate is collected which is one component and the redicual liquid in distillatin flask is the other component which can also be distilled at its boiling point and collected in pure form.

In chemical method it is essential to have some idea of the class of organic compounds to be separated. Hence preliminary investigation must be carried out to find if one of the component is an acid or base and then suitable procedure devised for its separation. The chemical method is illustrated here by taking a few examples.

Example 1

Separation of liquid mixture of toluene and o-toluidine. Treat the liquid mixture with excess dilute HCl when the o toluidine reacts with it to form

water soluble hydrochloride which, the, passes into aqueous layer. The toluene forms separate oily layer and the two layers are separated with the help of separating funnel.

The aqueous layer on treatment with dilute NaOH solution regenerates free o toluidine. Add sufficient ether (about 20-25 ml) to dissolve it, shake and transfer the liquids to a separating funnel. Reject the aqueous layer and evaporate the ether layer slowly to obtain pure o-toluidine.

Example 2

Separation of liquid mixture of an ether and hydrocarbon. To the liquid add sufficient amount of conc. H_2SO_4 in cold and shake when ether dissolves in conc H_2SO_4 leaving hydrocarbon to form separate layer. The two layers are separated with the help of a separating funnel. The H_2SO_4 layer on dilution with water regenerates free ether which forms a separate layer and can be separated easily.

Example 3

Separation of liquid mixture of an acid and some other water insoluble liquid. Add excess saturated sadium bicarbonate solution to the liquid mixture when acid reacts with $NaHCO_3$ and goes into aqueous layer while the other component forma a separate layer. These layers are separated by using a separating funnel. To the aquecous layer add excess dilute HCl and transfer it to a separating funnel. Add sufficient ether (about 25 ml), shake well and separate the ether layer which on slow evaporation leaves behind the acid. In case, the acid is not recovered on evaporating of ether layer, carry out the distillation of aqueous layer to obtain the acidic component.

3. Separation of mixtures of organic solid and liquid

(a) If one of the component is a solid and other a liquid then, advantage is taken of the difference in th volatility of the two components and separation can easily be achieved by distillation. One heating the liquid distills over leaving behind the solid residue.

The other method that can be employed is the chemical method based on the principle described under liquid mixtures. A few examples are given here.

Example 1

Separation of mixture of o-cresol and benzoic acid. To the mixture add excess saturated $NaHCO_3$ solution when benzoic acid forms sodium salt. To the resultant solutin add sufficient ether, shake and separate the two layers.

The ethereal layer on slow evaporation yields o-cresol. While the aqueous layer is first acidified with dilute HCl and then shaken with sufficient ether and the two layers separated. The ethereal layer on evaporation leaves behind acid as residue.

Example 2

Separation **of mixture of benzene and o-toluidine.** To the mixture add excess dilute HCl solution when o-toluidine forms the hydrochloride which passes into aqueous layer while benzene forms a separate layer. The two layers are separated.

The aqueous layer is treated with dilute NaOH solution when solid p-toluidine separates out. It can then be obtained by simple filtration or by extraction with ether.

(c) If the solid forms a suspension with the liquid then it can be easily separated by simple filtration but it must be confirmed that the liquid does not contain any dissolved solid component. In case solid component is even slightly soluble then though the pure solid compound can be obtained by filtration yet for obtaining the pure liquid component either the distillation or the chemical method will have to be applied.

Unit -3

Preliminary Examinations and Detection

Experiment - 1

Preliminary Examinations and test of unsaturation

(1)Preliminary Examinations

The following physical properties of the compound should be investigated.

(i) **Physical state.** Whether the compound is a liquid or solid, and if solid whether it is crystalline or amorphous. Similarly if liquid whether it is mobile or viscous. The list of compounds and their specific tests are arranged in this text on the basis of the fact that whether they are solids or liquids. Very few common organic compounds are amorphous solids and if the substance is amorphous it is unnecessary to apply tests of crystalline compounds for identification. In case of liquids their densities are helpful. Thus whether a water-immiscible liquid is lighter than or heavier than water may be useful in its identification.

(ii) **Colour:** The colour of the compound must be observed carefully. According to the theory of colour and chemical constitution' for a compound to be coloured presence of chromophoric groups (generally speaking groups with multiple linkages) is essential. Therefore if it is colourless or white in colour then the absence of these chromophoric groups is indicated. Similarly if the compound is coloured then depending on the colour some guess can be made about the class of compounds. Thus nitro compounds are yellow or orange in colour except few simple compounds are red, orange, brown or violet in colour. Some ketonic compounds like quinones, benzil, benzoin etc. and compounds lik anthracene, iodoform, iodoform etc. are yellow in colour. However the colour of the compound can be very misleading also. Many organic compounds described in the various dark colours on exposure to air or light. For example aromatic amines and phenolos are generally colourless or light. For coloured substances but one exposure to air, light and

moisture they acquire very dark colours. For this reason the colour of same compound given to student in practice and in the examination may not always be same.

(iii) Odour: Although there is no distinct relationship between the odour of organic compounds and their structures, yet in general aromatic compounds are associated with characteristic smells. There are many exceptions to this with many aromatic compounds being almost odourless and aliphatic compounds like alcohols, aldehydes, ketones and acids possessing characteristic or pungent smells. Many organic compounds possess such distinct smells that they many be even identified on its basis. For example odour of vanilla of vanillin, odour of thyme of thymol, odour of winter green of methyl salicylate are all very cahracteristic of these compounds. As a group isocyanides possess a very foul characteristic odour, aromatic aldehydes and nitro compounds may possess the smell of bitter almonds, aliphatic acids and acid halides possess pungent and penetrating smells. Similarly smell of DDT, iodoform, naphthalene etc. is very characteristic and gives a valuable clue to their identification. Sometimes an impurity may be responsible for the particular smell of the compound. Also, except in cases of very distinct smell the sense of smell varies greatly from person to person and hence much reliance cannot be placed on the smell for the identification of compound.

(iv) Solubility: The solubility of an organic compound in various solvents depends to some extent on the natures and structures of both the compound and solvent. According to the concept of like dissolves like, the compounds are soluble in solvents having structures similar to that of the compound but there are exceptions to this also. In general the solubility of organic compound gives valuable information regarding its chemical nature.

Aromatic hydrocarbons are immiscible and lighter than water but halogen compounds, aromatic nitro compounds, aromatic aldehydes etc. are immiscible and heavier than water.

The solubility of organic solids should be determined in various solvents like water, alcohol, ether etc. and also in dilute sodium hydroxide, dilute hydrochloric acids and concentrated sulfuric acid.

These observations are useful in revealing the chemical nature of the compound. Thus acids are soluble in either cold or hot water, alcohol and ether; polyhydric alcohols and carbohydrates are soluble in water but insoluble in ether; salts are soluble in water but insoluble in ether; hydrocarbons are insoluble n water but soluble in ether. Similarly compounds insoluble in water but soluble in sodium hydroxide must be acidic (either acids or phenols) and soluble in hydrochloric acid must be basic (amines etc.)

Ignition test. The organic compound is placed on a nicked spatula or metallic coin which is then heated at first slowly and then strongly in a burner flame. If the compound burns with a non-smoky flame it is an aliphatic compound but if it burns with a sooty or smoky flame it may be an aromatic compound. All aromatic compounds due to excess percentage of carbon in their molecule burn with a smoky flame whereas most aliphatic compounds burn with non-smoky flame with the exceptions of chloroform, chloral hydrate and ethyl acetate which burn with a smoky flame.

If on complete ignition of the compound a residue is left then the organic compound also contains a metal. This residue should be dissolved in dilute hydrochloric acid and tested for metals like sodium, potassium, calcium etc. by application of flame test technique or simple inorganic qualitative analysis.

At the time of ignition when the compound has started burning remove it from the flame, allow it to burn outside the flame, observes (i) if the compound melts, burns, boils, sublimes or decomposes; (ii) if the vapours are inflammable of not; (iii) if the vapours possess any particular smell (caution. The vapours may be poisonous). These may provide some due to the identity of the compound, thus a smell of burnt sugar or a charred residue indicates the probability of carbohydrates any dhyroxy acids.

Other tests employed for distinction between aromatic and aliphatic compounds are (i) nitration test and (ii) Le Rosen test.

Nitration test. To 1 gm. or 1 ml, of organic compound is a test but add 2 ml. conc. HNO_2 and 2 ml. conc. H_2SO_4. Heat the tube carefully for about 5 minutes, cool and then pour in excess cold water. If a yellow

oily liquid or solid separates the compound is an aromatic compound otherwise aliphatic.

Le Rosen test. To about 0.2 gm. or 3-4 drops of organic compound add 3-4 drops of formaldehyde solution and 5 ml. conc. H_2SO_4. Shake and warm gently. If a red, orange, violet or green colour or precipitate is produced then the compound is aromatic but if no colour change occurs the compound is aliphatic.

Melting and boiling points

Sometimes it may be necessary to obtain corrected melting or boiling point of the substance. In the determination of melting points of the solids and boiling points of the liquids only a part of thermometer (its bulb and adjoining stem) is maintained at the temperature of m.p. or b.p. whereas rest of it including the mercury thread is exposed to a much lower temperature.

(2) Test of Unsaturation

To find out if the compound is unsaturated following two tests are applied:

(i) Baeyer's test. To a solution of small amount of the compound in either water or alcohol add Baeyer's reagent (dilute alkaline $KMnO_4$ solution) drop by drop and with continuous shaking. If the purple colour of $KMnO_4$ disappears compound may be unsaturated. Add $KMnO_4$ solution till a light colour persists and allow the solution to stay or 1-2 minutes. If the colour of $KMnO_4$ is discharged again then the compound is unsaturated but if the colour persists the compound may be saturated.

(ii) Bromine decolourisation test: Dissolve a small amount of substance in 2 ml. CCl_4 and to this add 5 per cent solution of bromine in CCl_4 drop by drop and with shaking. If the brown colour of bromide disappears then the compound is unsaturated.

Classified on the basis of presence of absence of nitrogen, sulphur or halogens. With the functional group or groups known the next step is the find out the nature of compound i.e. whether aliphatic or aromatic generally be ignition, and determination of its boiling or melting point.

When all these things i.e. elements, functional groups, boiling or melting point and nature (aromatic or aliphatic) of the compound become known then the appropriate list of the compounds, (each of which is arranged in this text according to the order (i) aliphatic liquids, (ii) aliphatic solids, (iii) aromatic liquids and (iv) aromatic solids) is consulted. If the boiling or melting point (as the case may be depending on whether the substance is liquid or solid) of the compound corresponds to or is near that of one or more of the compounds described in the list, then the specific tests given therein are applied. In case the compound responds to the specific tests given under a particular compound in the list then this is the compound.

The Identity of the compound is finally confirmed by the preparations of suitable derivatives. For each type of compounds a number of derivatives with their m.p. are listed under specific tests and their methods of preparation are given at the end of each chapter describing the type of compounds. The m.p. of the derivative is determined and if this is identical to the m.p. of the derivative listed then the identity of the compound is confirmed. The preparation of the derivative is very essential for unambiguous identification of the compound particularly in cases where two or more compounds of the same class have their boiling or melting points within a range of $\pm 5^{\circ}$ of the compound. The requirements of suitable derivatives are (i) it must be a solid, easy to prepare and purify, (ii) the m.p. of the derivative must be definitely different from the original compound at least by nearly 20^{0}, (iii) the other compounds of the same class should also be capable of forming similar derivatives i.e. the derivative should preferably be prepared by a general reaction. Although strictly speaking, the preparation of the derivative and its significance does not come under the preliminary investigations but it has been dealt here in brief for the sake of continuity of the subject and the convenience of students.

Experiment -2

Detection of elements

Detection of Carbon and Hydrogen

As mentioned earlier also, it is not necessary to test for these elements, as their presence must be taken for granted. Nevertheless, if required, they may be detected by mixing the compound intimately with freshly ignited cupric oxide in 1:2 ratio in a hard glass tube fitted with a delivery tube having a bulb.The other end of delivery tube dips in lime water contained in a test tube. The mixture is heated strongly when carbon of the compound is converted to CO_2 and hydrogen to water. Water formed condenses in the form of droplets in the bulb and if desired can be tested by placing anhydrous $CuSO_4$ (white in colour) in the bulb of delivery tube which will turn blue if water is formed in the reaction. The CO_2 produced turns lime water in the test – tube milky.

$$C + 2CuO \rightarrow CO_2 + Cu; \quad \underset{\text{Lime water}}{CO_2 + Ca(OH)_2} \rightarrow \underset{\text{Insoluble (milky)}}{CaCO_3} + H_2O$$

$$2H + CuO \rightarrow H_2O + Cu; \quad \underset{\text{Water}}{5H_2O + CuSO_4} \rightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}$$

Detection of oxygen

Like carbon and hydrogen it is also not necessary to detect the presence of oxygen in the compound which may or may not be present. If necessary, it may be detected by following test.

Ferrox Text. A small amount of substance is dissolved in either benzene or toluene or a hydrocarbon and to this solution is added a strip of ferrox test paper (filter paper strip dipped in ferrox reagent and dried). If the solution becomes deep red the presence of oxygen in the compound is indicated.

The ferrox reagent is prepared by dissolving 1 mg potassium thiocyanate (KCNS) in 10 ml methyl alcohol and 1 gm $FeCl_3$ separately 10 ml methyl alcohol. The two solutions are mixed and the precipitate of KCl is removed by filtration. The filtrate contains a complex $Fe^{+3}[Fe(CNS)_4]^{-3}$ known as ferrox reagent.

Detection of Nitrogen, Sulphur and Halogens

The most important method for the detection of these elements was first introduced by J.L. Lassaigne in 1843 and is known as Lassaigne's test. Even after 134 years there is no better substitute and this is the most widely used test. The principle of this test is that on fusion with sodium the elements present in organic compounds are converted to ionic salts. Thus nitrogen in presence of

carbon (which in invariable present) gets converted to cyanide ions, sulphur to sulphide ions and halogens to halide ions. These ions are then tested in usual manner.

$$\overline{N} + C + Na \rightarrow \underset{(Sodium\ cyanide)}{NaCN}$$

$$S + 2Na \rightarrow \underset{(Sodium\ sulphide)}{Na_2S}$$

$$X(Cl,\ Br\ \text{or}\ I) + Na \rightarrow \underset{(Sodium\ halide)}{NaX}$$

Sometimes, when nitrogen and sulpher both are present in the compound, and the fusion is incomplete, sodium sulphocyanide is formed.

$$N + S + C + Na \rightarrow \underset{(Sodium\ Sulphocyanide)}{NaCNS}$$

(i) Preparation of Lassaigne's filtrate (sodium extract). A small piece of sodium (about half the size of a pea) is freshly cut and dried between the folds of filter paper. It is then introduced in an ignition tube held with a tong and the ignition tube is heated carefully and slowly by keeping it just above the flame of the burney. It will be noticed that that the sodium melts to form a shining globule like mercury. At this stage the ignition tube is removed from the flame and a very small amount (about 0.1 gm for solids and 2-3 drops for liquids) of the organic compound is added to it when an immediate reaction with sodium is observed. Allow the brisk reaction to subside and then insert a small piece of sodium (about half the size of piece used earlier) in the ignition tube. The ignition tube is then gently heated by keeping it just above the flame for a few seconds and as the reaction gains momentum it is removed from the flame. The process is repeated several times. Finally it is heated first over a low flame and then strongly for about 5 minutes. The tube will become red hot and probably start melting but continue heating for the time specified. Plunge the red hot ignition tube into 10 ml distilled water taken in a porcelain dish and crush any unshattered portion tube with the help of a glass rod. The contents of the porcelain dish are then boiled for a few minutes and filtered. The filtrate is known as Lassaigne's filtrate or sodium extract.

(ii) Test for nitrogen: To 2 ml of sodium extract add 2 ml freshly prepared solution of $FeSO_4$ when a green precipitate should be obtained. In case no green precipitate is obtained add NaOH solution till a green precipitate persists and boil the mixture. Cool and then

add dilute HCl or H_2SO_4 till the green precipitate of ferrous hydroxide dissolves. If a blue or green colour or precipitate is obtained the presence of nitrogen is confirmed.

The sodium cyanide formed as a result of fusion reacts with ferrous hydroxide formed by the reaction of ferrous sulphate with NaOH to form sodium ferrocyanide.

$$FeSO_4 + 2NaOH \rightarrow \underset{\text{Green Precipitate}}{Fe(OH)_2} + Na_2SO_4$$

$$Fe(OH)_2 + 2NaCN \rightarrow Fe(CN)_2 + 2NaOH$$

$$Fe(CN)_2 + 2NaCN \rightarrow \underset{\text{(Sodium Ferrocyanide)}}{Na_4Fe(CN)_6}$$

When the alkaline ferrous salt solution is boiled some ferric ions are produced by the action of air on ferrous salts and on acidification with dilute acid the hydroxides of ferros and ferric dissolves and the sodium ferrocyanide reacts with ferrictions to produce ferric ferrocyanide having a Prussian blue colour. But because a very small amount of this complex is formed the solution is either green or blue in colour,

$$3Na_4Fe(CN)_6 + 4Fe^{+3} \rightarrow \underset{\text{Ferric Ferrocyanide (Prussian blue)}}{Fe_4\left[Fe(CN)_6\right]_3} + 12Na^+$$

(iii) Test for sulphur. (a) To 2 ml sodium extract add 2-3 drops of freshly prepared sodium nitroprusside solution when a violet or purple colour confirms the presence of sulphur.

$$Na_2\left[Fe(CN)_5\,NO\right] + Na_2S \xrightarrow{NaOH} \underset{\text{Sodium sulphonitro prusside (violet)}}{Na_4\left[Fe(CN)_5\,NOS\right]}$$

(b) Acidify 2 ml sodium extract with dilute acetic acid and add 1 ml of lead acetate solution when a black precipitate of lead sulphide is produced confirming the presence of sulphur.

$$Na_2S + (CH_3COO)_2\,Pb \rightarrow \underset{\text{(Black)}}{PbS} + 2CH_3COONa$$

(iv) Test for nitrogen and sulphur together. If the fusion has been incompletely carried out and both nitrogen and sulphur are present in the compound, none of the above tests for these elements are shown by the sodium extract. Instead the following test should be performed.

Acidify 2 ml of sodium extract with dilute HCl and add 2 or 3 drops of $FeCl_3$ solution when a red or blood – red colour confirms the presence of both nitrogen and sulphur in the compound.

$$3NaCNS + FeCl_3 \rightarrow \underset{\substack{\text{Ferric thio}\\ \text{cyanate(blood-red)}}}{Fe(CNS)_3} + 3NaCl$$

(v) Test for halogens. (a) Acidify 2 ml sodium extract with conc. HNO_3 and boil. Coo and add 1 ml $AgNO_3$ solution. If a white precipitate is obtained which dissolves on addition of NH_4OH then chlorine is present in organic compoud.

$$NaCl + AgNO_3 \rightarrow NaNO_3 + \underset{\text{(While precipitates)}}{AgCl}$$

If a yellowish white precipitate is obtained which partially dissolves on addition of NH_4OH then bromine is present.

$$NaBr + AgNO_3 \rightarrow NaNO_3 + \underset{\text{(Yellowish white)}}{AgBr}$$

If a yellow precipitate insoluble in NH_4OH is obtained then iodine is present.

$$NaI + AgNO_3 \rightarrow NaNO_3 + \underset{\text{(Yellow)}}{AgI}$$

(b) However due to the minute amount of the precipitate it is often not possible to distinguish between yellow and white precipitates. Further, more than one halogen may be present in the compound. Hence the usual chloroform test is applied for distinction between the halogens.

Acidity 2 ml sodium extracts with conc. HNO_2 and boil. Cool, add 1 ml chloroform or CCl_4 and chlorine water in excess. Shake the solution.

If the chloroform layer becomes violet the presence of iodine is confirmed.

If the chloroform layer becomes yellow presence or reddish brown the presence of bromine is confirmed.

$$2NaI + Cl_2 \rightarrow 2NaCl + I_2$$

$$2NaBr + Cl_2 \rightarrow 2NaCl + \underset{\text{(Orange or brown)}}{Br_2}$$

To test for bromine in the presence of iodine, the chloroform test is performed as described above when the layer of chloroform turns violet due to the presence of iodine. To this add excess chlorine water and snake thoroughly when the violet colour will disappear due to oxidation of iodine to iodate. One

continuous shaking if the chloroform layer remains colourless then the bromine is absent.

$$2NaI + Cl_2 \rightarrow 2NaCl + \underset{(Violet)}{I_2}$$

$$I_2 + 5Cl_2 + 6H_2O \rightarrow 10HCl + \underset{\substack{\text{Iodic acid} \\ (\text{Colourless})}}{2HIO_3}$$

$$2NaBr + Cl_2 \rightarrow 2NaCl + \underset{\substack{(\text{Colourless orange} \\ \text{or brown})}}{Br_2}$$

To test chlorine in the presence of iodine and bromine take 2 ml sodium extract in a test tube and add 2 ml concentrated HNO_3. Boil the solution till the evolution of violet or brown coloured vapours continues. Cool and add 1ml $AgNO_3$ solution when a white precipitate soluble in NH_4OH confirms the presence of chlorine also.

Experiment -3

Determination of functional group:

Nature of Organic Compound:

Before proceeding for the tests of functional groups it is advisable that the nature of the organic compound, i.e.whether the compound is acidic, basic, neutral or phenolic may be known. This is done as follows:

(a)For substances acidic in nature

(i) To 0.1 gm. or 3- 3 drops of the organic compound add 1 ml. of distilled water shake and observe whether it is soluble, partly soluble Or insoluble, If soluble, test with litmus paper. If blue litmus paper turns red the organic compound may be an acid or phenol.

(ii) To 0.1 gm or 2.3 drops of the organic compound add $NaHCO_3$ solution. Observe the effervescence and filter. To the filtrate add dilute HCl till acidic. Shake well and observe. If no precipitate then it may be .aliphatic acid such as *succinic acid, oxalic acid etc.* If by adding dilute HCl precipitate appears then it may be an aromatic acid such as *benzole acid, cinnamic acid, phihalic acid* etc.

(b) For substances basic in nature

(i) Treat 0.l to 0.2 gnl. of a few drops of the organic compound with 10% dilute HCl. The compound dissolves. Add NaOH solution drop by drop till alkaline, precipitate or oily layer appears. The substance may be

basic in character, *e.g.,* aromatic such as *aniline, tolitidines, naphthylamines* etc.

(c) For substances phonelic in nature

If the compound turns blue litmus paper red but does not give any effervescence with $NaHCO_3$, then for such a substance add dilute NaOH solution to 0.1 to 0.2 gm. (or 0.2 to 0.3 ml) of the substances, shake well. If the substance dissolves fully or partly (or formation of oily layer) and reprecipitated by dilute HCl, then the substance may be a phenol such as phenol,α- naphthol, cresols etc.

(d)For substances neutral in nature

If tests given under *A, B* and *C* are negative then the compound belongs to this class, *i.e.,* it is said to be a neutral compound. It may be hydrocarbon, alcohol, aldehyde, ketone, ester, ether, carbohydrate etc.

Classification of Organic Compounds

After detection of the elements and having known the nature of the given organic compound sufficient hint for the possible functional group is available. These functional groups can be broadly classified as follows:

Group I

Elements present: C, H, (O)

Nature of organic compound	possible group
Neutral	Hydrocarbons, Alcohols, Aldehydes, Ketones, Esters, Ethers, Carbohydrates
Acidic Phenolic	Carboxylic acids
Phenols	Phenols

Group II

Elements Present: C, H, (O), N

Nature of organic compound	possible group
Neutral	Amides. Anilides, Nitro compounds
Basic	Primary, Secondary and Tertiary amines, Nitro anilines
Acidic	Amino acids, Nitro carboxylic acid, Nitro phenols

Group III

Elements Present: *C*, H, (O), Halogen

Nature of organic compound	possible group
Neutral	Halogen hydrocarbons
Acidic	Halogen carboxylic acids

Group IV

Elements Present: C, H, (O), S

Nature of organic compound	possible group
Neutral	Thiomides
Acidic	Amino aromatic sylphonic acids

Test for some individual Functional Groups

Having known the possibility of the functional group present, make the systematic tests for their detection as follows:

(1) For acid (-COOH group)

(i) Put a drop of aqueous solution of the original substance on a piece of blue litmus paper. It turns red.

(ii) Add 1-2 ml. aqueous solution of original substance (or 2-3 drops in case of liquid acid) to about 3 ml. of a 5% solution of $NaHCO_3$. Vigorous effervescence due to the evolution of carbon dioxide indicates the presence of –COOH group.

$$R-COOH + NaHCO_3 \rightarrow R-COONa + CO_2 + H_2O$$

(iii) To 0.5 gm. (or 0.5 ml.) of the substance add 1 ml of ethyl alcohol and 2 drops of conc. H_2SO_4. Heat gently for 1 to 2 minutes, cool and pour in into about 10 ml. of water. Characteristic fruity odour of an ester is formed

$$RCOOH + C_2H_5OH \xrightarrow{Conc.H_2SO_4} RCOOC_2H_5 + H_2O$$

(2) For Phenols (>C—OH group)

(i) All phenols possess characteristic carbolic odour.

(ii) All phenols are weakly acidic and aromatic.

(iii) $FeCl_3$ test: To 1 ml of the cold aqueous or alcoholic (if the original substance is not soluble in water even on warming) solution of original

substance add 1 drop of $FeCl_3$ solution-*blue, violet, red or deep-green* colouration of the solution indicates phenolic group.

(iv) Liebermann's test: To 0.5 gm. of the substance add a crystal of sodium nitrite. Heat, cool and add dilute sulphuric acid. Observe the change in colour. Dilute with water and further observe the change in colour again. The following table will give some idea of the colour changes in different media. In this reaction the indophenol is formed which gives different colouration as it acts as acid-base indicator.

Substance	Colour on adding $NaNO_2$ + H_2SO_4	Colour on dilu-tion with water	Colour on add-ing NaOH solution
Phenol	Intense blue or green	1 Red	Intense green or blue
o-Cresol	Intense blue or green	Red	Intense green or blue
m-Cresol	Intense blue or green	Brown	Dirty green
p-Cresol	Red or dirty brown	—	—
Resorcinol	Intense blue	Red	Brownish red
α-Naphthol	Intense green	—	—
β -Naphthol	Brownish black	—	

(v) Ceric ammonium nitrate test:Phenols give green or brown precipitate with eerie ammonium nitrate reagent, whereas alcohols give red colour.

The color change is due to the replacement of the nitrate group of the co-ordination complex by alcohol or phenol molecules.

$$(NH_4)_2[Ce(NO_3)_6] + 2ROH \longrightarrow [Ce(NO_3)_4(ROH)_2] + 2NH_4NO_3$$

Note—Aromatic amines also produce colour or ppt. the reagent.

Procedure—Add 3 or 4 drops of the substance or its concen-trated solution in water to 0.4 ml. of the reagent. Shake. Green or brown ppt. indicates the presence of phenol.

(3) For Alcohols (—OH group)

(i) All alcohols are neutral in reaction.

(ii) Ceric ammonium nitrate test: Add 3 to 4 drops of the substance or its concentrated solution in water to 0.5 ml. of the reagent diluted to 3 ml. Shake. Formation of red color indicates the presence of— OH group.

(iii) Take the substance in a dry test tube; add a small piece of sodium metal. Effervescence due to the evolution of hydrogen gas indicates the presence of alcohol.

(4) For Aldehydes (—CHO group).

(i) 2, 4-dinitro phenyl hydrazine test: To 2 ml. of the reagent solution add 1 or 2 drops or 0.5 gm. of substance. Shake vigorously or boil for 2 minute. A yellow or orange ppt, %how& the presence of carbonyl compounds *(aldehydes and ketones)*

$$C_6H_3(NO_2)_2 - NH - NH_2 + O = CHR \longrightarrow RCH = N.NHC_6H_2(NO_2)_2 + H_2O$$

$$C_6H_3(NO_2)_2 - NH - NH_2 + O = C\langle^{R}_{R'} \longrightarrow$$

$$\rangle^{R}_{R'} C = N.NHC_6H_3(NO_2)_2 + H_2O$$

(where R and R' are alkyl radicals.)

(ii) Schiff's reagent test—To 1-2 ml. of the Schiff's reagent add 0'2 gm. or 5-6 drops of the original substance, shake vigorously and wait for 1 -2 minutes. Do not warm or heat the mixture. A pink colour indicates presence of an aldehydic group.

Note—(1) Benzaldehyde restores the pink colour very slowly,

(2) Methyl ketones also give this test.

(iii) Tollen's reagent test: To 2 ml. of Tollen's reagent, (ammonical silver nitrate reagent) add 0.2 gm. or 4-5 drops of the original substance. Shake and warm. Black ppt. or silver mirror shows the presence of aldehydes.

* Salicylaldehyde does not give this test.

(iv) Fehling's solution test:To 2 ml. of Feeling's solution (A and B Disappearance of deep blue colour with the subsequent appearance of red ppt. indicates the presence of aldehydic group.

Note: Benzaldehyde and salicylaldehyde do not give this test.

(5) For Ketones (>C=O group).

(i) 2, 4-dinitrophenyl hydrazine test: Same as given for aldehydes.

(ii) Sodium nitroprusside test: To 2 ml. of 0-5% aqueous sodium nitroprusside solution add 0.2 gm. or 4-5 drops of the substance and then add 4-5 drops of NaOH solution. Red, purple or violet colour indicates the presence of a ketonic group.

Note: This test is given only by methyl ketones. (iii) To 0.2 gm. or 0.5 ml. of the original substance add excess of NaOH solution. Then add 0.l gm. of dinitrobenzene. Shake well. Red or violet colour shows the presence of a ketone.

Note: Only methyl and ethyl ketones give this test.

(6) For Esters (—COOR group).

(i) Phenolphthalein test: To a little of the substance in water add a drop of phenolphthalein and then a dilute Solution of NaOH drop by drop, till a pink colour appears. Now heat it. The pink colour disappears showing the presence of ester group. This pink colour is destroyed in the case of aldehydes also and is replaced by another colour.

The pink colour is destroyed due to the formation of acid as a result of hydrolysis of the ester.

$$CH_3COOR + HOH \longrightarrow \underset{\text{Acid}}{CH_3COOH} + \underset{\text{Alcohol}}{ROH}$$

(ii) Hydroxamic acid test (Feigl test)**:** To one drop of the original substance add 0.5 ml. of N solution of hydroxylamine hydrochloride in methyl alcohol and 0.5 ml. of 2N NaOH in CH_3OH. Heat to boiling. Acidify with 0-5 ml. of 2N HC1. Then add a drop of $FeCl_3$. Red-violet colour indicates

ester group. Hydroxylamine reacts with the ester to form hydroxamic acid which reacts with ferric chloride to give a red colour of ferric hydroxamate.

$$RCOOC_2H_5 + NH_2OH \longrightarrow RC0NHOH + C_2H_5OH$$

Hydroxamic acid

$$3RCONHOH + FeCl_3 \longrightarrow (RCONHO)_3Fe + 3HC1$$

Ferric hydroxaimate (red)

(7) For Carbohydrates: Carbohydrates are neutral solids, soluble or sparingly soluble in water. Most of them decompose on heating and do not show sharp melting points. Their presence can be confirmed by the following tests:

(i) Molisch's Test: To 2 ml. of the aqueous solution of original substance add 2 drops of Molisch's reagent and shake. Carefully pour about 1 ml. of cone. H_2SO_4 (contained in another test tube) down the side of the tube and allow to stand for two minutes. A red ring changing to violet red at the junction of the two layers indicates the presence of carbohydrates. On shaking, the whole mixture becomes violet-red or a dull blue-violet ppt. is formed.

(ii) Fehling's solution test: To 2 ml. of Fehling's solution add 1 ml. of the aqueous solution of the original substance and stand the test tube in boiling water for 1 minute—the whole mixture becomes red due to the formation of Ca_2O.

Note:

(1) Red ppt. is obtained in the case of glucose and fructose.

(2) The mixture remains blue, and only slightly yellowish turbidity is present if it is sucrose.

(3) No reduction takes place in the case of starch.

(4) Certain carbohydrates give yellow colouration when boiled with NaOH solution.

(iii) Tollen's reagent test**-** Take 1 ml. of Tollen's reagent solution. To this add 0.5 gm. of the original substance. Shake and warm. Formation of silver mirror for black ppt. shows the presence of aldo and keto hexoses.

Note: Sucrose does not give this test,

(iv) Seliwanoff's test ***(only for ketoses)****:* To 0.lgmof the substance add Seliwanoff's reagent. Boil, deep red colour within 2 minutes. In this test ketoses are decomposed to hydroxyl methyl furfural which condenses with resorcinol to produce a red dye.

(8) For Ethers (-O-groups)

(i) Take 1 ml. of the substance and to this cold and cone. H_2SO_4. The substance dissolves. Pour this clear solution in 3 ml. of ice cold water. The substance separates out as unchanged liquid.

(ii) To 1 ml. of the substance add 5 ml. of conc. HI. Heat it in an oil bath at 130°C. Pass the gaseous alkyl iodide thus formed into 1 ml. of alcoholic silver nitrate solution. A yellow ppt. confirms the presence of ether.

$$ROCH_3 + HI \xrightarrow{\text{Heat}} ROH + \underset{\text{Gas}}{CH_3I}$$

$$CH_3I + AgNO_3 \longrightarrow \underset{\text{Yellow PPt.}}{AgI} + CH_3NO_3$$

(9) For Aromatic Hydrocarbons:

(i) To 0.5 gm. or 1 ml of the original substance add 0.5 gm. of anhydrous $AlCl_3$, then add 1 ml. of dry chloroform. Warm gently and observe the obtained. The colors given by some of the aromatic 1 are shown in the following table.

Aromatic Hydrocarbon	Color
Benzene and its homologues	Orange yellow
Naphthalene	Blue or greenish blue
Anthracene	Green
Phenanthrene and diphenyl	Purple

(10) For Nitro Compounds: Nitro compounds may be neutral or acidic in character.

(i) To a small quantity of original substance in a test tube add about 1-2 ml. of NaOH solution. Shake well. Yellow, intense yellow or orange colour is developed.

(ii) Mullikan and Barker's Reaction: Dissolve a small quantity (0.l gm.) of the original substance in a small quantity (2 ml.) of alcohol. Add a few drops of 10% $CaCl_2$ solution (or about 0.1 gm. of NH_4Cl) and a pinch of Zn dust. Heat to boiling. Allow the reaction to proceed for 5 minutes. Nitro compounds are usually reduced to hydroxylamine derivatives. Cool, filter and to the filtrate add 2 ml. of Tollen's reagent. Reduction of Tollen's reagent to a black or grey ppt. of Ag indicates the presence nitro group in the original substance.

$$C_6H_5NO_2 + 2H \xrightarrow{Zn+alcohol} C_6H_5NHOH + H_2O$$

Phenyl hydroxyl-amine

$$C_6H_6NHOH + Ag_2O \longrightarrow C_6H_5NO + H_2O + 2\,Ag$$

Grey or black

Note: This test should not be done with those compounds which themselves reduce Tollen's reagent. For such compounds test (iii) should be applied.

(iii) Take 0.l gm. of the original substance, 0.5 ml. of cone. HC1 and 2-3 pieces of granulated tin (or 0.2 gm. of $SnCl_2$). Heat in the boiling water-bath for 3-4 minutes and shake continuously. Filter and cool under tap and test the filtrate for primary nitro group. Positive test indicates the presence of a nitro group in the original substance.

$$RNO_2 + 6H \longrightarrow R.NH_2 + 2H_2O$$

(11) For Amino Compounds: Primary amines ($-NH_2$ group). Amines are basic in character.

(a)For aliphatic primary amines.

(i) Isocyanide test: Characteristic reaction of primary amines, both aliphatic and aromatic, is the peculiar offensive odour produced, when they are warmed with chloroform and alcoholic KOH. This is due to the formation of isocyanide. The test is so sensitive that it is given by some derivatives of amines as well, which are likely to produce the base on hydrolysis e.g., the acetyl or benzoyl derivatives.

Procedure*:* To 0.5 gm. or 0.5 ml. of the substance add 1 ml. chloroform and 3 ml. alcoholic KOH, boil; very offensive; smell is obtained.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KC1 + 3H_2O$$

(ii) To 0.5 gm. or 0.5 ml. of the substance, add 2-3 ml.dil. HC1. Cool, now add saturated cold $NaNO_2$ solution drop-wise—brisk effervescence due to the evolution of nitrogen gas shows the presence of aliphatic primary amino ($—NH_2$) group.

$$RNH_2 + HCl + NaNO_2 \longrightarrow ROH + NaCl + H_2O + Na \uparrow$$

(iii) Rimini's test for aliphatic primary amino group: To 0.1 gm. or 2-3 drops of the substance add 1 ml. acetone and 1-2 drops of freshly prepared very dilute solution of sodium nitroprusside, appearance of violet-red colour within a minute shows the presence of aliphatic primary amino group.

(b) For aromatic primary amines.

(i) Isocyanide test-Perform the test as given above. Aro-matic amines also give very offensive smell due to the formation of isocyanide.

(ii) Diazotization test: To 2 drops or 0.1 gm. of the original substance add 2 ml. of water containing 1 ml. of cone. HCl Cool and add 4 ml. of $NaNO_2$ solution (3 - 5%) drop by drop frequently shaking the test tube. Pour the above clear solution in 10% causticsoda (2 ml.) containing 0.2gm. ofα- naphthol.An orange-red ppt. is obtained, if the compound is a primary aromatic amine.

(iii) To 0.5 gm. or 0.5 ml. substance, add 2-3 ml of dil. HCl and 1 ml H_2O_2 solution. Then add 2-2 drops of freshly prepared $FeSO_4$ solution, observe the colour of ppt., some aromatic amines give the following colours :

Substance	Colour of solution or of ppt.
Aniline	Bright-green
o-Toluidine	Bright-green
m-Toluidine	Bright-green
p-Toluidine	Yellow-brown

(12) For Amido group ($—C(=O)NH_2$)**:** Amides are neutral substances.

(i) Heat a small quantity of original substance with about 0.5 ml. of NaOH solution. Smell of NH_3 is detected if the original substance is an amide.

$RCONH_2 + NaOH \rightarrow RCOONa + NH_3$

Note:

(i) Ammonium salts also yield ammonia in cold.

(ii) To 0.2 gm. (or 0.3 ml.) of original substance add 1-2 ml. of dil. HCl. Add to it 2 ml. of 2-5% solution of $NaNO_2$; shake a little. Brisk effervescence due to the evolution of N_2 indicates an acid amide.

Unit – 4

Conformation of organic compounds

Experiment - 4

Conformation of organic compounds

Identification of Simple Mono functional Organic Compounds

[Containing Carbon, Hydrogen and (Oxygen)-C, H, (O)]

Carboxylic Acids:

A list of some of the compounds, which are highly acidic and discussed here, is given below:

Aliphatic*:* - Formic acid,Acetic acid,Propionic acid,n-Butyric acid, Oxalic acid

Malonic acid,Succinic acid,Glutaric acid,Adipic acid

Aromatic:-o-Toluic acid,m-Toluic acid, p-Toluic acid,Phthalic acid,Benzoic acid

(1) **Aliphatic liquids**

B.P.101°C Formic acid, HCOOH:

Miscible with water. On warming with conc. H_2SO_4 it gives CO_2 which burns with a blue flame at the mouth of the test tube. If decolourises acidified solution of $KMnO_4$, gives red colour with $FeCl_3$ solution and white precipitate with mercuric chloride solution. Its neutral solution reduces ammonical silver nitrate solution.

Derivative—Anilide M.P. 50°C, p-toluidine, M.P. 53°C.

118°C Acetic acid, CH_3COOH:

Miscible with water, possesses vinegar like smell.With neutral $FeCl_3$ a red colouration is obtained.

Derivative—Anilide, M.P. 114°C, Amide, M.P. 82°C, *p*-Toluidine, M.P. 147°C.

140°C Propionic acid, CH_3CH_2COOH

Miscible with water.

Derivative—Amide, m. p. 79°C, Anilide, m. p. 105°C, p-Toluidine, M.P. 141°C.

163°C *n*-Butyric **acid,** $CH_3CH_2CH_2COOH$

(i) Miscible with water. It is a thick liquid having a smell of rancid butter,

(ii) To 1 ml. of the original acid, add 1 ml. of ethyl alcohol and 1/2 ml. of cone. H_2SO_4. Heat. Smell of pine apple, due to the formation of ethyl butyrate, is observed.

Derivative. Amide, M.P. 114°C; Anilide, M.P. 96°C.

(2) Aliphatic solids:

101°C Oxalic acid (hydrated), $(COOH)_2.2H_2O$

Soluble in cold water

(i) Aqueous solution gives white precipitate with $CaCl_2$ solution.

(ii) It decolourises an acidified solution of $KMnO_4$ solution,

(iii) Take 0.5 gm. of the compound in a dry test tube and add 5 drops of cone. H_2SO_4 to it. Heat gently and burn the gas evolved at the mouth of the test tube. A blue flame is observed.

Derivative—Anilide, M.P. 245°C, *p*-Toluidine, M.P. 267°C.

133°C Malonic acid, $CH_2(COOH)_2$

(i) Heat a small amount of the substance in a dry tube until the solid melts and effervescence occurs (due to the formation of CO_2).

(ii) Take 0.5 gm. of the original substance in tube. Add 2 ml. of acetic anhydride and boil. Raddish yellow liquid with yellowish green fluorescence is obtained

Derivative— *p*-Nitrobenzyl ester, M.P. 8 5°C.

151°C Adipic acid

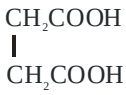
CH_2CH_2COOH
|
CH_2CH_2COOH

(i) Soluble in cold water, ether and alcohol.

(ii) Perform fluorescence test as given under succinic acid violet red colour after adding NaOH soln.

*Derivative :*Amide, M.P. 220°C, p-Nitrobenzyl ester, M.P. 106°C.

185°C Succinic acid

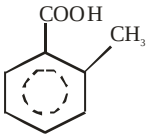


(i) Soluble in water, (ii) Mix a rice grain of the original substance with double the amount of resorcinol and 2 drops of cone. H_2SO_4. Gently heat the contents until the mixture attains a red brown colour. Cool. Add a few drops of water followed by aqueous NaOH solution till the solution becomes alkaline. Now take 1 ml. of this solution into another test tube and fill it with water. Yellow-green fluorescence.

Derivative. p-Nitrobenzyl ester, M.P. 88°C, Anilide, M.P.226°C.

(3) Aromatic solids

102°C *o*-Toluic acid

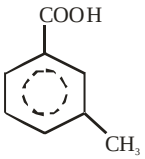


Sparingly soluble in water.

Derivative — Amide, M.P. 141°C, p-Nitrobenzyl ester, M.P.9l^{0}C.

When heated with alkaline $KMnO_4$ gives phthalic acid M.P. 195°C.

109°C *m*-Toluic acid,

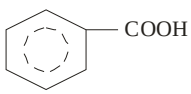


Sparingly soluble in water.

Derivative—Amide, M.P. 94°C, p-Nitrobenzyl ester, M.P.87°C.

When heated with alkaline $KMnO_4$ gives isophthalic acid, M.P. above 300°C.

121°C Benzoic acid



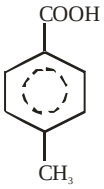
White glistening scales, sparingly soluble in cold water, readily soluble in hot water.

(i) To 1 ml, of the neutral soultion add 1 ml. of neutral ferric chloride solution. A buff coloured precipitate of ferric benzoate is obtained.

(ii) In a dry test tube heat original powder with dry soda lime. Burn the issuing vapours on the mouth of the test tube. Smoky flame due to the burning of benzene vapours is obtained.

Derivative—Amide, m. p. 128°C, Anilide, m. p. 160°C. COOH

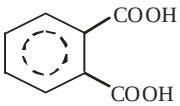
178°C *p*-Toluidine acid



Soluble in hot water.

Derivative — Amide, M.P. 158°C, Anilide, M.P. 140°C. p-Nitrobenzyl ester, m p. 104°C.

195°C Phthalic acid



Colourless prisms, sparingly soluble in cold water.

(i) Fluorescein reaction — Take 0.2 gm. of the substance in a dry test tube, add twice the amount of resorciaol and *2* drops of cone. H_aSO_4. Heat gently, until the Sjisture becomes reddish brown. Cool, add 1 ml. of aqueous NaOH solution and pour the contents in beaker containing about 50 ml. of water, An orange greenish fluorescence is observed.

(ii) Phenolphthalein test—Heat the original substance with phenol and cone. H_2SO_4 in a dry test tube. Add a drop of this solution to another test tube containing NaOH solution. Pink colour is obtained,

Derivative—Anhydride, M.P. 130°C, Anilide, M.P. 251°C, Amide, M.P. 219°C. **Alcohols:**

Some of the important alcohols, whose confirmatory tests have been given in the following pages, are listed below:

Aliphatic liquids: Methyl alcohol,Ethyl alcohol, Isopropyl alcohol,*n*-Propyl alcohol, Sec-Butyl alcohol,Isobutyl alcohol,*n*-Butyl alcohol,*n*-Amyl alcohol, Cylochexanol, Glycol, Glycerol

Aliphatic solids:*d*-Mannitol

Aromatic liquids: Benzyl alcohol, Phenyl ethyl alcohol

(1) Aliphatic liquids :

(a) O.S. Completely miscible with twice its volume of water.

B.P. 65°C Methyl alcohol, CH_3OH

Colourless liquid, characteristic odour, burns with a blue flame.

(i) Take 2 drops of O.S. in a dry test tube. Introduce red hot copper coil into the test tube. Pungent odour of formaldehyde.

(ii) Take 5 drops of the O.S. in a dry test tube. Add 3 drops of cone. H_2SO_4 and a pinch of salicylic acid.Heat gently. Cool and then pour the solution in flask containing water. Smell of oil of winter-green.

Derivative—3, 5-dinitrobenzoate&M.P. 109°C.

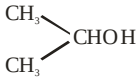
78°C Ethyl alcohol, C_2H_5OH

Colourless liquid, burns with a non-luminous flame.

(i) **Iodoform reaction**—O.S. + 2 ml iodine solution, add NaOH solution drop by drop. Deep brown colour changing to yellow and finally to give a finely divided yellow precipitate of iodoform with characteristic odour is observed.

Derivative—3, 5-dinitrobenzoate&M.P. 94°C.

82°C Isopropyl alcohol



This alcohol also gives iodoform test like ethyl alcohol.

Derivative—3, 5-dinitrobenzoate&M.P. 122°C.

97°C *n*-Propyl alcohol, $CH_3CH_2CH_2OH$

Burns with a non-luminous flame,

(i) *Iodoform test*—negative.

Derivative—3, 5-dinitrobenzoate&M.P. 73°C

(b) O S. floats on water.

100°C Sec-Butyl alcohol

Derivative—3, 5-dinitrobenzoate&M.P. 75°C.

108°C Iso-Butyl alcohol

Perform iodoform test. Generally iodoform is obtained in a minute's time.

Derivative—3,5-dinitrobenzoate&M.P.64°C.

117°C *n*-Butyl alcohol, $CH_3CH_2CH_2CH_2OH$

Does not burn.

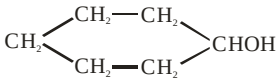
Derivative—3, 5-dinitrobenzoate&M.P. 64°C

138°*n*-Amyl alcohol, $CH_3(CH_2)_3CH_2OH$

Sparingly soluble in water.

Derivative—3, 5-dinitrobenzoate&M.P. 46°C

160°C Cyclohexanol



(i) Oxidation test:To 0.5 ml. of the O S. add 15 ml. of acidified $K_2Cr_2O_7$ solution. Heat to boiling for 5 minutes. Cool. Filter and wash the solid free from green chromium salt with cold water. Crystallise the solid from water, dry and determine the melting point. Adipic acid, M.P. 151°C is obtained.

Derivative—3, 5-dinitrobenzoate&M.P. 112°C.

197 °C Ethylene glycol,

Slightly viscous, miscible with water, sweet taste, does not burn.

Derivative—3, 5-dinitrobenzoate, M.P. 169°C.

290°C Glycerol, $CH_2OH.CHOH.CH_2OH$

Viscous, miscible with water, sweet in taste,

(i) To 2 ml. of the O.S. taxen in a dry test tube add 1.5 gms. of solid potassium hydrogen sulphate. Heat. Pungent and highly irritating smell of acrolein is observed.

Derivative—Tribenzoate, M.P. 76°C.

(2) Aromatic liquids

O.S. sinks in water.

BP. 205°C Benzyl alcohol, $C_6H_5CH_2OH$

Colourless pleasant smelling liquid.

(i) To 2 ml, of dil. HNO_3 (1 : 4) in a test tube add 1 drop of O.S. Stand the tube in boiling water for 5 minutes. Pale yellow emulsion and smell of bitter almonds (due to the formation of benzaldehyde).

Derivative—(i) 3,5-Dinitrobenzoate, m p. 112°C.

(ii) Reflux 1 ml. of O.S.+ 2 gm. of $KMnO_4$ and 30 ml. of water in 100 ml. round bottom flask shaking round periodically until purple colour disappears. Cool, filter and acidify the filtrate with cone. HC1. Filter the solid, wash with water. Crystallise with water. Dry and determine the M.P. Benzoic acid with m. p. 121°C is formed.

220°C Phenyl ethyl alcohol, $C_6H_5CH_2CH_2OH$

Odour of roses.

Oxidises to benzoic acid as given under benzyl alcohol.

Derivative—Benzoic acid, M.P.121°C.

(3) Aliphatic solids

M.P.**166°C *d*-Mannitol,** $CH_2OH[CH(OH)]_4CH_2OH$

It is readily soluble in water and insoluble in ether,

(i) To 2 ml. of aqueous $CuSO_4$ solution add dilute ammonium hydroxide till clear blue solution is obtained. Dilute by adding 25 ml of water. To 5 ml. of the solu-tion add rice grain of O.S. and shake, a precipitate is formed.

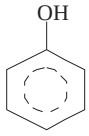
Derivative—Hexa-acetate, M.P. 119°C.

Method:To 4 ml. of acetic anhydride in a test tube, add 2 drops of cone. H_2SO_4. Pour this mixture on) gm. of O.S. contained in a small beaker. After the violent reaction stops, add 1 0 ml. of water, stir, filter off the solid. Wash it well with water, crystallize from alcohol, dry and determine M.P. 119°C.

10.3. Phenols

(i) Liquids :

B.P.**181°C Phenol**



Colourless deliquescent crystal, often coloured, due to soluble in light, characteristic carbolic odour, sparingly exposure in water, reedily soluble in ammonium hydroxide, M.P. 42°C.

(i) To one drop or 1 crystal of phenol dissolved in 15 ml. of water, add one drop of ferric chloride solution, *a,* violet colour is obtained.

(ii) *Phenolphthalein test*—Warm a few crystals of O.S. with a pinch of phtfaalic anhydride and 2 drops of cone. H_2SO_4. Cool and add NaOH solution pink colour indicates phenol.

(iii) *Liebermann's nitroso reaction*—Take a crystal of O.S. in a dry test tube. Add a crystal of sodium nitrate and pour 5 ml. of cone. H_2SO_4. Mix the contents by rotating the tube. Green or blue colour changing to red on dilution indicates phenol.

Derivative— (i) 2 4,6-tribromophenol, M.P. 93°C.

(ii) Phenyl benzoate, M.P. 68°C.

190°C *o*-Cresol, $C_6H_4(OH)CH_3$ (1 : 2), M.P. 31°C.

(i) Violet colour with aqueous $FeCl_3$ solution, green colour in alcoholic ferric chloride solution,

(ii) *Phenol'phthalaein test*—Gives a positive test like phenol,

(iii) o-Cre*sol* does not dissolve in ammonium hydroxide solution whereas phenol dissolves.

Derivative—(i) o-Cresol picrate, M.P. 88°C.

(ii) Dibromo-cresol, M.P. 56°C.

201°C p-Cresol, $C_6H_4(OH)CH_3$ (1 : 4), M.P. 36°C.

(i) Ferric chloride solution gives blue colouration in water and green in alcohol,

(ii) *Phenol phthalein test*—Negative.

(iii) *Liebermann's reaction*—In this test a red colour is obtained.

Derivative—(i) *p* Cresol benzoate, M.P. 71°C.

(ii) p-Cresol tetrabromide, M.P. 108°C.

202°C *m*-Cresol—$C_6H_4(OH)CH_3$ (1 : 3)

(i) With ferric chloride blue colouration in water and green in alcohol.

(ii) *Phenol phthalein test:* It gives a blue colouration where as phenol and *o*-cresol give red colouration.

Derivative— (i) *m*-Cresol benzoate, m p. 54°C.

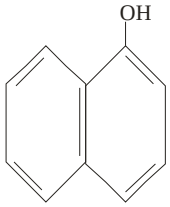
(iii) *m*-Cresol picrate, M.P. 188°C.

(iv) Tri-nitro/M-cresol, m p. 105°C.

(2) Solids

M.P. 42°C Phenol —See under liquids.

94°C α–Naphthol



$C_{10}H_7OH$

Colourless needles, sparingly soluble in water, soluble in ether.

(i) To a solution of titanic acid in cone. H_2SO_4, add a pinch of solid a-naphthol, green colour is obtained.

(ii) To the aqueous solution of a-naphthol add few drops of $FeCl_3$. White precipitate changing over to red and then to violet.

(iii) To 0.I gm. of O.S. add 10 ml. of a mixture (1 : 1) of iodine solution and NaOH. Shake. A violet colour changing to dark colour followed by a precipitate.

Derivative— (i) α -Naphthol picrate, M.P.189°C.

(ii) α -Naphthol benzoate, M.P. 56°C.

110°C Resorcinol, $C_6H_4(OH)_2$ (1 : 3)

Colourless needles, repidly soluble in water,

(i) With $FeCl_3$ violet colour in aqueous solution and green colour in alcoholic solution.

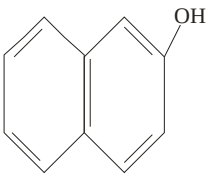
(ii) To 1 ml. of aqueous solution add an equal volume of aqueous NaOH solution and a drop of chloroform. Heat the mixture. Definite red colour appearing violet red on shaking.

(iii) Fluorescein test:To a dry test tube take a pinch of phthalic anhydride and a pinch of resorcinol. Add 2 drops of cone, sulphuric acid. Heat gently. Mixture assumes brown colour. Add NaOH solution till alkaline. Pour a small quantity of this alkaline solution in a beaker full of water. A yellow green fluorescence is observed.

Derivative— (i) Tribromoresorcinol, M.P. 11 2°C.

(ii) Resorcinol dibenzoate, M.P. 117°C.

122^{0}C β-Naphthol



Lustrous crystals, sparingly Soluble in water, faint

(i) Add 1 ml. of aqueous solution of **β** -naphthol to 1 mol. of aqueous ferric chloride solution. No colour, but white opalescence. If ferric chloride is added to alcoholic solution, green colour.

(ii) Add solid **β** -naphthol to a solution of titanic acid in cone, sulphuric acid. Red colour,

(iii) To an aqueous solution of **β** naphthol add NaOBr solution. Yellow colour. o-Naphthol under similar conditions produces violet colour.

Derivative— **β** -Naphthol benzoate, M.P. 107°C, **β** -naphthol picrate, M.P. 156°C.

132°C Pyrogallol, $C_6H_3(OH)_3$ (1, 2, 3)Colourless crystalline solid, readily soluble in water.

(i) To 1 ml. of aqueous solution add equal volume of 10% NaOH solution. Red colour turning slowly to brown,

(ii) To 1 ml. of aqueous solution add 1 ml. of ammoniacal silver nitrate solution (Tollen's reagent). An immediate grey or brown precipitate.

(iii) To 2 ml. of aqueous solution add 2 ml. of aqueous lead acetate solution, pale yellow emulsion changing over to white precipitate.

Derivative—Triacetate, M.P. 16l°C.

169°C Hydroquinone, $C_6H_4(OH)_2$ (1: 4)

Colourless crystalline solid, soluble in water.

(i) To the aqueous solution of O.S. add 2 drops of dilute ferric chloride solution. Transient blue changing over to red or reddish brown colour,

(ii) To 1 ml. of O.S. add 1 ml. of NaOH solution. Reddish brown solution,

(iii) To O.S. in water add Tollen's reagent. Immediate formation of a brown precipitate of metallic silver.

(iv) To a small quantity of the O.S. in a test tube add 2 ml. of dil. Sulphuric acid. Warm gently till the solid dissolves Cool. Add a small quantity of powdered $K_2Cr_2O_7$ solid. Immediately dark green needles of quinhydrone, are formed (M.P. 171°C).

***Derivative*—(i)** Quinhydrone, M.P. 171°C [see under test (iv)].

(ii) Hydroquinone dibenzoate, M.P. 199°C.

(iii) Hydroquinone diacetate, M.P. 120°C.

Carbohydrates

M.P. 102-10 4°C Fructose, $C_6H_{12}O_6$, $CH_2OHCO(CHOH)_3CH_2OH$

Colourless powder, soluble in cold water.

(i) To 1 ml. of aqueous solution of O.S. add 1 ml. of Benedict's solution. Heat to boiling. A red or yellow precipitate indicates a positive test.

(ii) Seliwanoff's test: To 2 ml. of cone, solution of O.S. add 2 ml of cone. HC1 and a pinch of resofcinol. Keep the tube in boiling water for 3 minutes. Deep red colour followed by a precipitate (distinction from glucose, where the colour develops after some time and is light pink).

(iii) Beredereck's test: To 2 ml. of aqueous solution of O.S. add 5 ml. of 4% solution of ammonium molybidate and 3-4 drops of glacial acetic acid. Heat in boiling water. A blue colour is formed.

(iv) In a test tube take a pinch of original substance and a small quantity of selenium dioxide. Add 2 ml. of dil. HC1. Heat in a water bath.

A red precipitate of selenium is formed. This reaction is shown by all compounds containing CH_2CO group.

Derivative — Osazone of fructose, M.P. 205°C. Osazone is formed in about 20 minutes. For the preparation of deri-vative see under the group tests for carbohydrates.

146-148 Glucose, $C_6H_{12}O_6$, $CH_2OH(CHOH)_4CHO$

Colourless powder, readily soluble in water.

(i) To the aqueous solution of O.S. add a-naphthol sol. and sulphuric acid. Violet colour *(Molisch's test).*

(ii) With Fehling's solution on heating, it gives a red precipitate.

(iv) To 1 ml. of aqueous solution of O.S. add 2 ml. of *Benedict's solution,* red precipitate is formed.

(v) To 2 ml. of the aqueous solution of O.S. add 2 ml. of lead acetate solution. Further add ammonium hydroxide solution slowly until a precipitate is formed. the contents. Selmon pink colour is obtained.

Derivative — Glucosazone, M.P. 205°C (for preparation of the derivative see under carbohydrates). Osazone is formed within four minutes.

185°C *(Decomposition)* **Cane Sugar,** Sucrose, $C_{12}H_{22}O_{11}$.

White crystalline solid, soluble in water.

(i) To 0.5 gm. of O.S. add 1 ml. of cone. H_4SO_4 in a dry test tube. Charring takes place.

(ii) Repeat Benedict and Fehling's solution tests as given under glucose. No reduction takes place (no red ppt.)

(iii) To 2 ml. of aqueous solution of O.S. add equal volume of NaOH solution and divide it in two parts :

a) To one part add a drop of $CuSO_4$ solution. A blue colour is obtained.

b) To another part add a drop of cobalt nitrate and warm. A violet colour is formed.

203°C(Decomposition) **Lactose,** $C_{12}H_{22}O_{11}$

Soluble in hot water.

(i) Reduces Fehling's solution.

(ii) Gives yellow osazone.

Derivative — Osazone, M.P. 208°C (decomposition) No Sharp Melting point Starch, $(C_6H_{10}O_5)_n$

White powder, insoluble in cold water.

In a dry test tube take a pinch of the solid. Heat, the powder chars, and a smell like burnt leather.

Make a paste of O.S. in hot water and dilute this with 10 ml. of hot water. Add a few drops of iodine solution. Deep blue colour.

*Derivative :*Does not give osazone.

Compounds Containing Carbonyl (>C = O) **group**

(a) Aldehydes

(1) Aliphatic liquids

B.P.21°C Acetaldehyde, CH_3CHO

Colourless volatile liquid having characteristic miscible with water.

(i) Take a few drops of O.S. arid add equal volume of NaOH solution. Heat gently. A brown resin is formed.

(ii) To 1 ml. of O.S. add a few drops of freshly prepared sodium nitroprusside solution. Add 2 drops of piperidine. A blue colour is formed.

(iii) Perform iodoform reaction given under ethyl alcohol. A positive test.

(iv) To 1 ml. of the aqueous solution of O.S. add 1 ml. of 0.5% sodium nitroprusside solution. Add 4-5 drops of NaOH solution. Deep wine red colour.

Derivative—Iodoform, M.P. 119°C, 2, 4-dinitrophenyl- hydrazone, M.P. 168°C.

97-98°C Formalin solution.

(25-30% solution of formaldehyde, HCHO in water, containing CH_3OH).Pungent penetrating smell.

(i) To I / 2 ml. of the O.S. add 1 /2 ml. of Schiff's reagent, pink colour is obtained. Add a drop of cone. HCl, the colour turns blue.

(ii) Pour cone. H_2SO_4, by the side of the test tube contain-ing 1 ml. of formalin. Add 1 ml. of resorcinol solution. Red ring is formed at the junction. White precipitate changing to violet red is formed in aqueous solution.

(iii) Add 1/2 ml. of 1% phenyl hydrazine hydrochloride solution and 1/2 ml. of sodium nitroprusside solution to a few drops of formalin. Now add excess of NaOH solution. Intense blue colour is formed.

*Derivative:*2, 4—Dinitrophenylhydrazone of formaldehyde, M.P. 166°C.

(2) Aromatic liquids

179°C Benzaldehyde, C_6H_5CHO

Colourless liquid, insoluble in water, smells like bitter almonds.

To 1 ml. of O. liquid add 2 ml. of $NaHSO_3$ solution. Shake vigorously. A white solid is formed.

Tollen's reagent is reduced slowly, whereas Fehling's solution is not reduced.

To 2 ml. of the O. liquid add 5 ml. of $KMnO_4$ solution. Heat to boiling for half an hour under reflux. Acidify with cone. HC1. Heat till the colour disappears. Cool. Crystalline benzoic acid separates.

Derivative—(i) 2, 4-dinitrophenylhydrazone of benzaldehyde M.P. 236°C, (ii) Prepare benzoic acid as given under test (iii), M.P.121^{C}C.

(b) Ketones

(1) Aliphatic liquids

B.P.56°C Acetone, CH_3COCH_3

Colourless liquid with a characteristic pleasant odour.

(i) Iodoform test—Positive. See under ethyl alcohol.

(ii) To 5 drops of acetone add 1 ml. of NaOH solution and 2 ml. of freshly prepared sodium nitroprusside solution. Red colouration is obtained. This is chara-cteristic of all ketones containing CH_3CO group.

(iii) To freshly prepared mercuric oxide add a few drops of acetone, yellow solid dissolves.

(iv) To 2 ml. of 1% solution of acetone add 1 ml. of Denige's solution. Heat in a water bath. A heavy white precipitate.

Derivative—2,4—Dinitrophenylhydrazone, M.P. 128°C, iodoform, M.P. 119°C.

80°C Methyl ethyl ketone, $CH_3COC_2H_5$

Colourless liquid with a pleasant smell, miscible with water.

Sodium nitroprusside test—Red colour same as given under acetone, test no (ii).

(ii) *Iodoform test*—Positive.

Derivative—2, 4-Dinitrophenylhydrazone of methyl ethyl ketone—orange needles, M.P. 111 °C.

(2) Aromatic liquids

B.P.202°C Acetophenone, $CH_3COC_6H_5$

Liquid having pleasant colour, insoluble in water.

(i) *Iodoform reaction*—Positive.

(ii) *Sodium nitroprusside test* — Wine red colouі\which turns blue on acidifying with acetic acid. Test given under acetone.

Derivative—2, 4-Dinurophenylhydrazone of acetophenone, orange red needles. Crystallise from acetic acid. Dry and determine the melting point (249°C).

(3) Aromatic solid

M.P.48°C Benzophenone, $C_6H_5COC_6H_5$

Colourless fragrant smelling solid, insoluble in water but dissolves in alcohol.

(i) O.S. + afew drops of conc. H_2SO_4. Yellow solution results.

(ii) Heat gently 0.2 gm. of the solid with a small piece of metallic sodium. A blue colour results.

Derivative — 2,4-Dinitrophenylhydrazone of benzophenone, M.P. 238°C.

Esters

(1) Aliphatic liquids

B.P.57°C Methyl acetate, CH_3COOCH_3

Colourless liquid, fruity smell, miscible with water.

(i) Decolourises the pink colour of aqueous NaOH solution containing a drop of phenolphthalein on heating.

(ii) Heat with aqueous NaOH and then add a drop of aqueous $FeCl_3$ soln. Red colour is obtained.

77°C Ethyl acetate, $CH_3COOC_2H_5$

Colourless liquid, pleasant fruity smell, miscible with water. Perform all the tests given under methyl acetate.

Derivative—Ethyl 3, 5-dinitrobenzoate, M.P. 94°C.

186°C Diethyl oxalate,

$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}$$

Sparingly soluble in water.

(i) On heating with cone. H_2SO_4 gives CO and CO_2 (test for CO_2 with lime water).

(ii) Hydrolysis with alcoholic NaOH and subsequently neutralize, and then add $CaCl_2$ solution. White precipitate of calcium oxalate is formed.

Derivative—Warm with aniline, oxanilide is formed, M.P. 247°C.

(2) Aliphatic solids

M.P.54°C Methyl oxalate

$$\begin{array}{l} COOCH_3 \\ | \\ COOCH_3 \end{array}$$

White solid, odourless, slightly acidic, miscible with cold water.

(i) *Feigl test*—Positive,

(ii) *Phenolphthalein test*—Positive.

(iii) Boil 2 gm. of ester with 10 ml. of dil. HCl for a long time. Concentrate the resulting solution until crystals begin to separate. Dry these crystals and determine the M.P., 101°C. (iv) Take 0.5 gm. of the ester and cover with 5 drops of conc. H_2SO_4. Heat. Burn carbon monoxide at the mouth of the test tube.

Derivative—Oxalic acid, M.P. 101°C, Oxamide, M.P. 300°C.

(3) Aromatic liquids

B.P.196°C Phenyl acetate, $CH_3COOC_6H_5$

Colourless liquid, characteristic odour, heavier than water.

(i) Take a flask and cover it with a funnel. Now pour 2 ml. of ester and 1 ml of alc. KOH. Heat gently for 40 mts. Cool, acidify with dil.

H_2SO_4. Again cool. Extract with ether. Remove solvent by evaporation and test the extract for phenol.

Derivative—Phenyl benzoate, preparethis compound by using phenol, separated in test above, M.P. 68°C.

213°C Ethyl benzoate, $C_6H_5COOC_2H_5$

Pleasant smelling colourless liquid, insoluble in water.

(i) Reflux 5ml. of ester and 25 ml. of 25% aqueous KOH in a 100 ml. round bottom flask fitted with air condenser for about 1/2 hour. Cool the contents acidify with dil. H_2SO_4. Crystals separate. Wash them with water. Crystallise with hot water, dry the crystals. Determine the melting point of benzoic acid thus formed.

Derivative-Benzoic acid, M.P. 121°C.

(4) Aromatic solid

M.P.68°C Phenyl benzoate, $C_6H_5COOC_6H_5$

Solid insoluble in water.

(ii) Reflux 1 gm. of ester with 20% NaOH for about an hour in a round bottom flask fitted with air condenser, Cool and smell phenol. Acidify the contents with dil. H_2SO_4. Filter, wash with water, crystallise the benzoic acid thus formed with hot water.

Derivative — Benzoic acid, M.P., 121°C.

Hydrocarbons

(1) Aromatic liquids

M.P.80°C Benzene, C_6H_6

Colourless liquid, characteristic smell. Highly inflammable, floats on water.

(i) Take 1 ml. of the compound and 1 ml. of nitrating mixture (equal volumes of cone. HNO_3 and cone. H_2SO_4). Shake vigorously and pour into 5 ml. of cold water in a beaker. Smell of bitter almonds due to the formation of nitrobenzene.

(ii) Take 1 ml. of the compound. Add 2 ml. of nitrating mixture. Heat to boiling and then pour into 20 ml. of ice cold water in a

beaker. A pale yellow solid due to the formation of m-dinitrobenzene.

Derivative — m-dinitrobenzene, M.P. 90°C.

110°C Toluene, $C_6H_5CH_3$

Colourless liquid, characteristic smell, lighter than water.

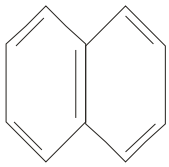
(i) Take 1 ml. of the compound. Add to it 2 ml. each of cone. HNO_3 and conc. H_2SO_4. Warm and pour into 20 ml. of ice cold water. Pale yellow crystals due to the formation of 2,4-dinitrotoluene, M.P. 76°C.

(ii) Take 1 ml. of the compound. Add a pinch of $K_2Cr_2O_7$ and 1 ml. of cone. H_2SO_4. Heat, cool, add 5 ml. of water. A white ppt. due to the formation of benzoic acid.

Derivative—2, 4-dinitrotoluene, M.P. 76°C, Benzoic acid, M.P. 121°C.

(2) Aromatic solids

M.P.80°C Naphthalene



$C_{I0}H_8$

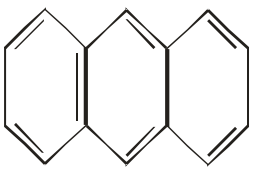
White solid, shining plates, insoluble in water.

(iii) Take a pinch of the O.S. add cone. H_2SO_4 and a small amount of benzal chloride. A magenta colour is obtained,

(iv) Dissolve 2.5 gms. of the O.S. in chloroform and add anhydrous $A1C1_3$. Green colour is obtained.

Derivative—Picrate, M.P. 149°C.

216°C Anthracene



$C_{14}H_{10}$

Commercial sample is greenish.

(i) Add 2rice grains of O.S. to 2 ml. of saturated solution, of picric acid is benzene and shake. Deep red solution due to the formation of picrate is formed, which on heating gives shining particles.

Derivative—Anthracene picrate, M.P. 138°C.

Identification of Simple Monofunctional Organic Compounds Containing Nitrogen[C, H, N, (O)]

Nitro group Containing Compounds

(1) Aromatic liquids

B.P.209°C Nitrobenzene, $C_6H_5NO_2$

Light pale yellow liquid, heavier than water, smelling like bitter almonds, insoluble in water.

Reduction—Boil 1 ml. of original liquid with 5 ml. of HC1 and 1 gin. of stannous chloride for about 10 minutes. Cool, make it alkaline with NaOH. Diazotise (add $NaNO_2$ and dil. HC1) and couple with alkaline α-naphthol. Make the contents more alkaline by adding NaOH. A bright red dye is obtained.

Derivative—m-Dinitrobenzene, M.P. 90°C.

220°C o-Nitrotoluene, $NO_2C_6H_3CH_3$ (1, 2)

Light yellow liquid, characteristic odour resembling bitter almonds, immiscible with water.

(i) *Reduction*—Reduce the original liquid by the proce-dure given under nitrobenzene. O-Toluidine will be formed. Test with diazotization and coupling with alkaline α-naphthol.

Derivative—2,4-Dinitrotoluene, M.P. 70°C.

230°C m-Nitrotoluene, $NO_2C_6H_4CH_3$ (1, 3)

Very pale yellow liquid, insoluble in water, smelling like bitter almonds,

(i) *Reduction*—Reduce to m-toluidine as given under nitrobenzene, and perform diazo-reaction.

Derivative—m-Nitrobenzoic acid, Oxidise O.S. with alkaline $KMnO_4$. m-nitrobenzoic acid is formed. Crystallise, dry and determine M.P. 142°C.

(2) Aromatic solids

M.P.54°C *p*-Nitrotohiene, $CH_3C_6N_4NO_2$ (1, 4)

Pale yellow solid, smelling like bitter almonds, insoluble in water.

(i) Boil 0.5 gm. of the solid with a small piece of metallic tin and 3 ml. of cone. HC1 for 15 minutes. Cool, diazotise and couple with alkaline α-naphthol. A beautiful red dye is obtained.

Derivative—2,4-Dinitrotoluene, M.P. 70°C.

61°C α-Nitronaphthalene, $C_{10}H_7NO_2$

Yellow crystals, odourless, insolillble in water.

(i) Gives deep red colouration, with cone. H_2SO_4.

(ii) *Reduction*—Take 0.5 gm. of the solid in a test tube. Add a small piece of metallic tin and 3 ml. of cone. HC1. Boil for 15 minutes. Cool, make it alkaline, diazotise and couple with alkaline α-naphthol. Orange red dye is obtained.

Derivative—α-Naphthylamine obtained by reduction as given above. Crystallise with dilute alcohol. Prism like crystals separate. Dry and determine the m. p. 50°C

70°C 2, 4-Dinitrotoluene, $CH_3C_6H_3(NO_2)_2$ (2, 4)

Light pale yellow solid insoluble in water,

Reduce the O.S. With tin and conc. HC1. Diazotise and couple with alkaline αnaphthol. Orange dye is formed.

Dissolve 0.l gm. of O.S. in 3 ml. of acetone. Add a drop of aqueous NaOH solution. Deep blue colour turning violet by adding acetic acid.

Derivative — Forms molecular compound with naphthalene in benzene, m p. 60°C.

90°C *m*-Dinitrobenzene, $C_6H_4(NO_2)_2$ (1, 3)

Light pale yellow solid insoluble in water.

Dissolve 0.l gm. of solid in 2 ml. of acetone. Add a drop of NaOH. Violet blue colour on shaking and turning to violet red on adding acetic acid.

To 0.l gm. of O.S. add a trace of $SnCl_2$ or dextrose in 5 ml. of boiling dilute NaOH solution. A violet colour.

Derivative — m-Nitroaniline, M.P. 1 1 4°C. Gives molecular compound with naphthalene in benzene, M.P. 52°C.

Amino group Containing Compounds

(1) Aromatic liquid

B.P.183°C Aniline, $C_6H_5NH_2$

Colourless liquid turning to brown on exposure to air, immiscible with water and heavier than it.

Isocyanide test—Boil a few drops of O.S. with alco-holic KOH and chloroform. Very unpleasant offensive smell due to the formation of phenyl isocyanide is obtained.

Diazo test — Dissolve 1/2 ml. of the O.S. in 5 ml. of HC1. Add 0-5 gm. of $NaNO_2$. Couple with alkaline α-naphthol. A beautiful orange red dye is obtained.

Runge's test — Suspend a trace of aniline in 5 ml. of water. Add one or two drops of sodium hypochlorite solution. Shake the solution, a violet colour is obtained.

Derivative—Acetanilide, plates, M.P. 114°C, Benzanilide, M.P. 163°C, 2,4,6-tribromoaniline, M.P. 11 8°C.

184°C Benzylamine, $C_6H_5CH_2NH_2$

Colourless liquid miscible with water, having characteristic ammoniacal smell.

Add nitrous acid ($NaNO_2$ and dil. HC1), brisk effervescence.

Derivative—2,4—Dinitrophenyl benzylamine, M.P. 1 15°C.

192°C Dimethyl aniline, $C_6H_5N(CH_3)_2$

Colourless liquid, lighter than water having characteristic odour.

Dissolve 1 /2 ml. of the liquid in 2 ml. of dil. HC1. Add sodium nitrite solution in cold with shaking, brown precipitate changing over to green by adding concentrated aqueous NaOH solution. On heating on ammoniacal smell is obtained.

Derivative—Picrate, M.P. 162°C.

198°C *o*-Tolnidine, $CH_3C_6H_4NH_2(1, 2)$

Colourless liquid, characteristic odour, insoluble in water,

(i) Dissolve 2gm. of original liquid in 50% H_2SO_4 solution. Add a few crystals of $K_2Cr_2O_7$. A blue colour changing to red on dilution is obtained,

(ii) Isocyanide test—Positive,

(iii) *Diazo test:* Diazotisation and coupling with alkaline α-naphthol gives orange red dye.

Derivative—Picrate, yellow prisms, M.P. 200°C, Dibromo-derivative, M.P. 50°C.

199°C *m*-Toluidine, $CH_3C_6H_4NH_2$ (1, 3)

Colourless liquid, insoluble and lighter than water.

Isocyanide test—Positive.

Diazotisation and coupling with alkaline α-naphthol gives orange-red dye.

Treat the ethereal solution of original-liquid with aqueous NaOCl. The layer becomes red, whereas the aqueous layer remains yellow.

Derivative—Benzoyl derivative, M.P. 125°C, 2, 4-dintro-phenyl derivative, M.P. 134°C.

(2) Aromatic solid

M.P.43°C *p*-Toluidine, $CH_3C_6H_4NH_2$ (1, 4)

(i) Crystalline solid sparingly soluble in hot water, possesses a strong characteristic odour.

(ii) Divide its solution in 50% H_2SO_4 in two parts. To one part add a small quantity of $K_2Cr_2O_7$, yellow colour is obtained. To another part add a few drops of conc. HNO_3. Blue colour changing slowly to violet and then to reddish brown is obtained.

Derivative—Picrate, yellow needles, M.P. 169°C, Acetyl derivative, M.P. 153°C

50°C α-Naphthylamine, $C_{10}H_7NH_2$

Light pinkish crystalline, sparingly soluble in hot water, unpleasant smell.

(i) Dissolve 0.5 in dil. HCl, and a drop of $FeCl_3$. A blue precipitate or colour is obtained.

Derivative—Acetyl derivative, M.P. 159°C, Benzoyl derivative, M.P. 1 60°C.

Compounds Containing Amido Group.

(1)Aliphatic solids

M.P.82°C Acetamide, CH_3CONH_2

Colourless crystalline solid, characteristic odour, readily soluble in water and deliquescent.

Heat the original solid with NaOH solution in a test tube, smell of ammonia,

Heat the O.S. with 1 ml. of cone. H_2SO_4, smell of acetic acid,

To 5 ml. of aqueous acetamide add 0.l gm. of freshly prepared HgO. The yellow solid dissolves.

Derivative—Picrate of acetamide, M.P. 107°C.

132°C Urea, NH_2CONH_2

Colourless crystalline solid, readily soluble in water.

(i) Give brisk effervescence with nitrous acid ($NaNO_2$ + dil. HC1).

(ii) *Biuret test:*Gently heat 0.5 gm. of O.S. in a dry test tube. The mass solidifies (smell of NH_3 is observed). Cool the mass add 2 ml. of water and warm, then add 1 drop of a very dilute $CuSO_4$ solution, followed by excess of NaOH solution. Violet colour develops.

Derivative—(i) Picrate, yellow needles, M.P. 148°C.

(ii) *Urea nitrate:*To the aqueous solution of O.S. add conc. HNO_3, crystalline solid of urea nitrate, M.P. 163°C.

(2)Aromatic solid

M.P.128°CBenzamide, $C_6H_5CONH_2$

Colourless crystalline solid, soluble in hot water,

(i) Heat 0.l gm. of 0.5 with 0.l gm. of soda lime in a dry test tube. Smell of bitter almonds due to the formation of benzo nitrile (similar to the odour of nitrobenzene).

(ii) Take 0.5gm of the compound. Add 1 ml. of cone. H_2SO_4. Heat strongly. Cool and add 2 ml. of water. A white solid due to the formation of benzoic acid is formed.

Derivative—(i) Benzoic acid, M.P. 1 21°C.

(ii) *Benzanilide*: on heating with aniline, benzanilide, M.P. 1 60°C is formed.

Unit -5

Thin Layer Chromatography & Determinations

Experiment -1

Thin Layer Chromatography

Chromatography

Chromatography is a separation process which depends on the differential distributions of the components of a mixture between mobile bulksphases may be either essentially thin film stationary phase. The stationary phase may be either in the form of a packed column (column chromatography) through which a mobile phase is allowed to flow, or in the form of a thin layer adhering to a suitable form of backing material (thing-layer chromatography) over which the mobile phase is allowed to ascend by capillary action.

The thin film stationary phase may be either a liquid or a solid, and the mobile phase a liquid or a gas. Possible combinations of these phases then give rise to the principle chromatography techniques in general use.

In partition chromatography the stationary phase is a thin liquid film adsorbed on the surface of an essentially inert support. The mobile phase may be either a liquid (liquid – liquid partition chromatography) or gas (gas – liquid partition chromatography or gas chromatography). In either system the separation depends largely upon partition between the two phases although the separation process may be complicated by the incursion of adsorption effects involving the inert support and the compounds undergoing chromatographic separation. Paper chromatography is an example of partition chromatography in which filter paper serves as a support for the immobile liquid phase.

In adsorption chromatography the mobile phase is usually a liquid and the stationary phase is a finely – divided solid adsorbent (liquid-solid chromatography). Separation here depends on the selective adsorption of the components of a mixture on the surface of the solid. Separations based on gas-solid chromatographic processes are of limited application to organic mixtures. The use of ion-exchange resins as the solid phase constitutes a special example

of liquid-solid chromatography in which electrostatic forces augment the relatively weak adsorption forces.

Apart from partition and adsorption process, chromatographic separations may also be based upon differences in molecular size (gel permeation chromatography, or gel filtration). In this technique gel-like material, which is commercially available in a range of porosities, serves as the stationary phase, and separation is achieved through differential diffusion into the pores of the matrix, of molecules which are not large enough to be completely excluded.

The chromatographic techniques which are principally of use to the synthetic organic chemist are described in the following sections. These are

1. Thing-layer chromatography (T.I.C.)
2. Liquid-solid column chromatography
3. Gas-liquid chromatography (G.L.C.)
4. High performance liquid chromatography (H.P.L.C.)

Thin Layer Chromatography (TlC)

Thin layer chromatography (TLC) like coloumn chromatography is a solid liquid chromatography based on the principle of adsorption. It is simple, inexpensive, fast efficient, sensitive and requires only milligram quantities of substance.

Princple

In TLC, as in coloumn – chromatography a liquid mobile phase moves along a solid stationary phase carrying with it the components of a mixture. In the process the components are separated by differential partitioning between the solid and liquid phases. The stationary phase is usually an adsorbent such as alumina or silica gel, so the separation is effected by the same mechanism as adsorption chromatography on a column.

Procedure

The operation of thin layer chromatography involves the following steps.

Preparation of TLC plates

A slurry of the adsorbent and the solvent is prepared by stirring 35g of silica gel. G in a mixture of 33 ml of methanol and 67 ml of chloroform taken in a 125 ml screw-cap jar. The G symbol stands for gypsum (calcium sulphate) which binds the adsorbent together and then glass plates. Holding two clean microscopic slides together back to back at the top are immensed in the slury

for about 2 seconds to coat them uniformly with the adsorbetn leaving the top 1 cm uncoated. The bottom of the slides are touched to the jar to drain off the excess slurry. The slides are air dried to evaporate the solvent, then separated and wiped the excess adsorbent off the edges with a tissue paper. The slides are activated by heating them in oven at 110^0 C for 15 minutes.

Application of sample

A small amount of the mixture (10-20) mg is dissolved in 1 ml of the suitable volatile organic solvent such as acetone or dichloromethane and tiny spot (2-3 mm) in diameter) of this solution is carefully applied with a micropipette or a dropping tube on to the bottom of the tlc plate, about 1.0-1.5 cm from the end the position of the spot is marked with a pencil to calculate the Rf value of the compound after separation when more than one spot of the sample is analyzed on the same plate the spot must be applied symmetrically atleast 5 mm apart. The spot is allowed to dry the plate is developed.

Development of TLC plate

When the solvent around the spot has evaporated, the plate is place vertically in a developing jar containing a small quantity of the solvent (moving phase) and lined with piece of filter paper moistened with the developing solvent. The solvent saturated lines help to keep the jar saturated with solvent vapours which speeds up the development process. The level of solvent in a jar (chambe) is adjusted so that the lower edge of the adsorbent layer is under the solvent but the spot should be above this level. The jar is then covered (figure) the solvent rises through the adsorbent layer and the components of the mixture ascent at different rates depending on their affinities for the adsorbent. When the solvent has reached the top of the adsorbent layer, the plate is removed from the jar. The position of the solvent is marked and it is allowed to evaporate from the plate.

The choice of solvent (moving phase) depends on the components to be separated. A solvent which causes all the spotted material to move with the solvent front is too polar. One which will not cause any of the material in the spot to move in not polar.

Solvents with their relative polarity are listed in column chromatography.

Chloroform and benzene are solvents of intermediate polarity and are a good choice for a wide variety of functional groups to be separated. Hexane or petroleum ether with varying proportions of benzene or ether give solvent

mixtures of moderate polarity which are useful for many common functional groups. For polar, compounds, ethylacetate, acetone or methanol can be used.

Location of the spot

a) The coloured components separated on the tlc can be visualised easily.

b) The colourless components are made visible by the use of visualization reagents. The most commonly used visualization reagent is iodine. Iodine reacts with many organic substances to form complexes, which are either brown or yellow. For this purpose a jar filled iodine vapours is used.

Another method used is charring of spots with sulphuric acid, i.e. concentrated sulphuric acid is sprayed on the plate and is heated in an oven it 110^0 C to complete the charring.

Certain reagents used for locating spots are as follows:

Table

Substance	Reagents
1) Acids	Bromcresol green
2) Aminoacids	nion hydrides or cupric nitrate
3) Aldehydes or ketones	2, 4-DNP
4) Phenols	$FeCl_3$ solution
5) Terpenoids	Antimony pentachloride $SbCl_5$ in CCl_4

An ultra violet lamp can also be used for visualization of spots. Under a UV light compound will often appear as bright spots on the plate.

Rf value: Under a given set of conditions (adsorbent, solvent, layer thickness and homogencity), Rf is the rate of movement of a compound with respect to the rate of movement of the solvent. Rf is a property of that compound. The value is determined by measuring the distance travelled by a substance from a standing line to middle of the spot and dividing this distance by the distance the solvent has travelled as measured from the same starting line.

Experiment -2

Monitoring of chemical reaction by thin-layer chromatography.

(1)Separation of amino acids:

Prepare solutions of DL-alanine, L-leucine and L-lysine hydrochloride by dissolving 5 mg of each separately in 0.33 ml of distilled water, measured with a graduated 1 ml pipette (leucine may require warming to effect solution). Mix one drop of each solution to provide a mixture of the three amino acids and dilute the remainder of each solution to 1 ml to give solutions of the respective amino acids. The latter will contain about 5 μg of each amino acid μl. Apply approximately 0.5 μl or each of the solutions to a Silica Gel G plate and allow to dry in the air (i.e. until the spots are no longer visible).

Prepare the developing solvent by mixing 70 ml of propan-1-ol with 30 ml of concentrated aqueous ammonia (d 0.88). Line the iside of the jar with filter paper reaching to within 3 cm of the bottom and moisten with the developing solvent. Insert the prepared plate into the jar and carefully introduce by means of a pipette sufficient of the developing solvent so that the lower edge of the adsorbent layer is immersed in the solvent; put the cover in position in the mouth of the jar, and allow the chromatogram to develop.

Remove the chromatogram, dry it at 100^0 C for 10 minutes and spray with ninhydrin reagent [0.2% solution in butan-1-ol, (1)]; heat at 110^0 C for 5-10 minutes in order to develop the colour. Mark the centre of each spot with the metal scriber and evaluate and record the R_F values.

Note. (1) Ninhydrin (p.630) is the 2-hydrate of indane-1,2,3 –trione. it reacts with *a*-amino acids to yield highly coloured products. Contact with the skin should be avoided since it produces a rather long-lasting purple discoloration.

(2)Separation of 2,4-dinitrophenylhydrazones:

The solutions are prepared by dissolving 10 mg of each of the 2,4-dinitrophenylhydrazones of acetone, butan-2-one and hexan-3-one (or hexan-2-one) in 0.5 ml of ethyl acetate. Prepare a flexible silica gel sheet of dimensions 20 × 5 cm in the manner already described and apply c. 0.5 μl of each of the tree solutions to give the marker spots of a diameter of between 2 and 3 mm. A mixed spot is conveniently obtained by loading sequentially to the same area further 0.5 μl aliquot portions of each of the solutions and allowing the solvent to evaporate completely between each addition.

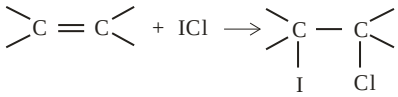
Charge the paper-lined jar with the developing solvent (toluene; light petroleum b.p. $40\text{-}60^0$ C, 3:1), insert the loaded flexible sheet and allow the development to proceed. Air dry thedeveloped chromatogram and record directly the R_F values of the components.

Experiment -3

Determination of Iodine value of given fat sample.

Theory

The iodine value of iodine number of an oil or fat is defined as the number of grams of iodine taken up by 100 g of the oil or fat. Oils and fats are triesters of glycerol with saturated and/or unsaturated higher. The degree of unsaturation of an oil of fat is measured in terms of iodine value. Linseed oil or cod liver oil, etc. have a large proportion of unsaturated fatty acids, hence their iodine value is high, whereas olive oil or almond oil possesses a low iodine value. Iodine value of coconut, olive and linseed oil are 10, 88 and 108, respectively. Iodine value is determined by reacting a known volume of iodine monochloride solution in acetic acid (Wij's solution) with the oil or dissolved in $CHCl_3$ or CCl_4 and then titrating the unsused iodine with a standard sodium thiosulphate (hypo) solution using as indicator.



$$ICl + Kl \rightarrow I_2 + KCl$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

Reagents

1. **Wij's solution:** This is a solution of iodine monochloride (ICl) in glacial acetic acid. Dissolve 3.0 g of iodine in 250 ml of glacial acetic acid and pass through it a slow current of chlorine gas until the deep red colour red colour changes to organe-yellow due to formation of iodine chloride. The Wij's solution must be stored in a well stoppered amber coloured bottle.
2. **Sodium thiosulphate solution (0.1 N):** Dissolve 6.2 g of $Na_2SO_3.5H_2O$ in 250 ml of water and standardise the solution iodometrically using a standard solution (0.1 N) of $CuSO_4.5H_2O$ or potassium and starch as indicator.
3. **Potassium iodide solution (15%):** Dissolve 15 g of KI in 100 ml of water.
4. **Indicator:** 1% Starch solution.

Procedure

Weight accurately about 1 g of the given oil or fat. Dissolve it in 10 ml of chloroform or carbron tetrachloride in a 500 ml control flask. Pipett out 25 ml of the Wij's solution and add to the flask. Mix the contents well, stopper the flask and keep in dark for 30 minutes with occasional shaking. Add 40 ml of 15% KI solution and 250 ml of water. Shake the flask for 5-10 minutes and titrate the contents against standard hypo solution using starch as indicator.

Standardisaton of the Wij's solution.

Take 25 ml of the Wij's solution in a 500 ml concial flask and add 75 ml of 15% KI solution. Dilute the mixture with 250 ml of water and standardise the solution iodometrically using 0.1 N standard copper sulphate potassium dichromate solution and starch in indicator.

Calculation:

Weight of the oil of fat = Wg

Normality of sodium thiosulphate (hypo) solution = N/*x*

Normally of hypo used for 25 ml of the Wij's solution blank = V_1 ml

Volume of hypo used for the sample = V_2 ml

1000 ml of 1 N hypo = 1 gequivalent of iodine

$\therefore$ $(V_1 - V_2)$ ml of *N/x* hypo = $\frac{(V_1 - V_2)}{1000} \times \frac{N}{x}$ g equivalent of iodine

$$= \frac{(V_1 - V_2)}{1000} \times \frac{N}{x} \times 127\text{g}$$ iodine

(Where 127 is equivalent weight of iodine)

$\because$ W g of the oil or fat takes up = $\frac{(V_1 - V_2)}{1000} \times \frac{N}{x} \times 127\text{g}$ of iodine

$\therefore$ 100g of oil or fat will take up $= \frac{(V_1 - V_2)}{1000} \times \frac{N}{x} \times 127 \times \frac{100}{W}$ g or iodine

$\therefore$ Iodine number of Iodine value $= \frac{(V_1 - V_2) \times 127 \times 100}{W \times 1000} \times \frac{N}{x}$

Experiment -4

Determination of the Percentage of amino group in given compound by Acetylation Method.

Theory:

Amino compounds react with acetic anhydride (known amount) in pyridine at room temperature to give acetyl derivative. The acetylation method involves heating of a known amount of amino with known volume of acetic anhydride (used in excess) and pyridine until acetylation is complete. The excess amount of unreacted acetic anhydride present in the reaction mixture is hydrolyzed to acetic acid by adding water to it. The total free acetic acid is then titrated with standard alkali solution. Simultaneously a blank experiment is also carried out excluding the amino sample. The difference in volumes of the alkali required in the two experiments in equivalent to the amount of acetylating agent taken up by the amine.

$$RNH_3 + (CH_3CO)_2O \xrightarrow{\text{Pyridine}} RNHCOCH_3 + CH_3COOH$$

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

$$-(NH_2)_n + n(CH_3CO)_2O \rightarrow -(NHCOCH_3)_n + nCH_3COOH$$

If the molecular which of amino compound is known then the number of amino groups present in the compound can be calculated. Various primary and secondary aliphatic, aromatic or heterocyclic amines may be estimated by using the acetylation method.

Reagents:

1. Acetylating mixture: Thoroughly mix one volume of acetic anhydride with three volumes of pyridine.
2. N/2 alcoholic NaOH solution: Prepare as described in the previous experiment.
3. Indicator : Phenolphthalein

Procedure:

Take an accurately weighted amount 1-1.5 g of amine in a 100 ml round-bottomed flask fitted with a reflux condenser. Add 10 ml of the acetylating mixture to the flask and heat on a water bath 30-45 minutes. Remove the heat source and add 20 ml of distilled water through the condenser and shake the flask thoroughly to ensure complete hydrolysis of the remaining acetic

anhydride. Remove the condenser and cool the flask to room temperature. Titrate the contents of the flask with standard N/2 NaOH solution using phenolphthalein as an indicator. Perform the blank titration after repeating the above experiment without adding the sample of the amine.

Calculation:

Weight of the amino compound = Wg

Volume of NaOH used with the sample = V_1 ml

Volume of NaOH used with the blank = V_2 ml

Normally of NaOH solution = N / *x*

1000 ml *N*NaOH = 1 g mole NaOH = 1 g mole CH_3COOH = 1 amino group

$\therefore$ $(V_2 - V_1)$ ml of N/*x*NaOH = $\frac{(V_2 - V_1)}{1000} \times N/x$ amino group

$\because$ W g of the amino compound contains = $\frac{(V_2 - V_1)}{1000} \times N/x$ amino group

$\therefore$ 100 g of the amino compound contains

$$= \frac{(V_2 - V_1)}{1000 \times W} \times N/x \times 100 \text{ amino group}$$

$$= \frac{(V_2 - V_1)}{10 \times W} \times N/x \text{ amino group}$$

Thus, the % of amino group in the sample of an unknown amino compound

$$= \frac{(V_2 - V_1)}{1000 \times W} \times N/x$$

Fi the molecular weight of the amino compound is known, suppose it is M, then the number of amine groups present in the compound will be

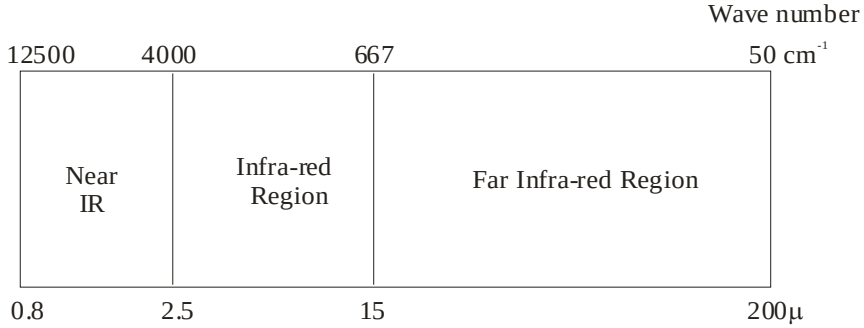
$$\frac{(V_2 - V_1) \times M}{1000 \times W} \times N/x$$

Unit -6

Infra-red Spectroscopy

Infra-red Spectroscopy

General Introduction: Infra-red spectrum is an important record which gives sufficient information about the structure of a compound. Unlike ultraviolet spectrum which com-prises of relatively few peaks, this technique provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of Infra-red radiations (quantized) causes the various bands in a molecule to stretch and bend with respect to one another. The most important region for an organic chemist is 2.5 μ to 15 μin which molecular vibrations can be detected and measured in an infra-red spectrum and in a Raman spectrum. The ordinary infra-red region extends from 2.5 $\mu$to 15 μ. The region from15 μ to 200 μ is called Far Infra-red region and that from0.8 μ to 2.5 μ is called Near infra-red.



The absorption of Infra-red radiations can be expressed either in terms of wavelength (X) or in wave number (v). Mostly infra-red spectra of organic compounds are plotted as percentage transmittance against wave number. The relationship between wavelength and wave number is as follows:

$$\text{Wave number} = \frac{1}{\text{wavelength in centimeters}}$$

Molecular Vibrations:

Absorption in the infra-red region is due to the changes in the vibrationaland rotational levels. When radiations with frequency rangeless than 100 cm^{-1} are absorbed, molecular rotation take place in the substance. As this absorption is quantized, discrete lines are formed in the spectrum due to molecular rotation.

Molecular vibrations are set in, which more energetic radiation in the region 10^4 to 10^2 cm^{-1} is passed through the sample of the substance. The absorption causing molecular vibration is alsoquantized. Clearly, a single vibrational energy change is accompanied by a large number of rotational energy changes. Thus,the vibrational spectra appear as vibrational-rotational bands.

Fundamental vibrations are classified as:

(i) **Stretching:**In this type of vibrations, the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.

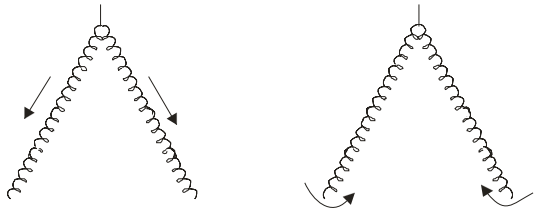


Fig. 1 Types of vibrations: (i) Stretching, (ii) Bending

(ii) Bending: In this type of vibrations, the positions of, the- atoms change with respect to the original bond axis. We know that more energy is required to stretch a spring .than that required to bend it. Thus, we can safely say that stretching absorptions of a bond appear at high frequencies (higher energy) as compared to the bending absorption of the same bond.

The various stretching and bending vibrations of a bond occur at certain quantized frequencies. When Infra-red radiation is passed through the sub-stance, energy is absorbed and the amplitude of that vibration is increased. From the excited state, the molecule returns to the ground state by the release of extra energy by rotational, collision or translational processes. As a result, the temperature of the sample under investigation increases.

Types ofstretching vibrations: There are two types of stretching vibrations:

(a) Symmetric stretching: Inthis type, the movement of the atoms with respect to a particular atom in a mole-cule is in the same direction.

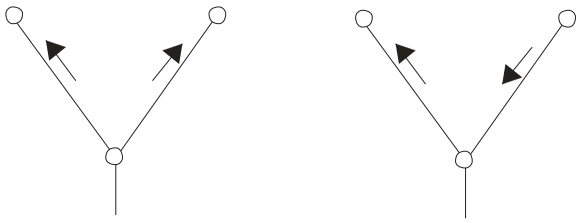


Fig. 2 Types of stretching vibrations.

(b) Asymmetric stretching. In these vibrations, one atom approaches the central atom while the other departs from it.

Types of bending vibrations: Bending vibrations are of four types:

a) **Scissoring.** In this type, two-atoms approach each other.

b) **Rocking.** In this type, the movement of the atoms takes place in the Same direction.

c) **Wagging.** Two atoms move up and below the plane with respect to the central atom.

d) **Twisting:** In this type one of the atoms moves up the plane which the other moves down the plane with respect to the central atoms.

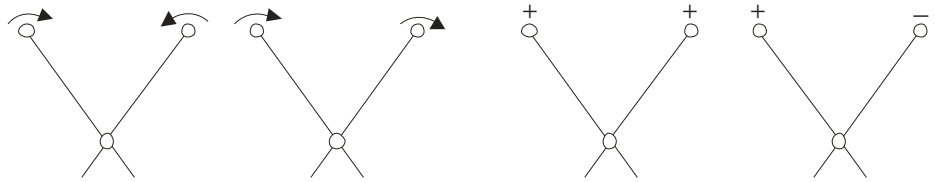


Fig. 3 : Types of bending vibrations (a) Scissoring (b) Rocking (c) Wagging (d) Twisting

Instrumentation

The most important source of Infra-red lightis Nernst glowerwhich consists of a rod of the sintered mixture of the oxides of Zirconium, Ytterium and Erbium. The rod is elec-trically heated to 1 500°C to produce Infra-red radiations.

A rod of silicon carbide (Globar) can also be electrically heated to pro-duce Infra-red radiations. To obtain monochromatic light, optical prisms or gratings can be used. For prism material, glass or quartz cannot be used since they absorb strongly through most of the Infra-red region. Sodium chloride or certain alkali metal halides are commonly used as cell containers or for prism materials as these are transparent to most of the infra-red region under consideration. Sodium chloride is hygroscopic and is, therefore, pro-tected from the condensation of moisture by working at suitable temperature. Gratings give better resolution than do prisms at high temperatures.

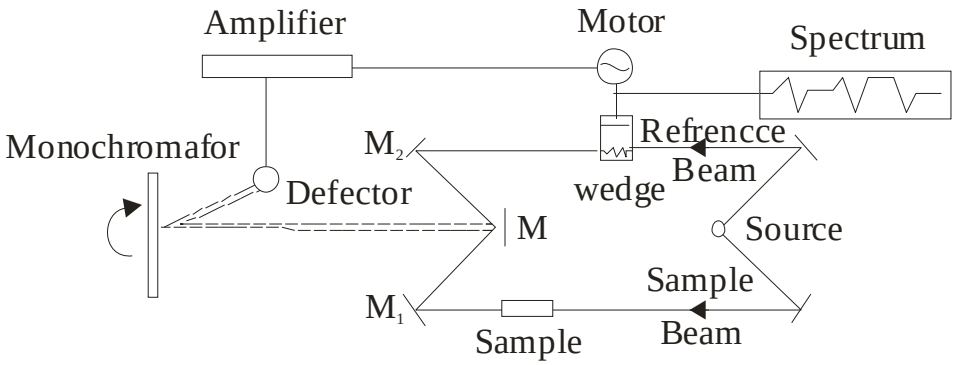


Fig 4: Infra-red Spectrometer

Light from the source is split into two beams. One of the beams ispassed through the sample under examination and is called the sample beam. The other beam is called the reference beam. When the beam passesthrough the sample, it becomes less intense due to the absorption of certain frequencies. Now, there will be a difference in the intensities of the twobeams. Let I_0 be the intensity of the reference beam and / be the intensity of the beam after interaction with the sample respectively.

The absorbance of the sample at a particular frequency can be calculated as:

$$A = \log (Io/I)$$

Also transmittance, $T = I/I_0$

or$A = \log (I/T)$

Intensities of the bands can be recorded as a linear function *T* against the corresponding wave-number. Intensities of the two beams, are converted into and measured as electrical energies with the help of detector thermopile. For this we proceed as follows:

The two beams (Sample and Reference) are made to fall on a segmented mirror with the help of two mirrors M, and M_2. The shopper *&&)* which rotates at a definite speed reflects the sample and the reference beams to a monochromator grating. As the grating rotates slowly, it sends individual frequencies to detector thermopilewhich converts Infra-red energy into electrical energy. It is then amplified with the help of amplifier. Due to the difference in intensities of the two beams, alter-nating currents start flowing from the detector thermopile to the amplifier. The amplifier is coupled to a small motor which drives an optical wedge. The movement of the wedge is in turn coupled to a pen recorder which draws absorption bands on the calibrated chart. The movement of the wedge continues till the detector receives, light of equal intensity from the sample and

the reference beams. Calibration can be carried out using spectrum of Polystyrene.

Sampling: Various techniques can be employed for placing the sample in the path of the Infra-red beam depending upon whether the sample is a gas, a liquid or a solid. The intermolecular forces of attraction are most operative in solids and least in case of gases. Thus, the sample of the same Substance shows shifts in the frequencies of absorption as we pass from the solid to the gase-ous state. In some cases, additional bands are also observed with the change in the state of the sample. Hence, it is always important to mention the state of the sample on the spectrum which is scanned for its correct interpretation. *(a)* Solids. Solids for the Infra-red spectrum may be examined as an alkali halide mixture. Alkali metal halides, -usually sodium chloride, which is transparent throughout the Infra-red region is commonly used for the purpose. Potassium bromide also serves the purpose well. The substance under investigation should be absolutely dry as water absorbs strongly atabout 3710 cm^{-1} and also near 1630 cm^{-2}. The sample (solid substance) is ground with KBr and is made into a disc after drying and then pressing it under elevated temperature at high pressure. Also a blank disc is prepared with pure potassium bromide which may be placed in the path of the reference beam. It is often advisable to carry out grinding under infer-red lamp to avoid condensation of atmospheric moisture. Grinding is usually done in agate mortar and pestle. Discs obtained from poorly ground mixture scatter more light than they disperse. The particle size of the ground mixture should be less than 2 μm to avoid scattering. Potassium bromide is transparent to the infrared region (2.5μ – 15 μ) and thus a complete spectrum can be scanned by mixing 1-2% of the solid sample with it and then grinding it to the desired particle size.

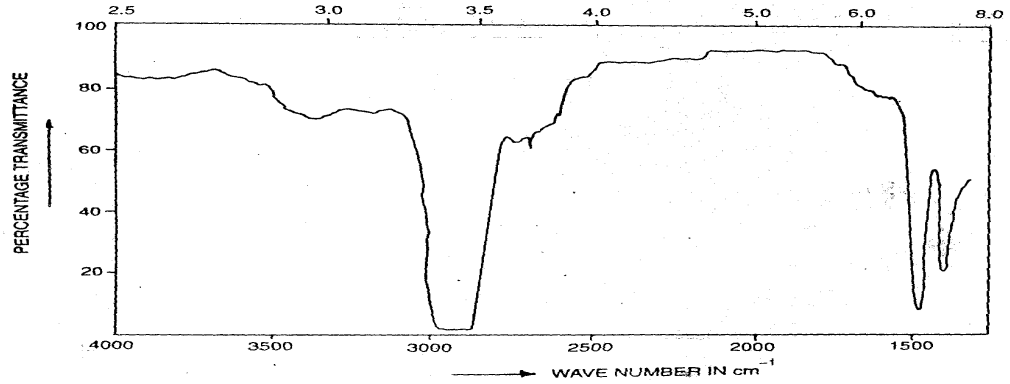


Fig. 5: Infra-red spectrum

The spectrum of the solid can also be conveniently determined as a mull or a paste. Some commonly used mulling reagents are (i) nujol (ii) Hexachlorobutadine (iii) chlorofluoro carbon oil etc. The most commonly used mulling regent is nujol which is a mixture of liquid paraffinic hydrocarbons with high molecular weights. When nujol is used as a mulling reagent [Spectrum show in figure 5 and 6).

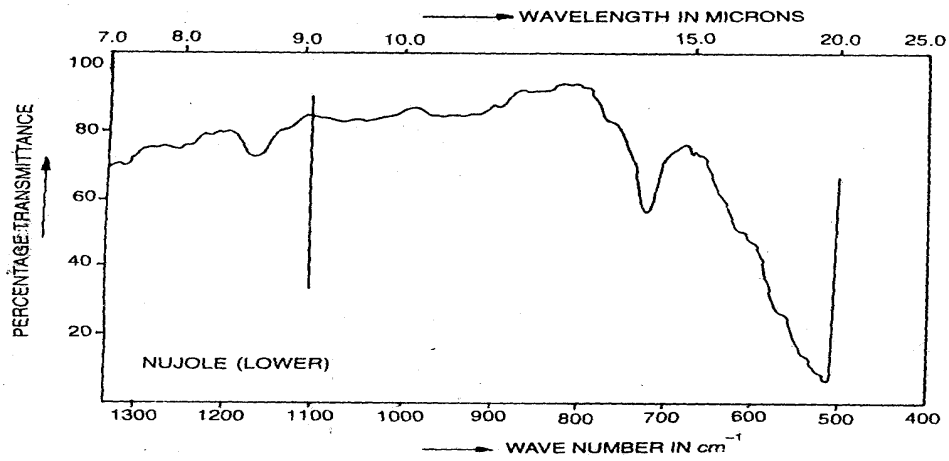


Fig. 6 Infra-red spectrum

Absorptions due to C-H stretching at 3030-2860 cm^{-1} and those for C-H bending at about 1460 cm^{-1} and 1374 cm^{-1} are observed. Clearly, no information about the sample can be recorded from these regions of absorptions. The regions of absorptions due to nujole can be studied only by taking another spectrum of the sample using hexachlorobutadiene as the mulling reagent. A solid film can also be deposited over the alkali metal halide (NaCl or KBr) disc by putting a drop of the solution of the sample (sample dissolved in the volatile solvent) on the disc and then evaporating the solvent.

Polymers, fats and waxy materials show excellent spectra in this way. Solid samples can also be examined in solutions. A polystyrene film is commonly used for calibration of wave numbers. For this, calibration is done using the bands at 3026, 3002, 2924, 1602, 1495 and 9.06 cm^{-1}.

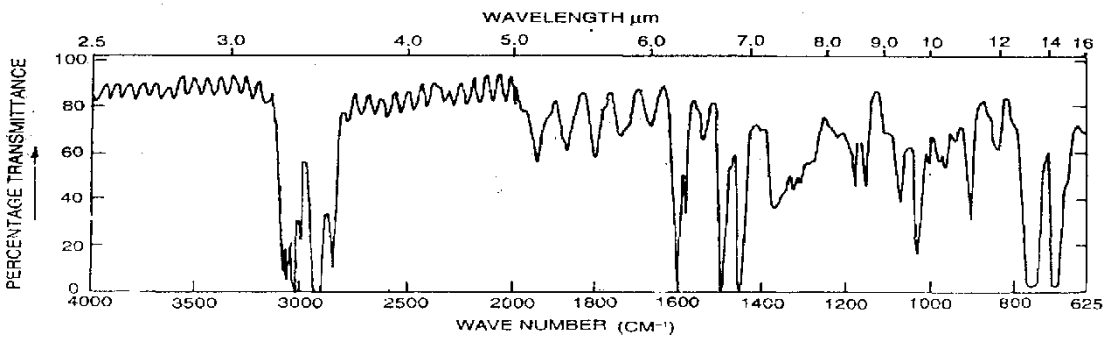


Fig.7- Polystyrene-wavelength v/s Percent transmittance

(b) **Liquids.** The simplest technique consists of sampling a liquid in a thin film (0.1 to 0.3 mm) squeezed between two sodium (chloride plates, *i.e.*, plates made of the material transparent to Infra-red light. For samples that contain water, plates may be constructed with calcium fluoride. A drop of the liquid sample is placed on the top of the sodium chloride plate and another sodium chloride plate is placed on it. The pair of sodium chloride plates enclosing the liquid film is then placed in the path of the sample beam. Similarly, a drop of the low melting substance can be likewise placed between two plates for spectral analysis.

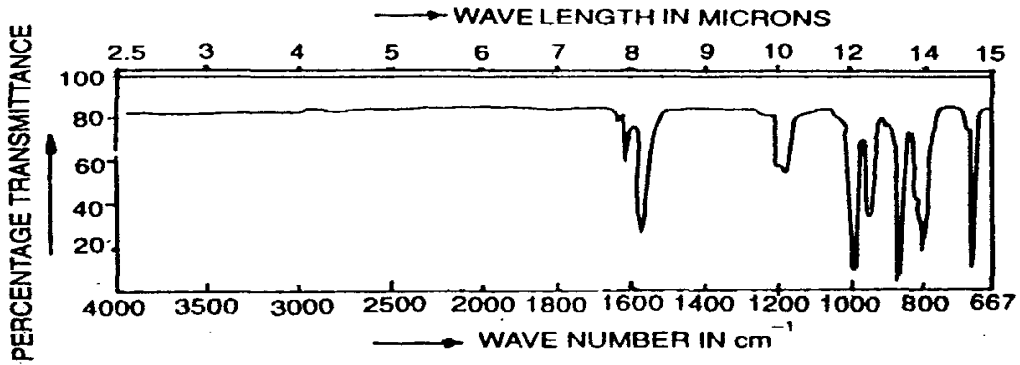


Fig. 8 Infra-red spectrum of Hexachlorobutadiene 1. 3.

(c)Gases. The gaseous sample is introduced into a gas cell. The walls of the cell are made of sodium chloride. Sodium chloride windows allow the cell to be placed directly in the path of the sample beam. The gas cell is usually 10 cm long. Very few organic compounds can be examined as gases. The low frequency rotational changes in the gaseous phase often split the high frequency vibrational bands.

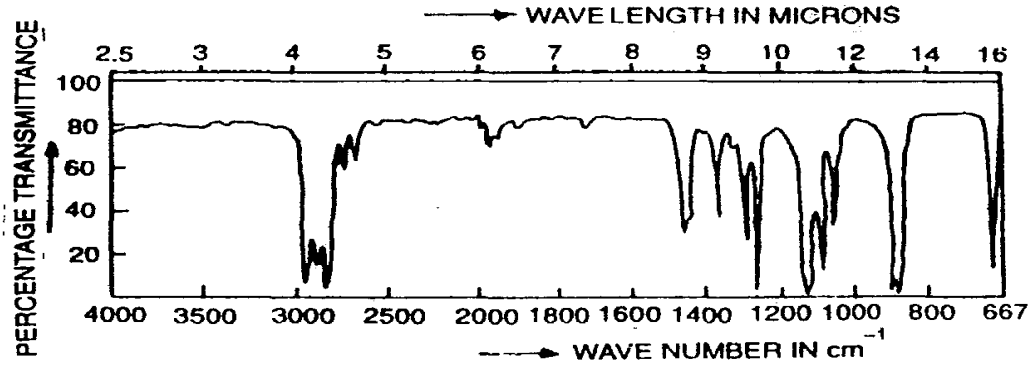


Fig. 9 Infra-red spectrum of 1, 4 Dioxane.

(d) **Solutions.** It is most convenient to determine the spectrum in solu-tions. Excellent solvents are those which have poor absorptions of their own. Unlike ultraviolet spectroscopy, too many solvents cannot be used in this technique. In Infra-red technique, all solvents do absorb in one region or the other. Some important solvents which may be used are:

(i) Chloroform, (ii) Carbon tetrachloride, (iii) Carbon disulphide etc.

Water cannot be used as a solvent as it absorbs in several regions ofthe infra-red spectrum.

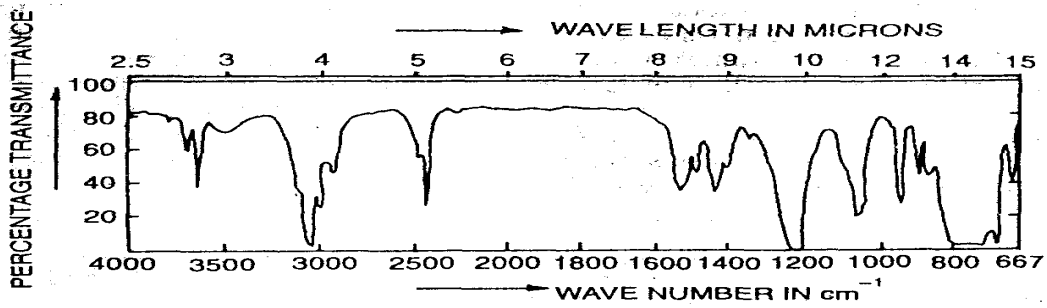


Fig. 10.Infra-red spectrum of Chloroform.

The sample under analysis is dissolved in a solvent. Its 1-5% solution is placed in a solution cell consisting of transparent windows (made of alkali metal halide). A second cell containing the pure solvent is placed inthe path of the reference beam to cancel out solvent interferences. In facl solvents do absorb in one region or the other.

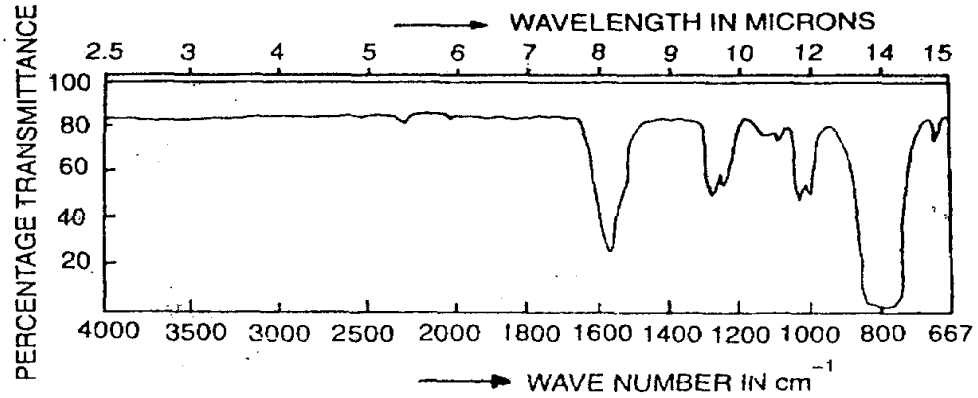


Fig. 11Infra-red spectrum of Carbon tetrachloride.

Hence, for correct analysis, two spectra should be run by dissolving the sample in two different solvents;

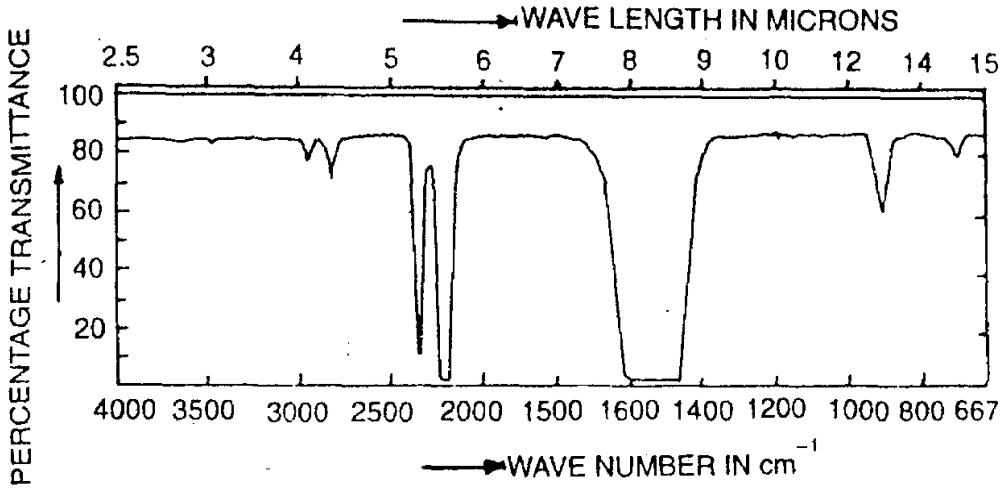


Fig. 12 Infra-red spectrum of Carbon disulphide.

Applications of Infra-Red Spectroscopy

Infra-fed spectrum of a compound provides more information than is nor-mally available from the electronic spectra. In this technique, almost all groups absorb characteristically within a definite range. The shift in the po-sition of absorption for a particular group may change (within the range) with the changes in the structure of the molecule.Impurities in a compound can be detected from the nature of the bands which no longer remain sharp and well defined. If the spectrum contains a strong absorption band between 1900-1600 cm^{-1}, the presence of carbonyl group [>C – O]in a compound is suspected. The position of the peakor the band not only tells the presence of a particular group but also reveals a good deal about the environments affecting the group. Further study of the spectrum reveals whether it is aldehydic, ketonic, ester, amide etc. Al-dehydes can be recognised from its characteristic C—H stretching; esters from C—O-stretching and amides show absorptions for N—H stretching and N—H bending absorptions in addition to vC=O in the said range.

Presence of conjugation with carbonyl group can be detected as it shifts vC=O stretching to the lower wave number. The absorption values for certain groups such as C=O, O—H are also important in detecting hydro-gen bonding. In case of hydroge.n bonding, the wave nurnber-of absorption is shifted downwards for both the donor as well as the acceptor group. It can also make distinction between intermolecular hydrogen bonding and intra-molecular hydrogen bonding; the absorption position due to the latter being independent of the change in concentration.

A molecule is constantly vibrating: its bonds *stretch* (and contract), and *bend* with respect to each other. Changes in vibrations of a molecule are caused by

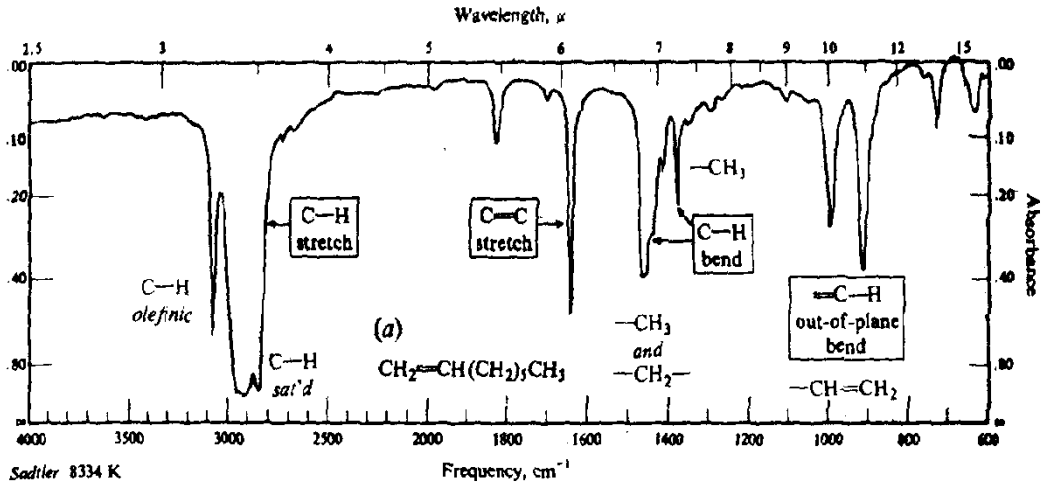
absorption of infrared light: light lying beyond (lower frequency, longer wave-length^ less energy) the red of the visible spectrum.

Like the mass spectrum, an infrared spectrum is a highly characteristic propertyof an organic compound—see, for example, the spectra in Fig. 13 and can be used both to establish the identity of two compounds and to reveal the structure of a new compound.

Two substances that have identical infrared spectra are, in effect, identical in thousands of different physical properties—the absorption of light at thousands of different frequencies—and must almost certainly be the same compound. (One region of the infrared spectrum is called, appropriately, the *fingerprint* region.)

The infrared spectrum helps to reveal the structure of a new compound by telling us what groups are present in—or absent from—the molecule. A particular group of atoms gives rise to *characteristic absorption bands;* that is to say, a particu-lar group absorbs light of certain frequencies that are much the same from com-pound to compound. For example, the —OH group of alcohols absorbs strongly at 3200-3600 cm^{-1} the C=O group of ketones at 1710 cm^{-1} the —C ≡ N group at 2250 cm^{-1}; the —CH group at 1450 and 1375 cm^{-1}.

Interpretation of an infrared spectrum is not a simple matter. Band; may beobscured by the overlapping of other bands. Overtones (harmonics) mayappearat just twice the frequency of the fundamental band. The absorption band of aparticular group may be *shifted* by various structural features—conjugation, electron withdrawal by a neighboring constituent, angle strain or Van der Waals strain



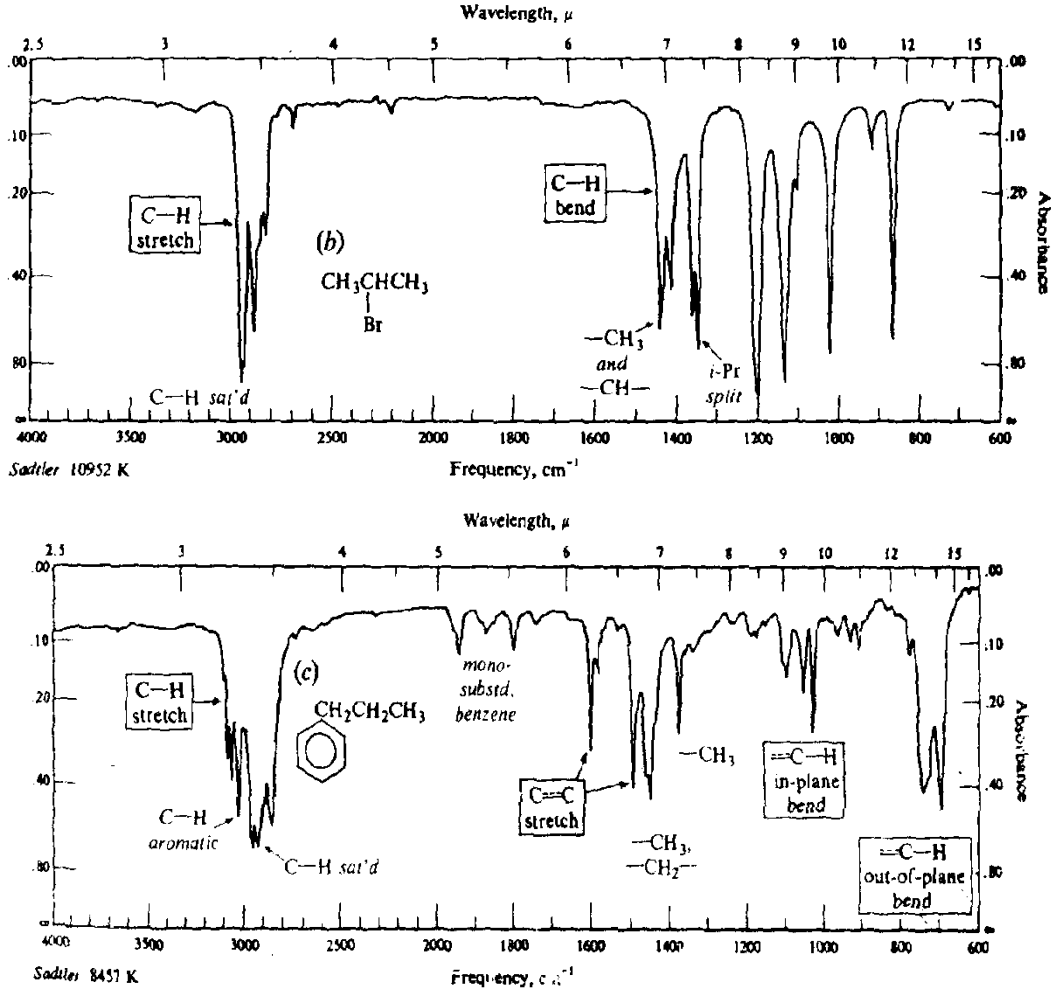


Fig. 13: Infrared spectra (a) 1-Octene, (b) Isopropyl bromide

Table 1:-lists infrared absorption frequencies characteristic of variousgroups.

Table 1CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES

Bond	Compound type	Frequency range, cm^{-1}
C-H	Alkenes	2850-2960
C—H	Alkenes	1350-1470
C—H	Aromatic rings	3020-3080 (m)
C-H	Alkynes	675-1000
O=C	Alkenes	3000-3100 (m)
C—H	Alkenes	3300
C=C	Alkenes	1640-1680(v)
C=H	Alkenes	2100-2260 (v)
C=C	Aromatic rings	1500,1600(v)
C—O	Alcohols, ethers, carboxylic acids, esters	1080-1300
O—H	Monomeric alcohols, phenols	3610-3640 (v)

C=O	Aldehydes, ketones, carboxylic acids, esters	3610-3640
	Hydrogen-bonded alcohols, phenols	3200-3600 *(broad)*
	Carboxylic acids	2500-3000 *(broad)*
N—H	Amines	3300-3500 (m)
C—N	Amines	1180-1360
C= N	Nitriles	2210-2260 (v)
—NO_2	Nitro compounds	1515-1560

Infrared spectra of hydrocarbons

In this first encounter with infrared spectra, we shall see absorption bands due to vibrations of carbon-hydrogen and carbon-carbon bonds: bands that will constantly reappear in all the spectra we meet, since along with their various functional groups, compounds of all kinds contain carbon and hydrogen. We mustexpect to find these spectra complicated and, at first, confusing. Our aim is to learn to pick out of the confusion those bands that are most characteristic of certain structural features.

Bands due to carbon-carbon stretching may appear at about 1500 and 1600 "1 for aromatic bonds, at 1650cm^{-1} for double bonds (shifted to about 1600 by conjugation), and at 2100 cm^{-1} for triple bonds. These bands, however, are often unreliable. (They may disappear entirely for fairly symmetrically substi-tuted alkynes and alkenes, because the vibrations do not cause the changein dipole moment that is essential for infrared absorption.) More generally useful bands are due to the various carbon-hydrogen vibrations.

Absorption due to carbon-hydrogen stretching, which occurs at the high-frequency end of the spectrum, is characteristic of the hybridization of the carbon holding the hydrogen: at 2800-3000 cm^{-1} for tetrahedral carbon; at 3000-3100 cm^{-1} for trigonal carbon (alkenes and aromatic rings); and at 3300$cm^{-1}$for diagonal carbon (alkynes).

Absorption due to various kinds of carbon-hydrogen bending, which occurs at lower frequencies, can also be characteristic of structure. Methyl and methylene groups absorb at about 1430-1470 cm^{-1}; for methyl, there is another band, quite characteristic, at 1375cm^{-1}. The isopropyl "split" is characteristic: a doublet, with equal intensity of the two peaks, at 1370 and 1385 cm^{-1} (confirmed by a band at 1170cm^{-1}). tert-Butyl gives an unsymmetrical doublet : 1370cm^{-1} (strong) and 1395 cm^{-1}*(moderate).*

Carbon-hydrogen bending in alkenes and aromatic rings is both in-plane and out-of-plane, and of these the latter kind is more useful. For alkenes, out-of-plane bending gives strong bands in the 800-1000 cm^{-1} region, the exact location depending upon the nature and number of substituents.

For aromatic rings, out-of-plane C—H bending gives strong absorption in the 675-870 cm^{-1}region, the exact frequency depending upon the number and location of substituents; for many compounds absorption occurs at:

Monosubstituted	690-710 cm^{-1}	m-disubstituted	690-710 cm^{-1}
o-disubstituted	735-770	p-disubstituted	810-840

Now, what do we look for in the infrared spectrum of a hydrocarbon? To begin with, we can readily tell whether the compound is aromatic or purely aliphatic. The spectra in Fig. 13 show the contrast that is typical: aliphatic absorption is strongest at higher frequency and is essentially missing below 900 cm^{-1}; aromatic absorption is strong at lower frequencies (C—H out-of-plane bending) between 650 and 900 cm^{-1}. In addition, an aromatic ring will show C H stretching at 3000-3100 cm^{-1}; often, there is carbon-carbon stretching at 1500 and 1600 cm^{-1} and C—H in-plane bending in the 1000-1100 cm^{-1} region.

An alkene shows C—H stretching at 3000-3100 cm^{-1} and, most characteristically, strong out-of-plane C—H bending between 800 and 1000 cm^{-1}, as discussed above.

A terminal alkyne, RC=CH, is characterized by its C—H stretching band, a strong and sharp band at 3300 cm^{-1}, and by carbon-carbon stretching at 2100 cm^{-1}. A disubstituted alkyne, on the other hand, does not show the 3300 cm^{-1}band and, if the two groups are fairly similar, the 2100 cm^{-1} band may be missing too.

Infrared spectra of alcohols

In the infrared spectrum of a hydrogen-bonded alcohol — and this is the kind that we commonly see — the most conspicuous feature is a strong, broad band in the 3200-3600 cm^{-1} region due to O— H stretching.

O— H stretching, *strong, broad*

Alcohols, ROH (or phenols, ArOH) 3200-3600 cm^{-1}

(A monomeric alcohol gives a sharp, variable band at 3610-3640 cm^{-1})

Another strong, broad band, due to C— O stretching, appears in the 1000-1200 cm^{-1} region, the exact frequency depending on the nature of the alcohol:

C— O stretching, *strong, broad*

1°ROH about 1050 cm^{-1} 3° ROH about 1150cm^{-1}

2°ROH about 1100 cm^{-1}ArOH about 1230cm^{-1}

Phenols (ArOH) also show both these bands, but the C—O stretching appears at somewhat higher frequencies. Ethers show C—O stretching, but the O—H band is absent. Carboxylic acids and esters show C—O stretching, but give absorption characteristic of the carbonyl group, O=O, as well

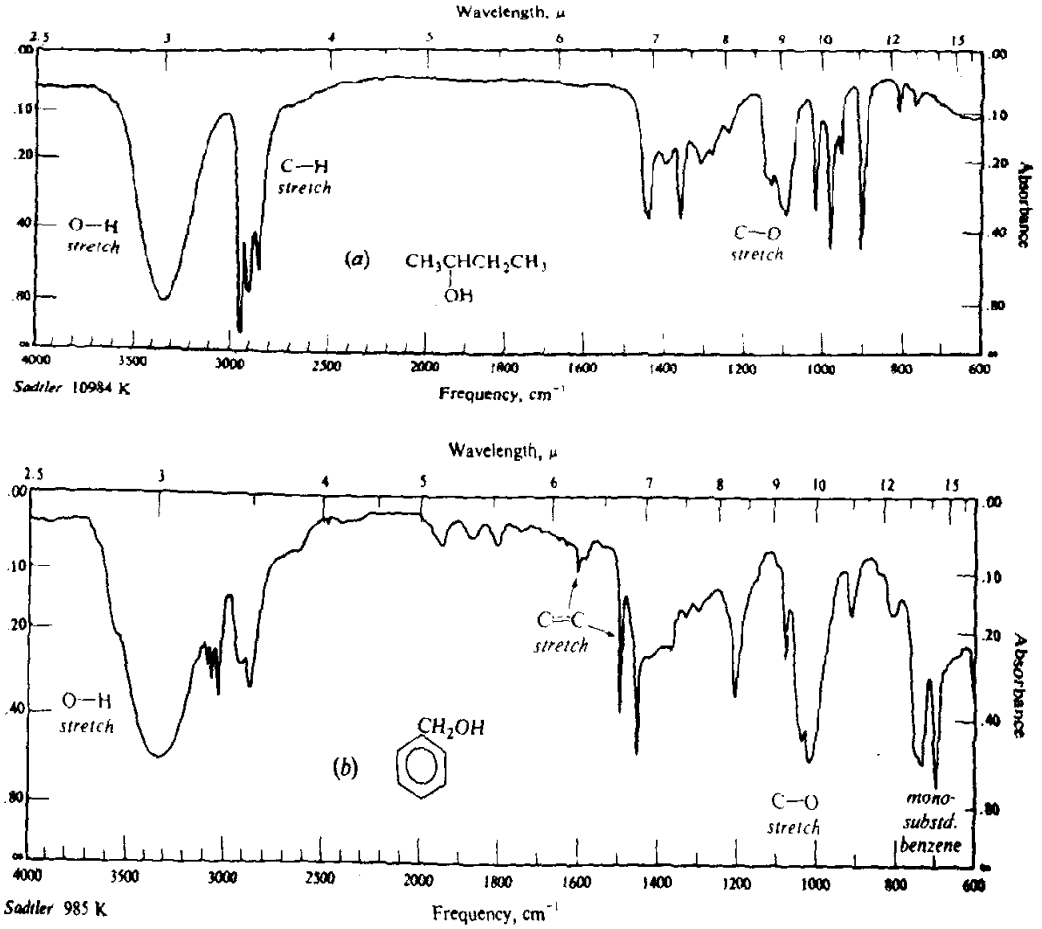


Fig. 14: Infrared spectra of (a) sec-butyl alcohol and *(b)* benzyl alcohol.

Infrared spectra of ethers

The infrared spectrum of ether does not, of course, show the O—H band characteristic of alcohols; but the strong band due to C—O stretching is still present, in the 1060-1300 cm^{-1} range, and is the striking feature of the spectrum.

C—O stretching, *strong, broad*

Alkylethers 1060-1150 cm^{-1}

Aryl and vinyl ethers 1200-1275 cm^{-1} (and, weaker, at 1200-1075 cm^{-1})

Carboxylic acids and esters show C—O stretching, but show carbonyl absorption aswell.

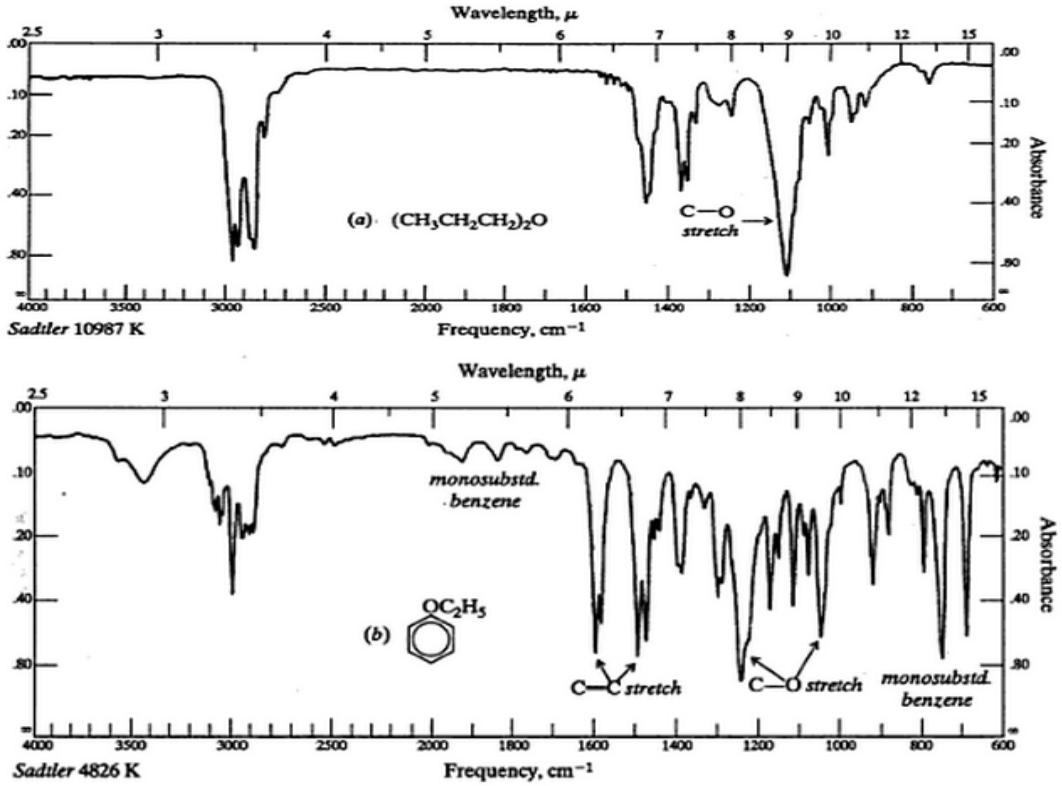


Figure 15: Infrared spectra of (a) di-n-propyl ether and (b) ethyl

Infrared spectra of an acyl compound:

The infrared spectrum of an acyl compound shows the strong band ion the neighborhood of 1700cm^{-1} that we have come to expect of C=O stretching. (See fig. 16)

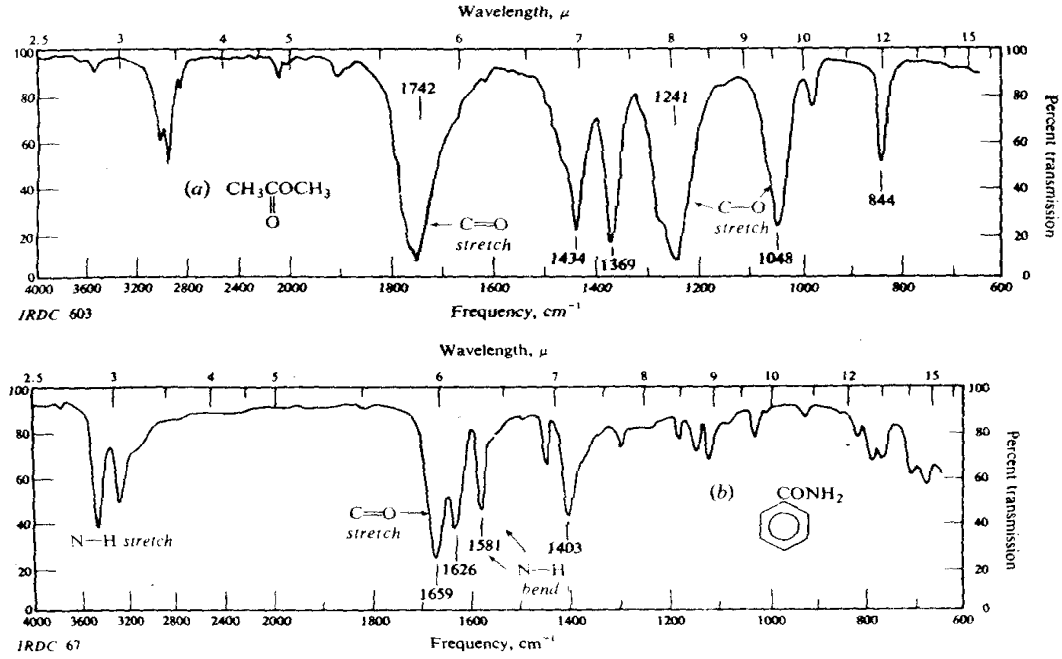


Fig. 16 Infrared spectra of (a) methyl acetate and *(b)* benzamide.

The exact frequency depends on the family the compound belongs to (Table 2) and, for a member of a particular family, on its exact structure. For esters, for example:

C=O stretching, *strong*

RCOOR 1740cm^{-1} ArCOOR 1715-1730 cm^{-1} RCOOAr 1770cm^{-1}

Or Or

TABLE 2

Compound	O-H	C-O	C= O
Alcohols	3200-3600 cm^{-1}	1000-1200 cm^{-1}	_
Phenols	3200-3600	1140-1230	—
Ethers, aliphatic	—	1060-1150	—
Ethers, aromatic	—	1200-1275 1020-1075	—
Aldehydes, ketones cm^{-1}	—	—	1675-1725
Carboxylic acids	2500-3000	1250	1680-1725
Esters	—	1050-1300 *(two bands)*	1715-1740
Acid chlorides	—	—	1750-1810
Amides ($RCONH_2$)	(N— H 3050-3550)—		1650-1690

Esters are distinguished from acids by the absence of the O—H band. They are distinguished from ketones by two strong C—O stretching bands in the 1050-1300 cm^{-1} region; the exact position of these bands, too, depends on the ester's structure.

Besides the carbonyl band, amides ($RCONH_2$) show absorption due to N—H stretching in the 3050-3550 cm^{-1} region (the number of bands and their location depending on the degree of hydrogen bonding), and absorption due to N—H bending in the 1600-1640 cm^{-1}region.

Infrared spectra of amines and substituted amides

The number and positions of absorption bands depend on the class which the amine belongs.An amide, substituted or unsubstituted, shows the C=O band in the 1640-1690 cm^{-1} region. In addition, if it contains a free N—H group, it will show ft stretching at 3050-3550 cm^{-1} and —NH bending at 1600-1640 cm^{-1}($RCONH_2$) or 1530-1570 cm^{-1} (RCONHR').

N—H stretching 3200-3500 cm^{-1}

1° Amines	2°Amines	3° Amines
Often two bands	*One band*	*No band*

N—H bending

1° Amines Strong bands 650-900 cm^{-1}*(broad)* and 1560-1650 cm^{-1}

C— N stretching

Aliphatic 1030-1230 cm^{-1}*(weak)* Aromatic 1180-1360 cm^{-1}*(strong)*

(3°: *usually a doublet)* *Two bands*

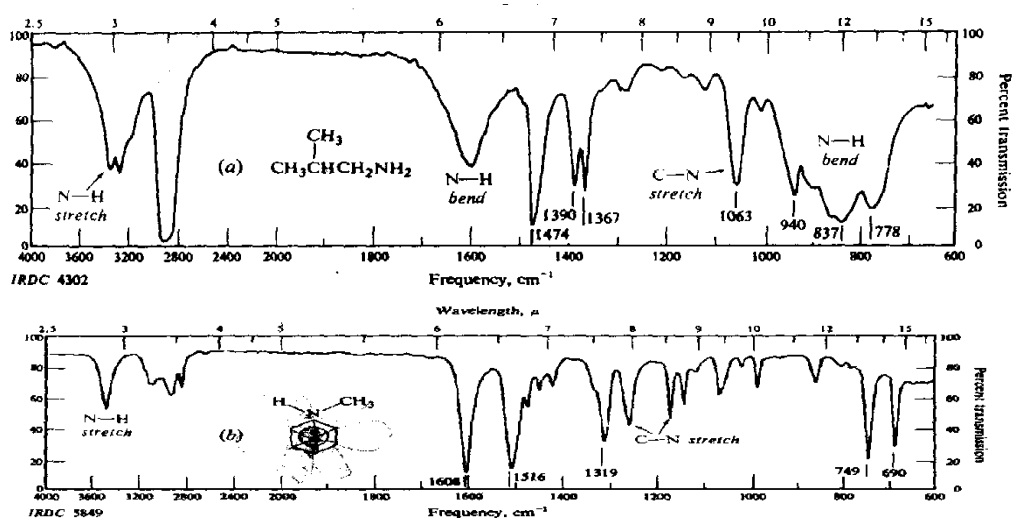
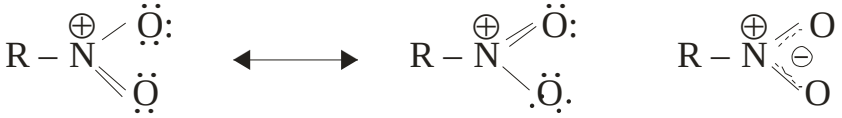


Fig. 17 Infrared spectra of (a) aliphatic amine (b) aromatic amine

Infrared spectra of Nitro-compounds

The electron diffraction method and X-ray analysis have shown that the two oxygen atoms are equidistant from the nitrogen atom (1 .22A) and also πELECTRONS are equally distributed between the two N—O bonds by isovalent conjugation. The uniform TCelectron distribution in the nitro group can be expressed as follows:



The vibrational behaviour of the nitro group also supports this structure. The presence of nitro group in a compound is characterized by the presence of two strong bands in its Infra-red spectrum which arise from the sym-metrical and asymmetrical stretching modes which occur in the region (i) 1620-1535 cm^{-1} and *(ii)* 1375-1275 cm^{-1}. Bands arising from deformation modes are difficult to distinguish from other bands occurring in the low frequency region. Primary derivatives ($RCH_2—NO_2$) absorb at higher fre-quency as compared to secondary (R_2CHNO_2). Tertiary nitro compounds ($R_3C.NO_2$) absorb at still lower frequency.

Aromatic compounds show two strong bands (i) 1570-1500 cm^{-1} and (ii) 1370-1300 cm^{-1}. Nitrites (—O—N= O) can be readily recognised from the two strong bands in the regions (i) 1680-1650 cm^{-1} and (ii) 1625-1605 cm^{-1}.

Table 3. Nitro compounds

Group	Type of vibration	Region in cm-1 And intensity
$C—NO_2$	N = O str	1620-1535 (s)
		1375-1274 (s)
$Ar—NO_2$	N = O str	1570-1500 (s)
		1370-1300 (s)
—O—N=O	N = O str	1680-1650 (s)
		1625-1605 (s)
$O—NO_2$	N = O str	1650-1600 (s)
		1270-1250 (s)

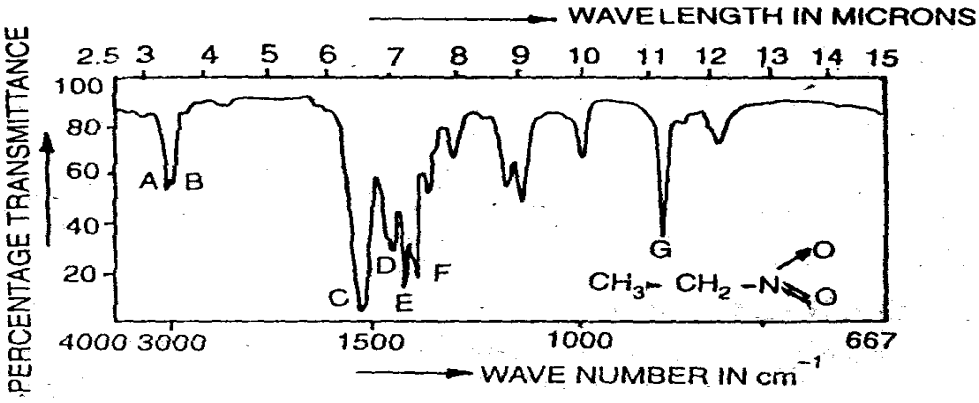


Fig18. Infra-red spectrum of Nitroethane as a film.

Positions of some characteristic absorption

A and B 3003 and 2940 cm^{-1}; C—H str in CH_3

C and E 1562 and 1394 cm^{-1};	Characteristic of nitro group
D = 1440 cm	C—H def in methyl
F = 1362 cm^{-1}	C—H def
G = 875 cm^{-1}	C—N str

Infrared spectra of nitriles and related compounds

Nitriles are the functional derivatives of the carboxylic acids containing C=N groups. Various equivalent structures of cyanides can be written as

$$R-C\equiv N \qquad R-C=\overset{\oplus}{N}: \qquad \overset{\oplus}{C}-C=C=\overset{\ominus}{N}$$

(a) (b) (c)

The electronegative nitrogen atom makes the carbon atom more positive and the polar-CN group has -I effect on the adjacent bond. The infra-red spectra of various cyanides (nitriles) have shown that the predominant form is *(a)* .with a triple bond between carbon and nitrogen atoms. Thus, the infra-red absorption occurs in the triple bond region between 2280-2200 cm^{-1}

The shift in υ C= N stretching absorption depends upon the electronic effect of atoms of groups attached to C= N group.

In aliphatic nitriles, the intensity of C = N stretching band is low.

$CH_3—O=N$ 2280 cm^{-1}

$CH_3—CH_2—C\equiv N$ 2257cm^{-1}

The decrease in the wave number of absorption is due to +I effect of the alkyl group/groups attached to C= N group. In asaturated nitriles, conjugation of electrons of the double bond with C=N group lowers the force constant and hence the wave number of absorption is also lowered.

Conjugative effect dominates and υC=N stretching occurs at a lower wave number if a group exerting -I and +E effects is attached with the C = N group.

For example, acrylonitrile shows υC=N stretching at 2231 cm^{-1}.

In aromatic nitriles, the υ C = N stretching decreases by about 20 cm^{-1}but band intensity increases as compared to the saturated compounds.

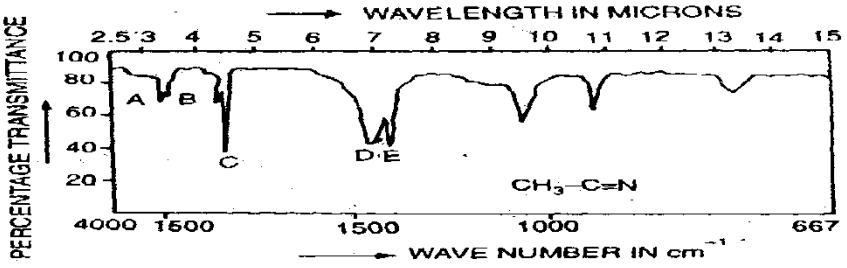


Fig. 19Infra-red spectrum of Methyl cyanide.

Positions of some characteristic absorption

A = 3002 cm^{-1} C—H str in CH3

B = 2940 cm^{-1} C—H str

D = 1440 cm^{-1} C—H def in CH_3

E = 1370 cm^{-1} C—H def

C = 2256 cm^{-1} C= N str in alkyl cyanides

Alkyl nitrile vC= N -2250 cm^{-1}

Benzonitrile vCs N - 2230 cm^{-1}

Isocyanides show an absorption band in the region 2200-2075 cm^{-1}.

Isocyanates absorb in the region 2275-2250 $cm^{-1.}$

In the case of azo compounds (— N= N —), the N= N stretching vibrations occur in the region 1630-1570 cm^{-1}. In case of diamides, azides etc.,absorption in the Infra-red spectrum occurs in the region 2160-2120 cm^{-1}.

Example. An organic compound (A) with molecular formula, C_3H_9N shows the following peaks in the Infra-red spectrum;

(i) 3012 cm^{-1} (m) (ii) 3423 cm^{-1}(s)

(iii) 3236 cm^{-1} (m) and (iv) 1615 cm^{-1} (m)

When the compound A is treated with nitrous acid, we get a compound Bwhich shows a strong peak at 3430 cm^{-1}. What are A and B and explain thereactions involved?

Solution. (i) The two bands at 3423 cm^{-1} and 3236 cm^{-1} are due to asymmetrical and symmetrical N — H str. Clearly, die compound contains— NH_2 group.

(ii) The band at 3012 cm^{-1} is due to C — H str.

(iii) 'The band at 1615, cm^{-1} is due to N — H bending.

The probable structure of (A) consistant with the given molecular for-mula and data is $CH_3CH_2CH_2NH_2$. When it is treated with nitrous acid,

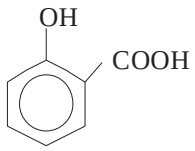
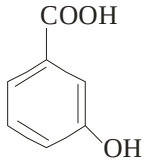
— NH_2 is converted into OH group which forms a strong peak at 3430 cm^{-1}.

The reaction involved is written as:

$$CH_3CH_2CH_2NH_2 + HONO \longrightarrow CH_3CH_2CH_2OH + N_2 + H_2O$$

n-Propylamine n-Propylalcohol

Example. How will you differentiate between the following pairs ofcompounds using Infra-red spectra:

(a)  and  (b) (i) CH_3CH_2CHO and (ii) $CH_2= CH - CH_2OH$

Solution.*(a)* o-hydroxy benzoic acid (salicylic acid) and w-hydroxy benzoic acid shows a similar broad band due to O—H str in —COOH between 3000—2500 cm^{-1}.

Difference.(i) In salicylic acid, intramolecular hydrogen bonding takes place. Therefore, the O—H str shifts to some lower wave number. As it is intramolecular, change in concentration does not cause any shift in O—H str absorption. In case of /n-hydroxy benzoic acid, vO—H str occurs at a still lower value due to intermolecular hydrogen bonding. Moreover, the absorption band will be broad and position of absorption shifts with dilution.

(i) o-hydroxy benzoic acid shows one band at 735—770 cm^{-1} while w-hydroxy benzoic acid shows two bands at 690-710 cm^{-1} and 730-770 cm^{-1}.

Propanal (CH_3GH_2CHO) shows characteristic absorption bands at

(i) 1720-1740 cm^{-1} due to vC—H str

(ii) vC—H str in aldehyde ~ 2720 cm^{-1}

(ifi) C—C str at 1400—1000 cm^{-1}

CH_2= CH—CH_2OH shows characteristic absorption at

(0 vO—H str 3300-3600 cm^{-1}

(if) vC= C str 1650 cn^{-1}

Example. How would the Infra-red spectrum of $C_6H_5CH_2NH_2$ CH_3—CO—$N(CH_3)_2$ differ?

Solution. Benzylamine shows the following characteristic absorptions.

(i)vC—H str -3100-3040 cm^{-1}

(ii) vC— C str -1600 cm^{-1}, - 1500 cm^{-1}, - 1460 cm^{-1}

(in aromatics)

(iii) vN—H str -3250-3500 cm^{-1}

NN-Dimethyl acatamide shows bands at

vC= O str 1675 cm^{-1} (s)

vC—H str -3300 cm^{-1}

Infrared Spectra of HeteroaromaticCompounds:Heteroaromatic compound such as pyridine, furan, thiophene etc. show C—H strbands in the region 3077-3000 cm^{-1}. Such compounds containing N—Hgroup shows N—H str absorption in

the region 3500-3220 cm^{-1}. In this region of absorption, the exact position depends upon the degree of hydrogen bonding and hence upon the physical state of the sample or the polarity of the solvent. Pyrrole and Indole in dilute solution in non-polar solvents show a sharp band near 3495 cm^{-1}

Ring stretching vibrations occur in the general region between 1600-1300 cm^{-1}. The absorption involves stretching and contraction of all the bonds in the ring and interaction between these stretching modes, Pyridineshows four absorption bands in this region. In this respect, it closely resembles monosubstituted benzene.

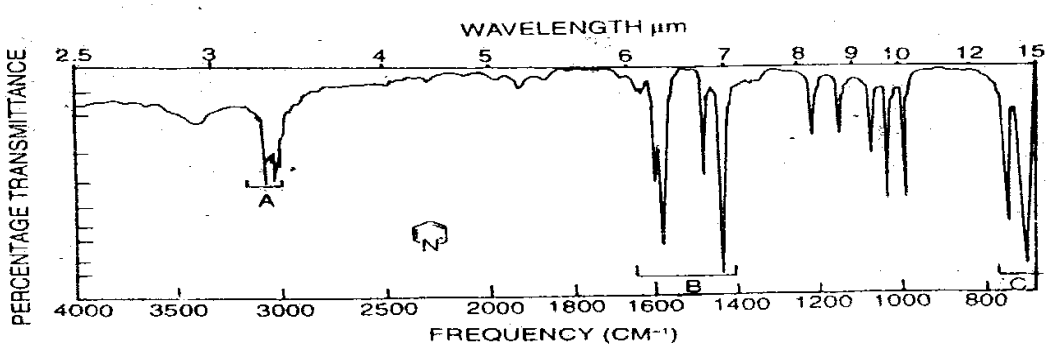


Fig. 20 Infra-red spectrum of Pyridine

*Courtesy :*Sadtler Research Laboratories, Philadalphia.

Positions of some characteristic absorptions

A = 3080-3010 cm^{-1}	C — H str aromatic
B = 1600-1430	C=C and C = N str (in ring)
C = 748, 703 cm^{-1}	C — Hdef out of plane

Unit -7

Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR)

The nucleus of a hydrogen atom (Proton) behaves as a spinning bar magnet because it possesses both electric and magnetic spin. Like any other spinning charged body, the nucleus of hydrogen atom generates a magnetic field (Fig.1)

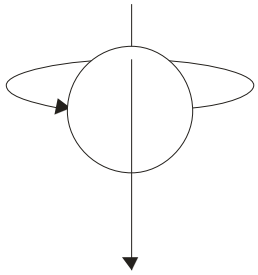


Fig. 1: Spinning charge in nucleus generates magnetic dipole

Nuclear magnetic resonance involves the interaction between an oscillating magnetic field of electromagnetic radiation and the magnetic energy of the hydrogen nucleus or some other type of nuclei when these are placed in an external static magnetic field. The sample absords electromagnetic radiations in radio wave region at different frequencies since absorption depends upon the type of protons or certain nuclei contained in the sample.

All nuclei carry a charge. So they will process spin angular momentum. The moment of the spin angular momentum is quantized, i.e, only those nuclei which have a finite value spin quantum number (I>O) will precess along the axis of rotation. It is known that the spin quantum number I is associated with mass number and atomic number of the nuclei.

Mass number	Atomic number	Spin quantum number I
Odd	odd or even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ldots$
even	even	0
even	odd	1,2,3

The circulation of the nuclear charge generates a magnetic moment along the axis. The intrinsic magnitude of the generated dipole is expressed in terms of magnetic moment μ.

If a proton is placed in a magnetic field, then it starts precessing at a certain frequency in the radio wave region and thus, will be capable of taking up one of the two orientations with respect to the axis of the external field.

(i) Alignment with the field and

(ii) Alignment against the field

If a proton is processing in the aligned orientation, it can pass into the opposed orientation by absorbing energy. From the high energy opposed orientation, it comes back to the low energy aligned orientation (more stable) by losing energy. The transition from one energy state to the other is called flipping of the proton. The transition between the two energy states can be brought about by the absorption of a quantum of electromagnetic radiation in the radio wave with energy hυ.

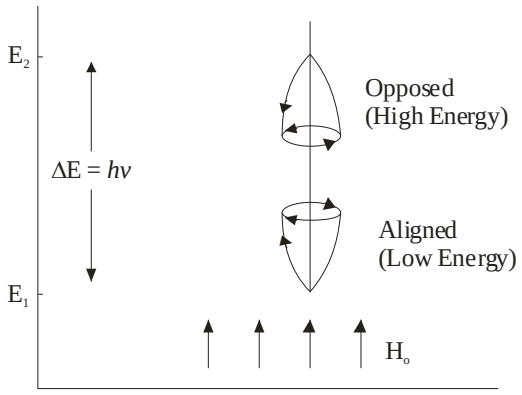


Fig.2: Energy level of a proton.

The energy required to bring about the transition $(\Delta E = h\nu)$ or to flip the proton depends upon the strength of the external field. Stronger the field, greater will be the tendency of the nuclear magnet to remain lined up with it and higher will be the frequency of the radiation needed to flip the proton to the higher energy state. Proton will absorb energy from the radio-frequency source only if the precessing frequency is the same as the frequency of the radio frequency beam, i.e., when the quantum energy(hυ) of electromagnetic radiation matches up the energy difference between the two energy states at the field strength H_0. When this occurs, the nucleus and the radio- frequency beam are said to be in resonance. Hence, the term nuclear magnetic resonance.

This technique consists in exposing the protons (placing the substance) in an organic molecule to as powerful field. The protons will process at different

frequencies. Now we irradiate these processing protons with steadily changing frequencies (For promoting or flipping protons from the low energy state to high energy state) and observe the frequency/ frequencies at which absorptions occur. It is generally more convenient to keep the radio- frequency constant and the strength of the magnetic field constantly varied. At some value of the field strength, the energy required to flip the protons matches a spectrum is called Nuclear magnetic resonance spectrum.

Number of Signals

The number of signals in the NMR spectrum tell the number different sets of equivalent protons in a molecule. Each signal corresponds to a set if equivalent protons. It may be noted that magnetically equivalent protons are chemically equivalent protons. Let us find the various sets of equivalent protons (signals) in the following types of compounds:

In acetone all the six protons are in exactly similar environment. Therefore, only one signal is observed. Similarly, we see only one signal for cyclobutance.

Some compounds showing more than one signal are as follows:

Just as the number of signals in an NMR spectrum tells us how many kinds of protons a molecule contains, so the positions of the signals help to tell us what kinds of protons they are: aromatic, aliphatic, primary, secondary, tertiary; benzylic, vinylic, acetylenic ; adjacent to halogen or to other atoms or groups. These different kinds of protons have different electronic environments, and it is the electronic that determines just where in the spectrum a proton absorbs.

When a molecule is placed in a magnetic field-as it is when one determines an NMR spectrum-its electrons are caused to circulate and, in circulating, they generate secondary magnetic fields: induced magnetic fields: induced magnetic fields.

Circulation of electrons about the proton in a magnetic field-as it is when one determines an a way that-at the proton-it oppose the applied fields. The field felt by the proton is thus diminished, and the proton is said to be shielded.

Circulation of electrons-specifically, π electrons-about nearby nuclei generates a field that can either oppose the applies field at the proton, depending on the proton's location (Fig.3). If the induced field opposes the applied field, the proton is shielded, as before. If the induced field reinforces the applied field, then the felt by the proton is said to be dishelmed.

Compared with a naked proton, a shielded proton requires a higher applied field strength-and a deshielded proton requires a lower applied field strength-to

provide the particular effective field strength at which absorption occurs, shielding thus shifts the absorption up field, and dishelming shifts the absorption downfield. Such shifts in the position of NMR absorptions. Arising from shielding and dishelming by electrons, are called chemical shifts.

The unit in which a chemical shift is most conveniently expressed is parts per million of the total applied magnetic field. Since shielding and dishelming arise from induced secondary fields, the magnitude of a chemical shift is proportional to the strength of the applied field-or, what is equivalent, proportional to the radiofrequency the field must match. If, However, it is expressed as a fraction of the applied field- that is, if the observed shifts is divided by the particular radiofrequency used-then a chemical shift has a constant value that is independent of the radiofrequency and the magnetic field that the NMR spectrometer employs.

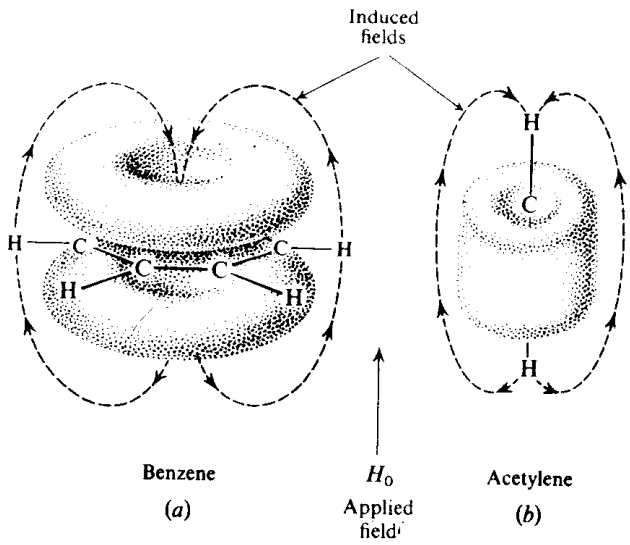


Fig. 3: Induced field (a) reinforces the applied field at the aromatic protons, and (b) opposes the applied field at the acetylenic protons. Aromatic protons are deshielded; acetylenic protons are shielded.

The reference point from a naked proton, but the signal from actual reasons, not the signal from naked proton, but the signal from an actual compound: usually tetramethylsilane, $(CH_3)_4Si$. Because of the low electro negativity of silicon, the shielding of the protons in the silage is greater than in most other organic molecules; as a result, most NMR signals appear in the same direction from the tetramethylsilane signal: downfield.

The most commonly used scale is the δ (Delta) scale. The position of the tetramethylsilane signal is taken 0.0ppm. Most chemical shift have δ values

between 0 and 10 (minus10, actually). A small δ value represents a small downfield shift, and a large value represents a large downfield shift.

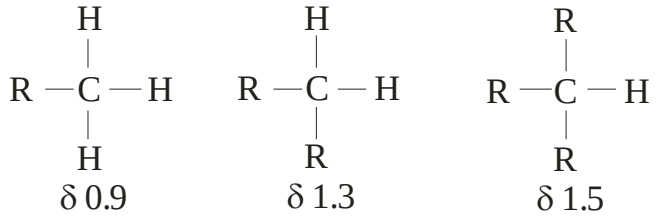
One sometimes encounters another scale: the τ (tau) scale, on which the tetramethylsilane signal is taken as 10.0ppm. Most τ values lie between 0 and 10. The two scales are related by the expression $\tau = 10 - \delta$.

An NMR signal from a particular proton appears at a different field strength than the signal from tetramethylsilane. The difference-the chemical shift-is measured not is gauss, as we might expect, but in the equivalent frequency units and it is divided by the frequency of the spectrometer used. Thus, For a spectrometer operating at 60MHz, that is at $60 \times 10^6\, Hz$

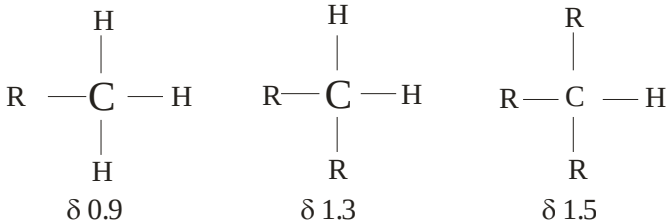
$$\delta = \frac{observedshift(Hz) \times 10^6}{60 \times 10^6 (Hz)}$$

The chemical shift for a proton is determined then, by thee electronic environment of the proton. In a given molecule, protons with different environments-non-equivalent protons-have different chemical shifts. Protons with the same environments-equivalent protons-have the same chemical shift.

Furthermore, it has been found that a proton with a particular environment shows much the same chemical shift, whatever the molecule it happens to be part of. Take, for example, our familiar classes of hydrogen's: primary, secondary, and tertiary. In the absence of other nearby substituents, absorption occurs at about these values:



Attachment of chlorine to the carbon bearing the proton causes a downfield shift. If the chlorine is attached to the carbon once removed from the carbon bearing the proton, there is again a downfield shift, but this time much weaker.



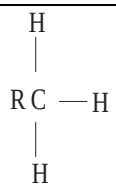
Two chlorines cause a greater downfield shift. Other halogens show similar effects.

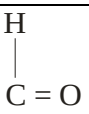
The downfield shift caused by chlorine is what we might have expected from its inductive effect: electron withdrawal lowers the electron density in the vicinity of the proton and thus causes deshielding. As we can see in table 1 the electronegative oxygen of alcohols and ethers similarly causes deshielding. The effect of a substitution on the chemical shift is unquestionably the net result of many factors; yet we shall often observe chemical shifts which strongly suggest that an inductive effect is at least one of the factors at work.

The NMR spectra (Fig 14) of the alkylbenzenes toluene, p-xylems, and mestiylene illustrate the points we have just made. In each spectrum there are two signals: one of the side chain protons, and one for the ring protons.(Here as in some-though not most-aromatic compounds, the ortho, meta, and para protons have nearly the same chemical shifts.)

In each spectrum the ring protons show the low-field absorption we have said is characteristic of aromatic protons. A absorption is not only at low field, but at nearly the same field strength for the three compounds: at δ 7.17, 7.05 and 6.78 (These values are not exactly the same, however, since the environments of the aromatic protons are not exactly the same in the three compounds.)

Table 1: Characteristic Proton Chemical Shifts

	Types of Proton	**Chemical shift δ, ppm**
Cyclopropane		0.2
Primary		0.9
Secondary	R_2C-H	1.3
Tertiary	R_3C-H	1.5
Vinylic	$C=C-H$	4.6 – 5.9
Acetylenic	$C\equiv C-H$	2 – 3
Aromatic	Ar – H	6 – 8.5
Benzylic	Ar – C – H	2.2 – 3
Allylic	C = C – C – H	1.7
Fluorides	H – C – F	4 – 4.5
Chlorides	H – C – Cl	3 – 4
Bromides	H – C – Br	2.5 – 4

Iodides	H – C – I	2 – 4
Alcohols	H – C – OH	3.4 – 4
Ethers	H – C – OR	3.3 – 4
Esters	RCOO – C – H	3.7 – 4.1
Esters	H – C – COOR	2 – 2.2
Acids	H – C – COOH	2 – 2.6
Carbonyl compounds	H – C – C = 0	2 – 2.7
Aldehydic		9 – 10
Hydroxylic	RO – H	1 – 5.5
Phenolic	ArO – H	4 – 12
Enolic	C = C – O – H	15 – 17
Carboxylic	RCOO – H	10.5 – 12
Amino		1 - 5

In each compound, side-chain protons-benzylic protons-are close enough to the ring to feel a little of the deshielding effect of the π electrons and hence absorb somewhat downfield from ordinary alkyl protons: at δ 2.32, 2.25 and 2.25. In all three compounds, the environment of the side-chain protons is almost identical, and so are the chemical shifts.

The similarity in structure among these three alkybenzencea is thus reflected in the similarity of their NMR spectra. There is However, a major difference in their structures-a difference in numbers of aromatic and side-chain protons-and, as we shall see in the next section, this is reflected in a major difference in their NMR spectra.

The chemical shift is fundamental to the NMR spectrum since, by separating the absorption peaks due to the various protons of a molecule, it reveals all the other features of the spectrum. The numerical values of chemical shifts, although significant, do not have the overriding importance that absorption frequencies have in the infrared spectrum. In our work with NMR, we shall escape much of the uncertainty that accompanies the beginner's attempts to identify infrared absorption bands precisely; at the same time, we have a greater

variety of concepts to learn about-but these, at our present level, we may find more satisfying and intellectually more stimulating.

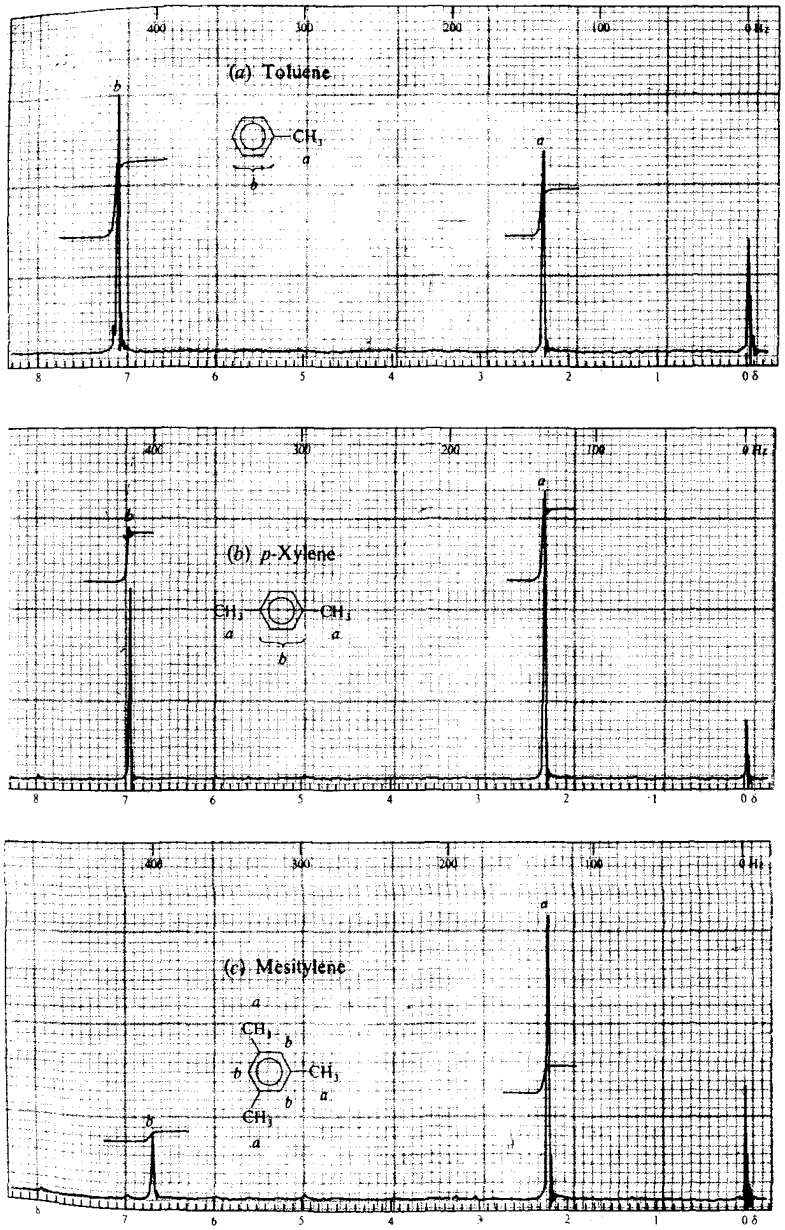


Fig. 4: NMR spectra : chemical shift. (a) Toluene; (b) p-xylene; (c) mesitylene

Peak area and proton counting

Let us look again at the NMR spectra of toluene, p-xylems, and mesitylene, and this time focus our attention, not on the positions of the signals, but on their relative intensities, as indicated by the sizes of the absorption peaks.

Judging roughly from the peak heights, we see that the (high-field) peak for side-chain protons is smaller than the (low-field) peak for a aromatic protons in the case of toluene, somewhat larger in the case of p-xylene, and considerably larger in the case of mesitylene. More exact comparison, based on the areas

under the peaks, shows that the peaks for side-chain and aromatic protons have sizes in the ratio 3:5 (or 6:4) for p-xylene; and 3:1 (or 9:3) for mesitylene.

This illustrates a general quality of all NMR spectra. The area under an NMR signal is directly proportional to the number giving rise to the signal.

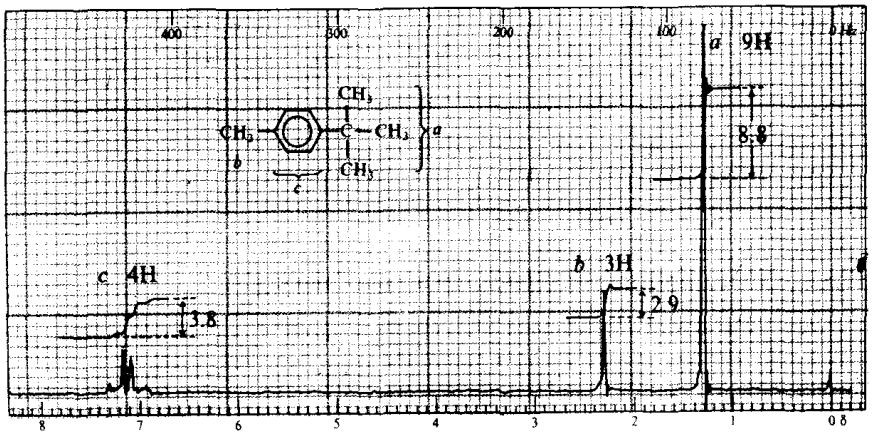


Figure 5:NMR spectrum of p-tert-butyltoluene. Proton counting

the ratio of step heights a:b:c is

8:8:2:9:3:8=3.0:1.0:1:3=9.0:3.0:3.9

Alternatively, since the molecular formula $C_{11}H_{16}$ is known,

$\frac{16H}{15.5units}=1.03H$ per unit

$a-1.03\times 8.8=9.1 \qquad b=1.03\times 2.9=3.0 \qquad c=1.03\times 3.8=3.9$

Either way, we find: a,9H; b,3H; c,4H.

The 4H of $c(\delta 7.1)$ are in the aromatic range, suggesting a disubstitutedbenzene . The 3H $b(\delta 2.28)$ of have a shift expected for benzylic protons, giving $CH_3-C_6H_4-$. There is left C_4H_9 which, in view of the 9H of $a(\delta 1.28)$ must be $-C(CH_3)_3$; since these are once removed from the butyl toluene (actually as shown by the absorption pattern of the aromatic protons, the para isomer).

Areas under NMR signals are measured by an electronic integrator, and are often given on the spectrum chart in the form of a stepped curve; height of steps is proportional to peak areas. NMR chart paper is cross-hatched, and we can conveniently estimate step heights by simply counting squares. We arrive at a set of numbers that are in the same ratio as the numbers of different kinds of protons. We convert this set of numbers into a set of a smallest whole numbers just as we did in calculating empirical formulas. The numbers of protons giving rise to each signal is equal to the whole number for that signal-or to some multiple of it. See, for example, Fig.5

We take any shortcuts we can. If we know the molecular formula and hence the total number of protons, we can calculate from the combined step heights the number of squares per proton. If we suspect a particular structural feature that gives a characteristic signal-an aldehydic (-CHO) or carboxylic (-COOH) proton, say, which gives a far-downfield peak-we can use this step height as a starting point.

Splitting of signals.:

An NMR spectrum, we have said, shows a signal for each kind of proton in a molecule; the few spectra we have examined so far bear this out. If we look much further, however, we soon find that most spectra are-or appear to be-much more complicated than this. Figure 7, for example , shows the NMR spectra for three compounds.

$CH_2Br-CHBr_2$ CH_3-CHBr_2 CH_3-CH_2Br

1,1,2-Tribromoethane 1,1 – DibromoethaneEthyl bromide

Each of which contains only two kinds of protons; yet, instead of two peaks, these spectra show five, six and seven peaks, respectively.

What does this multiplicity of peaks mean? How does it arise, and what can id tell us about molecular structure?

The answer is that we are observing the splitting of NMR signals caused by spin-spin coupling. The signal we expect from each set of equivalent protons is appearing, not as a single peak, but as a group of peaks. Splitting reflects the environment of the absorbing protons: not with respect to electrons, but with respect to other, nearby protons. It is a though we were permitted to sit on a proton and look about in all directions: we can see and count the protons attached to the carbon atoms next to our own carbon atom and , sometimes, even see protons still farther away.

Let us take the case of adjacent carbon atoms carrying, respectively, a pair of secondary protons and a tertiary proton, and consider first the absorption by one of the secondary protons:

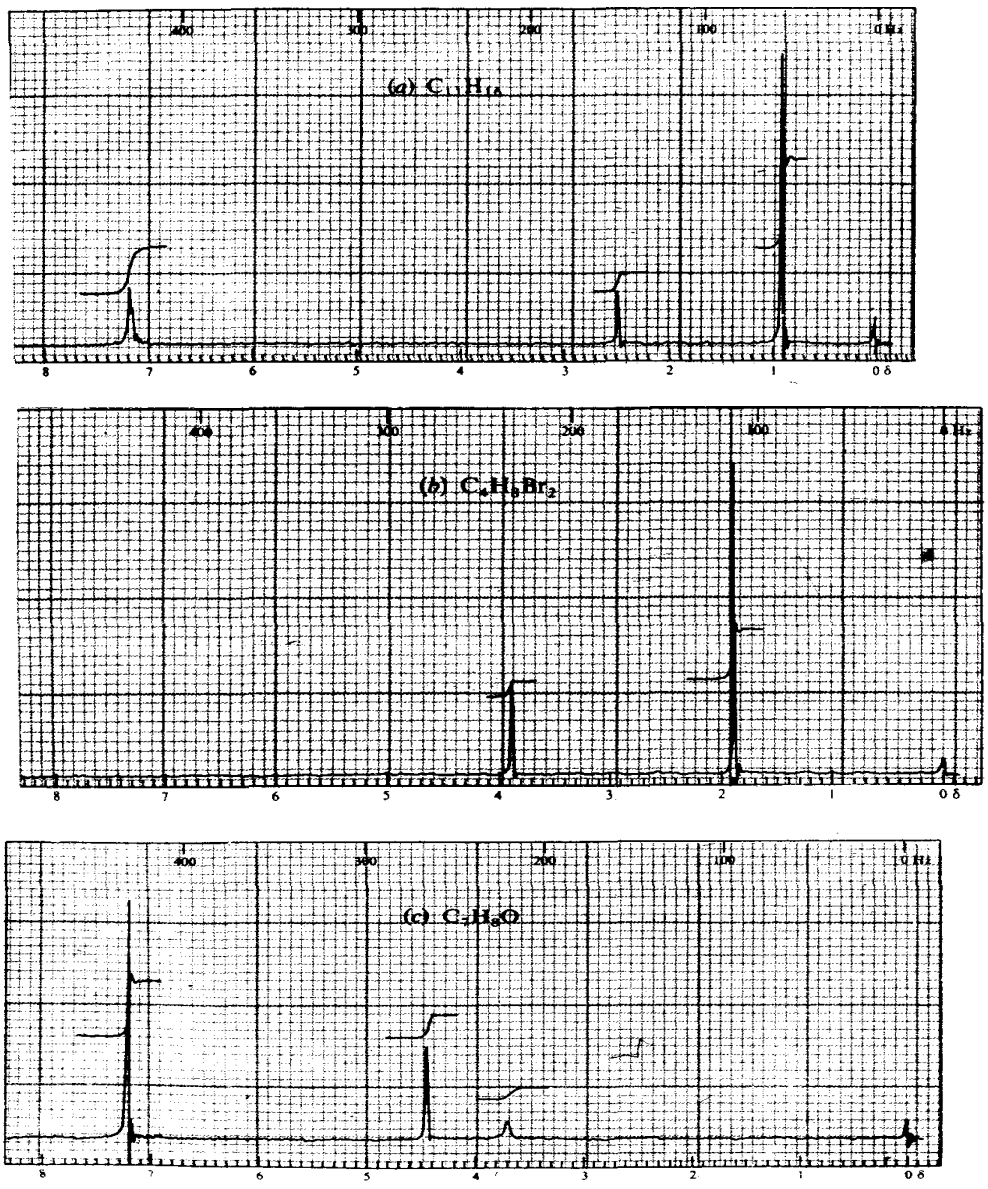
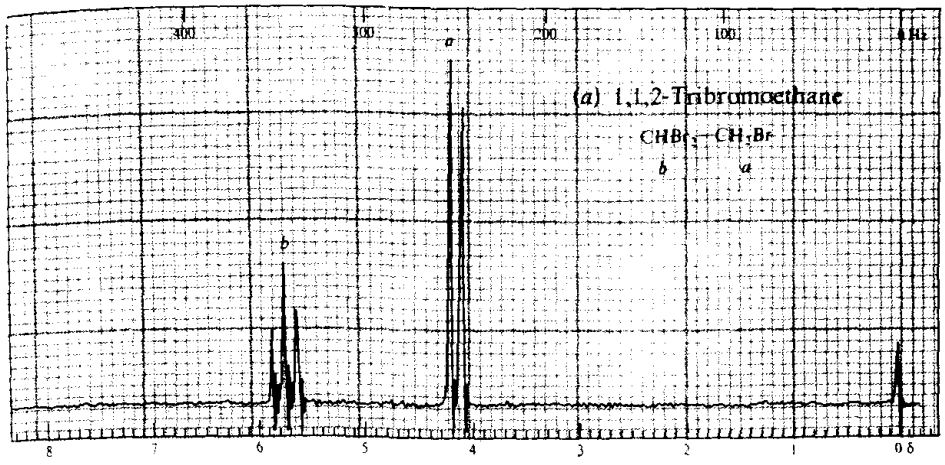


Fig. 6: NMR spectra



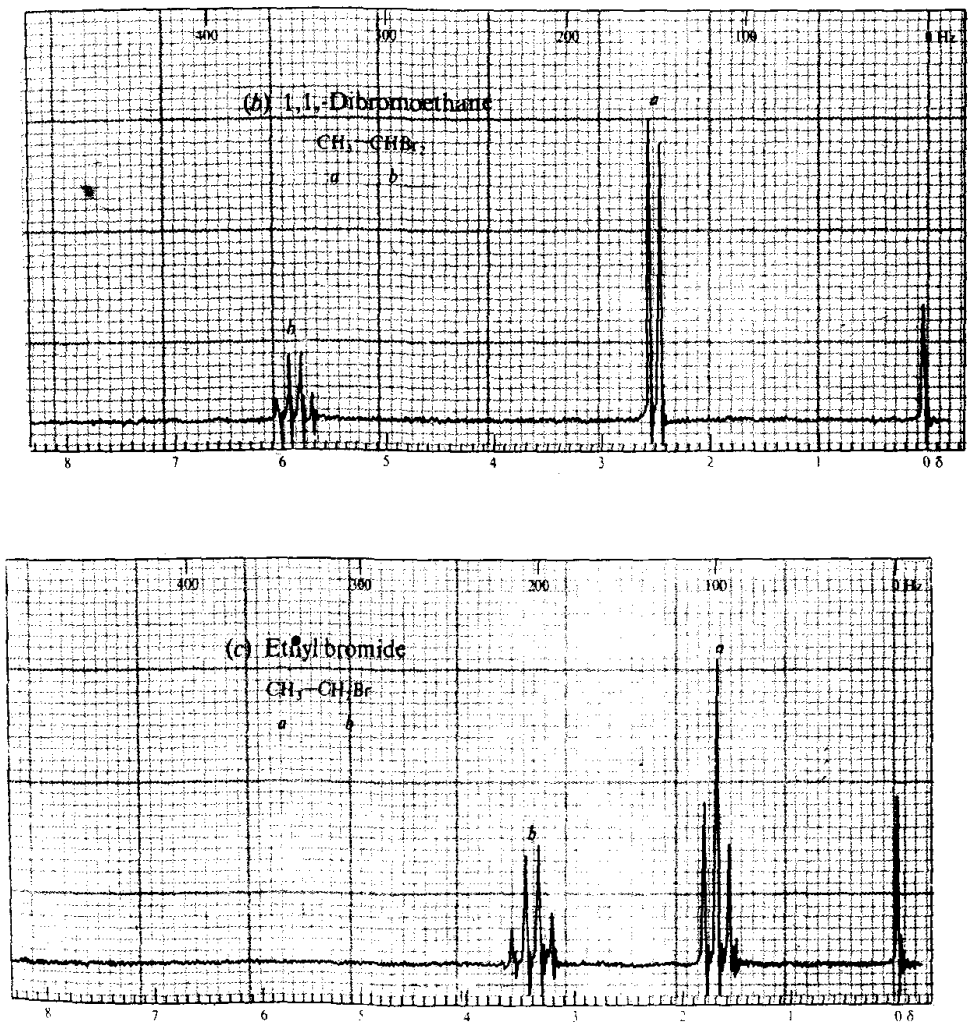
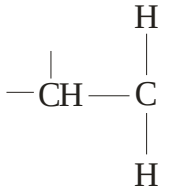


Fig. 7 : NMR spectra : splitting of signals. (a) 1, 1, 2-Tribromoethane; (b) 1, 1-dibromoethane; (c) ethyl bromide



The magnetic field that a secondary proton feels at a particular instant is slightly increased or slightly decreased by the spin of the neighboring tertiary proton: increased if the tertiary proton happens at that instant to be aligned with the applied field; or decreased if the tertiary proton happens to be aligned against the applied field.

For half the molecules, then, absorption by a secondary proton is shifted slightly downfield, and for the other half of the molecules the absorption is shifted slightly up filed. The signal is split into two peaks: a doublet, with equal peak intensities (Fig.8)

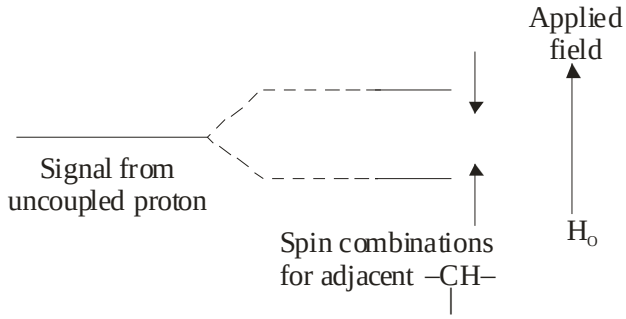
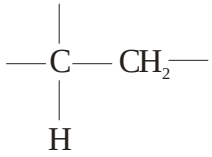


Figure.8 spin-spin coupling. Coupling with one proton gives 1:1

Next what can we say about the absorption by the tertiary proton?



It is, in its turn, affected by the spin of the neighboring secondary protons. But now there are two protons whose alignments in the applied field we must consider. There are four equally probable combinations of spin alignments for these two protons, of which two are equivalent. At any instant, therefore, the tertiary proton feels any one of these fields, and its signal is split into three equally spaced peaks: a triplet, with relative peak intensities 1:2:1, reflecting the combined (double) probability of the two equivalent combinations (Fig.9).

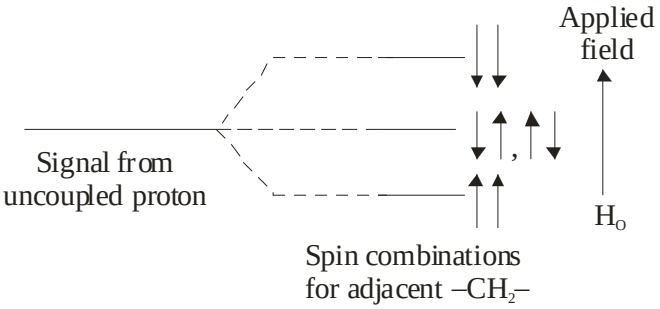


Figure.9 Spin-spin coupling. Coupling with two protons gives a 1:2:1

Figure 10 shows an idealized NMR spectrum due to the grouping $-CH-CH_2-$. we see a 1:1 doublet (from the $-CH_2-$) and a 1:2:1 triplet (from the $-CH-$). The total area (both peaks) under the doublet is twice as big as the total area (all three peaks) of the triplet, since the doublet is due to absorption by twice as many protons as the triplet.

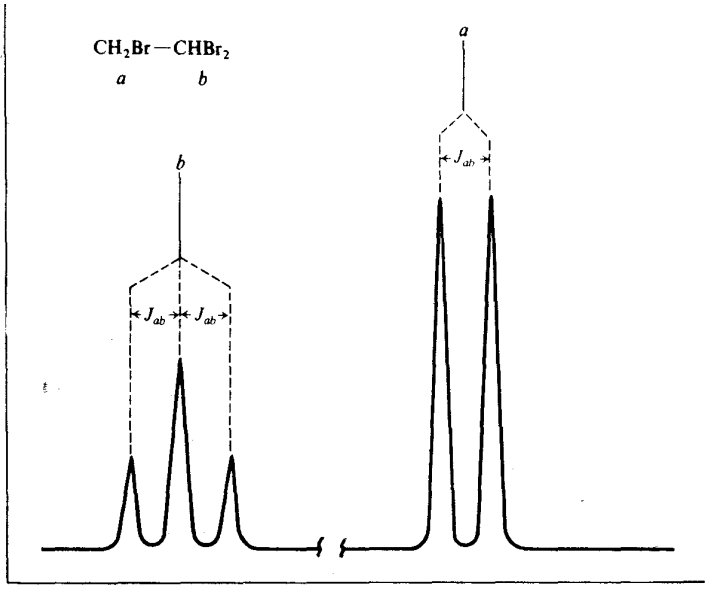


Figure.10: Signal a is split into a doublet by coupling with one proton; signal b is split into a triplet by two protons. Spacing in both sets are the same (j_{ab})

A little measuring shows us that the separation of peaks in the doublet is exactly the same as the separation of peaks in the triplet. (spin-spin coupling is a reciprocal affair, and the effect of the secondary protons on the tertiary proton must be identical with the effect of the tertiary proton on the secondary proton) even if they were to appear in a complicated spectrum of many absorption peaks, the identical peak separations would tell us that this doublet and triplet were related: that the (two) proton giving the doublet and the (one) proton giving the triplet are coupled, and hence are attached to adjacent carbon atoms.

We have seen that the NMR signal is split in to a doublet by one nearby proton, and into a triplet by two (equivalent) nearby protons what splitting can we expect more than two proton to produce? In fig11 we see that three equivalent proton split signal into four peaks-a quartet-with the intensity pattern 1:3:3:1.

It can be shown that, in general, a set of n equivalent proton will split an NMR signal into (n + 1) peak.

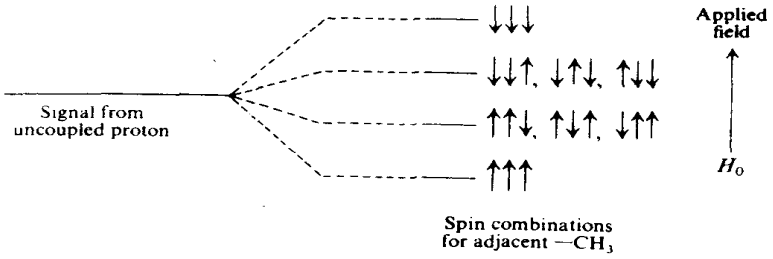


Figure.11 Coupling with three protons gives a 1:3:3:1 quartet.

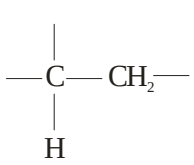
We now see not just five or six or seven peaks, but instead a doublet and a triplet, or a doublet and a quartet, or a triplet and a quartet. We recognize each of these multiplets from the even spacing within it, and form its symmetrical intensity pattern (1:1, or 1:2:1 or 1:3:3:1). Each spectrum does show absorption by just two kinds of proton; but clearly it shows a great deal more than that.

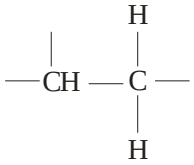
If we keep in mind that the peak area reflects the number of absorbing protons, and the multiplicity of splitting reflects the number of neighboring protons, we find in each spectrum just what we would expect.

In the spectrum of $CHBr_2 - CH_2Br$ we see

Downfield triplet and Upfield doublet

Area: 1 **Area: 2**

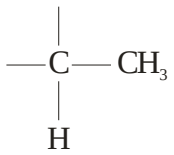


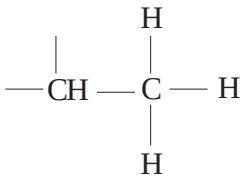


In the spectrum of $CH_3 - CHBr_2$ we see

Downfield triplet and Upfield doublet

Area: 1 **Area: 2**

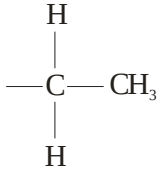


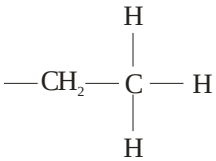


In the spectrum of $CH_3 - CH_2Br$ we see

Downfield triplet and Upfield doublet

Area: 1 **Area: 2**



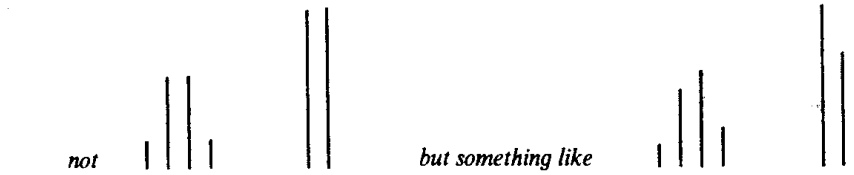


We see chemical shifts that are consistent with the deshielding effect of halogens: in each spectrum, the proton on the carbon carrying the greater number of halogens absorbs farther downfield (larger δ).

In each spectrum, we see that the spacing of the peaks within one multiplet is the same as within the other, so that even in a spectrum, with many other peaks, we could pick out these two multiples as being coupled.

Finally, we see a feature that we have not yet discussed: the various multiplets do not show quite the symmetry we have attributed to them. In spectrum, (a) we see

and in spectrum (*b*)



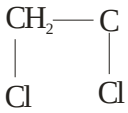
and in spectrum (*c*)

In each case, the inner peaks-the peaks nearer the other, coupled multiplets are larger than the outer peaks.

Perfectly symmetrical multiplets are to be expected only when the separation between multiplets is very large relative to the separation within multiplets-that is, when the chemical shift is much larger than the coupling constant .The patterns we see here are very commonly observed, and are helpful in matching up multiplets: we know in which direction-upfield or downfield-to look for the second multiple.

We have not yet answered a very basic question: just which protons in a molecule can be coupled? We may expect to observe spin-spin splitting only between non-equivalent neighboring protons. By "non-equivalent" protons we mean protons with different chemical shifts, as we mean most commonly protons on adjacent carbons, as in the examples we have just looked at (Fig.7); sometimes protons farther removed from each other may also be coupled, particularly if π bonds intervene. (If protons on the same carbon are non-equivalent as they sometime are- they may show coupling.)

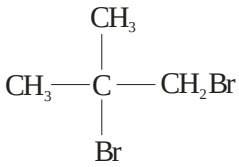
We do not observe splitting due to coupling between the protons making up the same $-CH_3$ group, since they are equivalent. We do not observe splitting due to coupling between the protons on C-1 of 1, 2- dichloromethane.



1, 2-Dichloroethane

Since although on different carbons, they too are equivalent

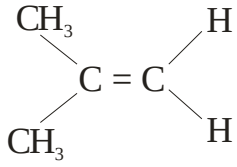
In the spectrum of 1, 2-dibromo-2methtypropane,



1,2-Dibromo-2-methylpropane

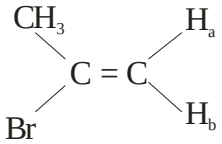
We do not observe splitting between the six methy1 protons, on the one hand and the two protons on the other hand. They are non-equivalent, and give rise to different NMR signals, but they are not on adjacent carbons and their spins do not (noticeably) affect each other. The NMR spectrum contains two singlets with a peak area ratio of 3:1 (or 6:2). For the same reason, we do not observe splitting due to coupling between ring and side-chain protons in alkyl benzenes (Fig.4)

We do not observe splitting between the two vinyl protons of isobutylene since



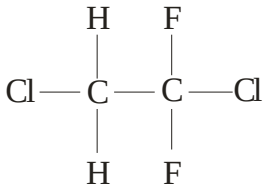
Isobutylene

they are equivalent. On the other hand, we may observe splitting between the two vinyl protons on the same carbon if, as in 2-bromopropene, they are non-equivalent.



2-Bromopropene

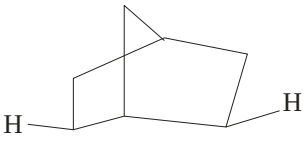
The fluorine nucleus has magnetic properties of the same kind as the proton. It gives rise to NMR spectra, although at a quite different frequency-field proton. Fluorine nuclei can be coupled not only with each other, but also with protons. Absorption by fluorine does not appear in the proton NMR spectrum it is far off the scale. But the splitting by fluorine of proton signals can be seen. The signal for the two protons of 1, 2-dichloro-1, 1- difluoroethane, for example



Coupling Constant (J):

The spacing between the splitted lines is known as the coupling constant and measured in hertz (Hz). This gives valuable information about the relative positions of the interacting nuclei. By convention a superscript before the symbol J represents the number of intervening bonds between the coupled nuclei. Labels identifying the coupled nuclei are usually indicated as subscript after the symbol 'j' e.g. 2 jab=2.7 Hz would indicate a coupling of 2.7 Hz between the nuclei a and b which are separated by two intervening bond.

Coupling constant (J) depends only on the number, type and spatial arrangement of the bonds separating the two nuclei, it is the molecule and is independent of the applied magnetic field. The magnitude of j and splitting pattern gives valuable structural information.

Typical Group consisting	J(Htz)
$CH_2CH_2CH_2CH_3$	2JH=-16
$CH_3CH_2CH_2CH_3$	3JH.H=7.2
$CH_3CH_2CH_2CH_3$	4JH H=0.3
$CH_2=C=C=CH_2$	5JHH=7
$H_2C=CH-CH=CH_2$	5JHH=1.3
	4 JHH = 1.5

In NMR spectra no molecular spin-spin coupling is observed. Spin-spin coupling is transmitted through the bonds of a molecule and does not occur between nuclei in hetero molecules.

Multiplicity of Signals –The (n+1) Rule:

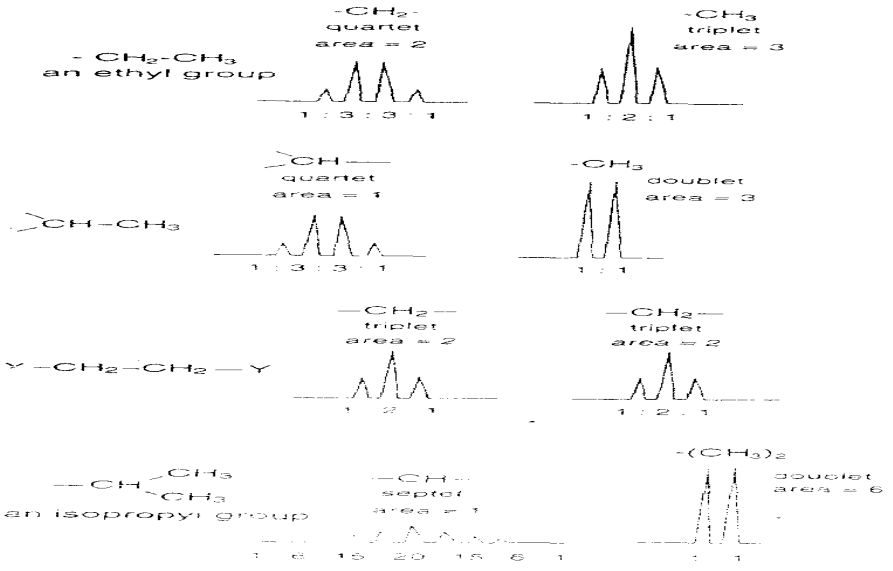
Spin-spin coupling gives rise to multiple splitting in ^1H-NMR spectra. According to (n+1) rule the NMR signal of nucleus coupled to 'n' equivalent hydrogen's will be split into a multiplet with (n+1) lines. The relative intensity

if lines in multiplet are given by the binomial coefficient of order 'n' or by Pascal famous triangle .

n	Multiplicity (n+1)	Relative line intensities	Name of the number
0	1	1	Singlet (s)
1	2	1:1	Doublet (d)
2	3	1:2:1	Triplet (t)
3	4	1:3:3:1	Quartet (q)
4	5	1:4:6:4:1	Quintet
5	6	1:5:10:10:5:1	Sextet
6	7	1:6:15:20:15:6:1	Septet

A methyl group- CH_3 (isolated from coupling to other protons in the molecule) will give a singlet. A CH_3CH_2 - group (isolated from coupling to other protons in the molecule) will appear as a quarter (CH_3) and a triplet (CH_3-)

Characteristic multiplet patterns

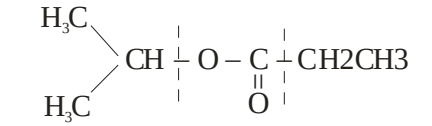


Analysis of ^1H NMR spectra:

Structural information from the NMR spectra can obtained by first knowing the two parameters (Chemical shifts and coupling constants) for all the protons and

then interpret the values of the coupling Constant in terms of the relationship between these parameters and structure.

1. A spin system or a group of coupled protons in the molecule should be located. For example isopropyl propionate comprises two separate proton system a seven proton system for the isopropyl group and a five proton system for the propionate residue as the ester group provides a barrier (5 bonds) against effective coupling between the two parts.



Isopropyl Propionate

2. Strongly and weekly coupled spins:these terms refer to the ratio of the separation of chemical shifts expressed in Hz (Δv) to the coupling constant J between them. For most purposes $(\Delta v / j)$ are larger than m3 the spin system is termed weakly coupled and when this ratio is smaller than m3, spins are strongly coupled.

This gives two important conclusions:

(a) The chemical shift separation (Δv) is expressed in Hz than in the dimensionless units (δ), its value changes with the operating frequency of the spectrometer while the j value remains constant. It follows that two spin systems will become progressively more weakly coupled as the spectrometer frequency increases. Weakly coupled spin system are easier to analyze than strongly coupled spin systems and this operation at higher frequencies or higher frequencies applied magnetic fields will yield spectra which are easily interpreted. This has been the important reason for the development NMR spectrometer operating at higher magnetic fields.

(b) Within a spin system some pairs of nuclei system some pairs of nuclei or groups of nuclei may be strongly coupled and other weakly coupled. Thus a spin system may be partially strongly coupled.

(4) Conventions used is naming spin system:

Consecutive letters of the alphabets A, B, C, D are used to denote the strongly coupled protons. Subscripts give the number of protons which are magnetically equivalent magnetically. A break in the alphabets indicates weakly coupled protons for example:

ABC : denotes a strongly coupled 3-spin system.

AMX : shows a weakly coupled 3-spin system

ABX : denotes a partially strong coupled 3-spin system

ABMXY : shows a spin system in which the three magnetically equivalent.

Nuclei are strongly coupled to the nucleus B, but weakly coupled to M, X and Y nuclei. The nucleus is strongly coupled to the nucleus Y but weakly coupled to all the other nuclei. The nucleus M is weekly coupled to all other 6 nuclei.

$AA^{I}XX^{I}--$ is a 4. Spin system described by two chemical shift parameters (for the nuclei A and X) but where $JAX \neq JAX^{I}$, and A and (X and X^{I}) are pairs of nuclei which are chemically equivalent but magnetically nonequivalent.

Analysis of the spectrum:

The process of deriving δ and j from set multiplets in a spin system is known as the analysis of the NMR spectrum. Any spectrum arising from a spin system can be analyzed by calculations on a computer.

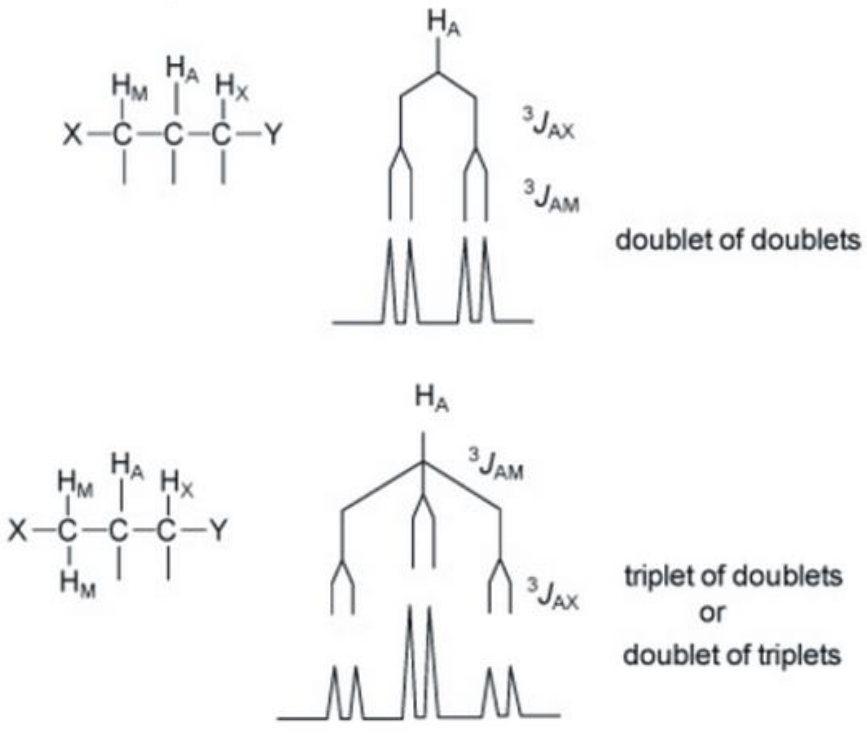
First order spectra:

In a large number of spectra multiples can be correctly analyzed by inspection and direct measurements. Such are known as first order spectra, which arise from weekly coupled spin system. By applying molecular magnetic field a large number of $^{I}HNMR$ spectra can be shown to exhibit the first order type.

Rules for the analysis of NMR Spectra:

1. A group of n magnetically equivalent protons will split a resonance of interacting group protons in to (n+1) lines. Then the resonance due to A protons is an XM system will be split into (m+1) lines while the resonance due to X protons will split into (n+1) lines.
2. The coupling constant j value in the above example in both parts of the spectrum will be equal J_{AX}.
3. The chemical shift of each group of interacting protons lies in the centre of the multiplet.

4. The relative intensities of the lines within each multiplet will be in the ratio of the binomical coefficients (table 3, 4). In the case of higher multiplets the outside components of the multiplets are relatively weak and may be lost into instrumental noise for ex. a septet may appear as a quintet if the outer lines are not visible. The intensity relationship is distorted in non-ideal cases.
5. When a group of magnetically equivalent protons interacts with more than one group of protons, its resonance will take the form of a multiplet of multiplets. Thus the resonance due to the A proton in a system The multiplet pattern are chained e.g. A proton coupled to 2 different protons will be split to a doublet by coupling to the first proton then each of the component of the doublet will be split further by coupling to the second proton resulting in a symmetrically multiplet with 4 lines.(doublet of doublets). The appropriate coupling constants will control splitting and relative intensitive obey rule 4.



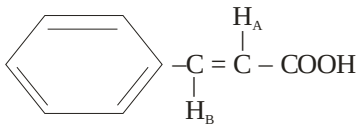
6. Protons which are magnetically equivalent do not split each other any system and will give rise to a singlet.
7. Spin system that contain groups of chemically equivalent protons but not magnetically equivalent cannot be analyses nu first order method.

8. Strongly and partly coupled spectra cannot be analysed by first order method.

   First order spectra: some examples of multiplicity:

   Following the above mentioned rules the multiplicities of the signals in the proton NMR spectra of the typical compounds can be predicated.

NMR spectrum of trans – cinnamicacid:



AX – System

The NMR spectrum of Trans cinnamic acid as shown below gives rise to the peaks at $\delta 7.4$ and $\delta 7.5$ and carbonyl protons at $\delta 12.5$ as experted. Following the (n+1) rule of multiplicity of the simple first order spectrum H_A appears as a doublet centered at $\delta 5.45$ due to splitting by neighboring HX and HX due to the splitting of the spin of HA appears similarly as two lines or a doublet. The separation between the two HA lines (J coupling constant) is the same as the separation between the two HA (J value the coupling constant) fig.11 intensity of signals HA and HX is in the ratio of 1:1.

NMR spectrum of trans – cinnamic acid:

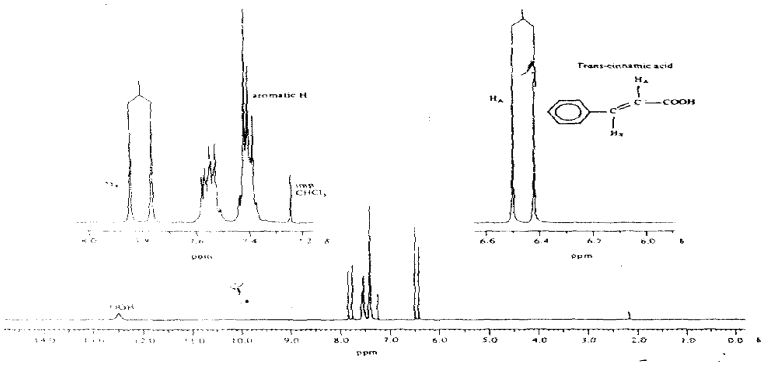


Fig. 11: H-NMR Spectrum of Trans – cinnamic acid (200 MHZ in $CDCl_3$) lower traces (full spectrum) upper trace, expanded × 6

Splitting of proton signals in styrene epoxide:

A Knowledge of the splitting or multiplicity of the protons as mentioned earlier in the first order spectra helps to develop a simple procedure for the analysis of any spectrum. The first step consists of drawing a splitting diagram from which the line spacing can be measured and related Splitting can be identified (fig.12).

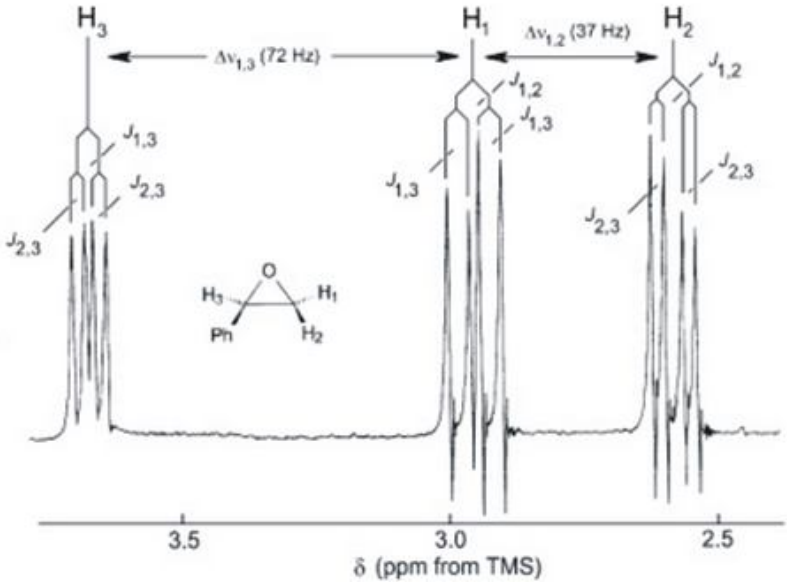


Fig.12 a portion of the NMR spectrum of styrene (100 Mz , as a 5% solution in CCI_4)

The NMR spectrum oxide (fig.12) contains the signals from 3 protons identified as H_1, H_2 and H_3 with H_1 at $\delta 2.95$, H_2 at $\delta 2.58$ and H_3 at $\delta 3.67$ ppm. Each signal appears as a doublet and the chemical shift of each proton is obtained by locating the center of the multiplet. The pair of nuclei giving rise to each splitting is clearly indicated by the splitting diagram above each multiplet with $2JH_{1-H2} = 5.9Hz$ $3JH_{1-H3} = 4.0Hz$ and $3JH_{2-H3} = 2.5Hz$

The first order analysis can be verified by calculating the ratio, for each pair of nuclei & establishing that it is greater than 3.

From fig. (12)

$$\frac{\Delta u12}{j12} = \frac{37}{5.9} = 6.3 \quad \frac{\Delta u1,3}{j1,3} = \frac{72}{4.0} = 18 \quad \frac{\Delta u2,3}{j2,3} = \frac{109}{2.5} = 43.6$$

Each ratio greater than 3.0 so a first order analysis is justified and the 100 MHz spectrum of the aliphatic protons of styrene oxide is a first order spectrum and could be labeled as AMX spin system.

Instrumentation

Nuclear magnetic resonance spectrophotometer makes use of a magnet, a radio-frequency, a detector and an amplifier. The detection system is used to note that energy is being transferred from the radio-frequency beam to the note that energy is being transferred from the radio-frequency beam to the nucleus.

The sample under investigation is taken in a glass tube which is placed between the pole faces of a magnet. A radio-frequency source (υ=60 mega cycles sec^{-1}) is made to fall on the sample. It can be done by feeding energy (radio-frequency

source) into a coil wound round the sample tube. A signal is detected if the nuclei in the sample resonates with the source, i.e., ΔE , energy required to flip the proton is the same as that of the source. Energy is transferred from the source via nuclei to the detector coil. The output from the detector can be fed to a cathode ray oscillograph or to a strip chart recorder after amplicationetc.

Protons being in different electronic environments in a molecule cannot resonate at exactly 60 mega cycles sec^{-1}. For practical purpose, radio-frequency source is held steady at the said frequency and field strength is varied by placing small electromagnet to the pole faces of the main magnet. By increasing the current flowing through these electromagnet, the total field strength is increased.

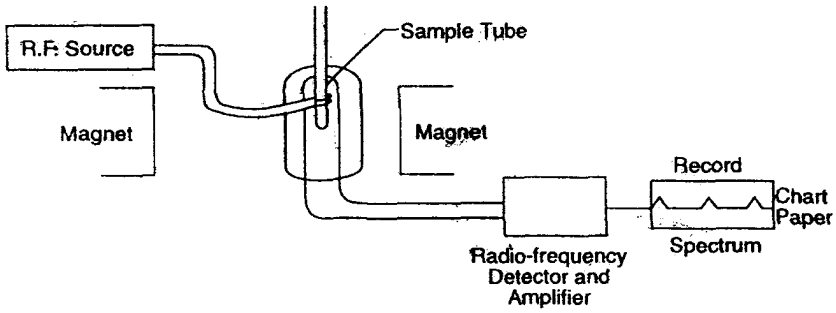


Fig. 13 : NMR spectrophotometer

As the field strength increases, the precessional frequency of each proton increase until resonance with the radio-frequency source takes place. As a proton (or a set of equivalent protons) comes to the chart paper. The signal from the detector produces a peak on the chart paper. The nmr spectrum consists of series of peaks that correspond to different applied field strength. Each peak means a set of protons.

Interpretation of ^{1}H NMR Spectra of some simple molecules

(a) Ethyl bromide, CH_3CH_2Br

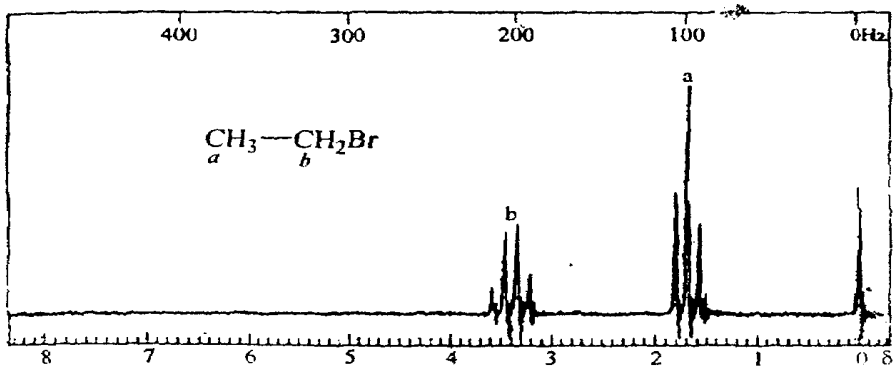


Fig. 14: NMR spectrum of ethyl bromide

1. A triplet (J=6Hz) centered at $\delta 1.7$ equivalent to 3H indicates the methyl protons (a).
2. A quartet (J=6Hz) centered at $\delta 3.4$ equivalent to 2H, indicated the methylene protons (b). the methylene protons (b) being adjacent to the electronegative bromine atom, resonate at a lower field. 3H upfield triplet and 2H downfield quartet indicate the ethyl group.

(b) Ethanol, $CH_3 - CH_2 - OH$

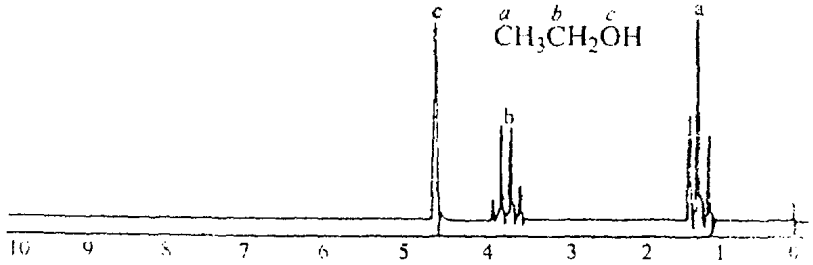


Fig. 15: NMR spectrum of ethyl alcohol

1. A triplet (J=6Hz) centered at $\delta 1.2$ integrated for 3H, represents the methyl protons(a).
2. A quartet (J=6Hz) centered at $\delta 3.63$ integrated for 2H, indicated the methylene protons (b). this signal is shifted downfield because it is bonded to oxygen, an electronegative element.
3. A singlet at $\delta 4.6$ equivalent to 1H, exhibits the OH proton (c). there is no coupling between the methylene protons (b) and the hydroxyl proton (c). hydroxyl proton exhibits the phenomenon of chemical exchange.

(c) Acetaldehyde $CH_3 - CHO$

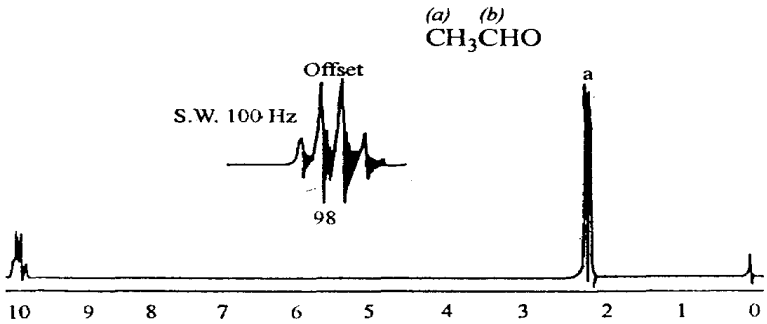


Fig. 16: NMR spectrum of acetaldehyde

1. A doublet (J=8Hz) at equivalent to 3H, reveals the methyl protons (a).
2. A quartet, centered at, equivalent to I H, indicates the aldehydic proton (b). anisotropic effect of carbonyl group shifts the signal very downfield.

(d) 1,1,2-Tribromoethane, $CHBr_2 - CH_2Br$

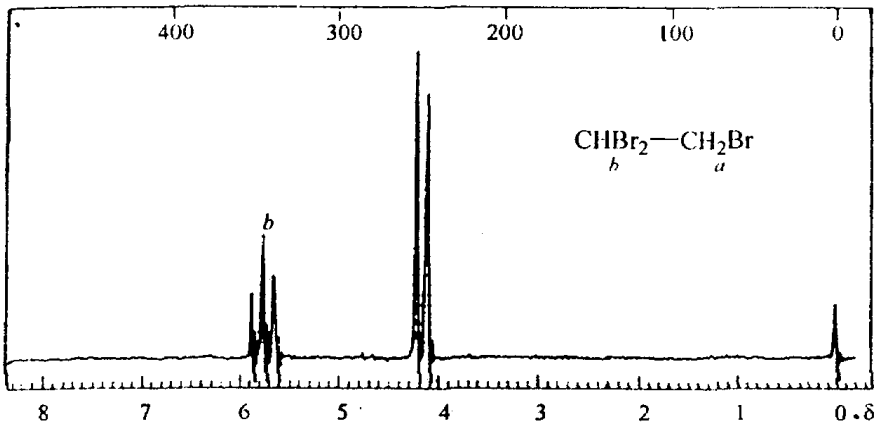


Fig. 17: NMR spectrum of 1,1,2-tribromoethane

1. A doublet (J=6Hz) centered at $\delta 5.8$, equivalent to 2H, indicates the methylene proton(a).
2. A triplet (J=6Hz) centered at $\delta 5.8$, equivalent to 1H, exhibits the methane proton (b). being adjacent to two bromine atoms, it resonates at downfield as compared to two methylene protons which are adjacent to one bromine atom.

(e) Ethyl acetate, $CH_3COOCH_2CH_3$

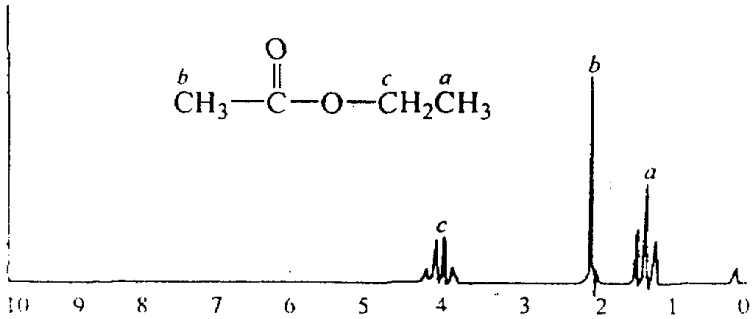


Fig. 18: NMR Spectrum of ethyl acetate

1. A triplet (J=7 Hz) at $\delta 1.23$, equivalent to 3H, indicates the methylene proton(a).

2. A singlet at $\delta 1.97$ equivalent to 3H, exhibits the methylene proton (b). its multiplicity and chemical shift indicate the presence of nearby carbonyl group.
3. A quartet (J=7 Hz) at $\delta 4.06$, equivalent to 2H, indicates the methylene proton(c) attached to electronegative oxygen function.

(f) Toluene, $C_6H_5-CH_3$

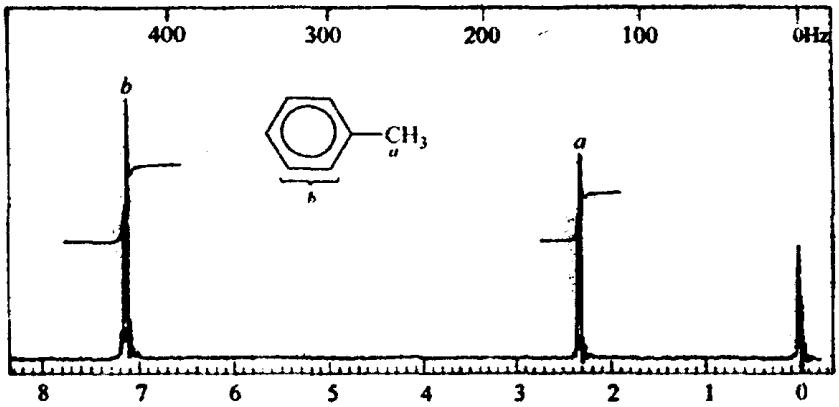


Fig. 19: NMR spectrum of toluene

1. A singlet at $\delta 2.3$ equivalent to 3H represents methyl protons (a). They appear at lower field because they are attached to the benzene ring.
2. The signals from five protons (b) on phenyl ring occur at the same place at and are characteristic of mono substituted benzene with a non-electronegative substituent.

(g) Acetophenone, $C_6H_5COCH_3$

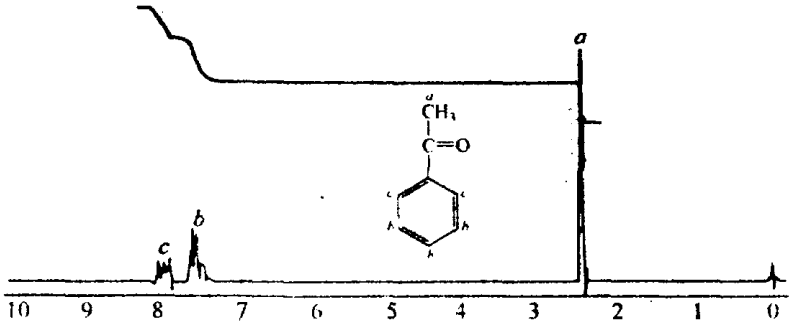


Fig. 20: NMR spectrum of acetophenone

1. A singlet at $\delta 2.47$ equivalent to 3H, revels methyl protons (a). Attached to unit.

2. Two sets downfield multiplets centered at $\delta 7.50$ and 7.80 indicate respectively the aromatic protons (b) and (c). the two ortho protons (c) are deshecilded by the anisotropic effect of C=O group in comparison to protons (b).

Problem

1. Product the chemical shift position in methyl acetate and ethyl acrylate $(CH_2 = CHCOOCH_2CH_3)$
2. Preduct the chemical shift positions for the protons in

a) Butanone $CH_2COCH_2CH_3$

b) ethyl propanoate $CH_3CH_2COOCH_2CH_3$

c) Vinyl propionate $CH_3CH_2COOCH = CH_3$

d) n-propyl acetate $CH_3COOCH_2CH_2CH_3$

3. Preduct the chemical shift positions for the protons in
   4-nitroanisole
4. How do yoe differentiate the following compounds on the basis of NMR spectroscopy?
   a) $CH_3CH_2COOCH_2CH_3$ From $CH_3COOCH_2CH_2CH_3$
   b) $C_6H_5NCOCH_3$ From $C_6H_5NHCOCC_6H_5$
   c) $CHCI_3$ From CH_3CH_2CI
   d) 1,1-Dichlorethane from 1,1-dichloro-2,2-bromoethane

5. Preduct the multiplicities of the signals in the proton NMR spectra of
   a) 1,3-dichloropropane $CICH_2CH_2CHCI$
   b) 1,1,3,3-tetrachloropropane $CI_2CHCH_2CHCI_2$
   c) Diisopropylether $(CH_3)_2 CH - O - (CH_3)_2$
6. The 60 MHZ ^1H NMR spectrum shown in below figure ( ) that of a hydrocarbon C_9H_{12}. Deduce its structure by accounting for
   a) chemical shift values
   b) integrals and
   c) Coupling constant.

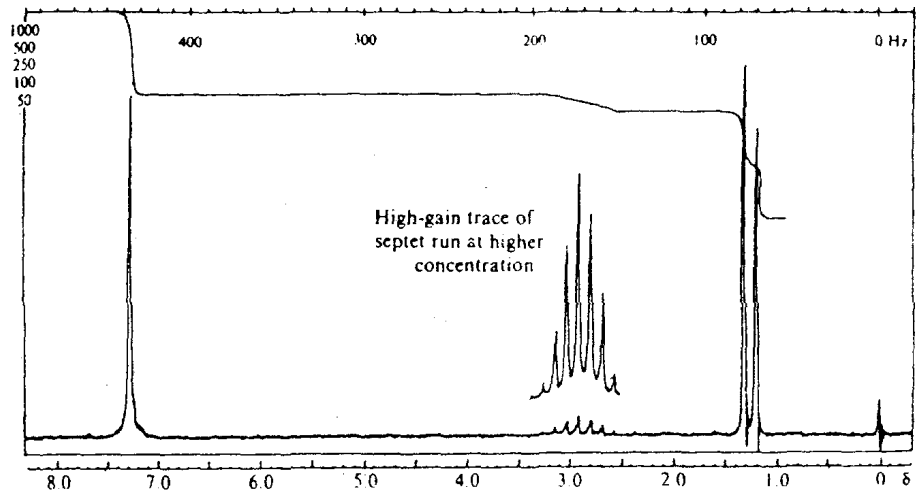


Fig. : H-NMR spectrum for C_9H_{12} in problem (6)

7. The 60 MHZ ^{1}H NMR spectrum in below figure is of a compound infrared evidence shows it to be a carboxylic acid. Deduce its structure by according for
    a) Chemical shift values
    b) Integrals and
    c) Coupling constants.

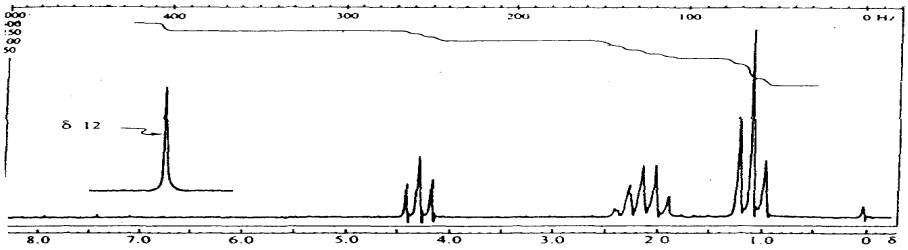


Fig. ^{1} H NMR spectrum for $C_4H_7BrO_2$ in problem (7)

8. Give a structure consistent with each of the following sets of NMR data.
    a) $C_3H_3CI_5$
    a triplet, $\delta 4.52, 1H$
    b doublet, $\delta 6.07, 2H$
    b) $C_2H_5CI_3$
    a singlet, $\delta 2.20, 3H$
    b singlet, $\delta 4.02, 2H$
    c) C_4H_9Br
    a doublet, $\delta 1.04, 6H$

bmultiplet, $\delta 1.95, 1H$

c doublet, $\delta 3.33, 2H$

d) $C_{10}H_{14}$

a singlet, $\delta 1.30, 9H$

b singlet, $\delta 7.28, 5H$

e) $C_{10}H_{14}$

a doublet, $\delta 0.88, 6H$

bmultiplet, $\delta 1.86, 1H$

c doublet, $\delta 2.45, 2H$

b doublet, $\delta 7.12, 5H$

f) C_9H_{10}

a quintet, $\delta 2.04, 2H$

b triplet, $\delta 2.91, 4H$

c singlet, $\delta 7.17, 4H$

g) $C_{10}H_{13}CI$

a singlet, $\delta 1.57, 6H$

b singlet, $\delta 3.07, 2H$

c singlet, $\delta 7.27, 5H$

h) $C_{10}H_{12}$

amultiplet, $\delta 0.65, 2H$

bmultiplet, $\delta 0.81, 2H$

c triplet, $\delta 1.37, 3H$

d singlet, $\delta 7.17, 5H$

i) $C_9H_{11}Br$

a quintet, $\delta 2.15, 2H$

b triplet, $\delta 2.75, 2H$

c triplet, $\delta 3.38, 2H$

d singlet, $\delta 7.22, 5H$

j) C_3H_5CIF

a triplet, $\delta 1.75, 3H$

b triplet, $\delta 3.63, 2H$

9. Give a structure or structures consistent with each of the following sets of CMR data.

a) $C_3H_5CI_3$

a triplet	$\delta 45.3$
b doublet	$\delta 59.0$

b) C_4H_9Br

a quartet	$\delta 20.9$
b doublet	$\delta 30.7$
c triplet	$\delta 42.2$

c) $C_3H_6CI_{12}$

a quartet	$\delta 22.4$
b triplet	$\delta 49.5$
c doublet	$\delta 55.8$

d) C_3H_5Br

a triplet	$\delta 32.6$
b triplet	$\delta 118.8$
c doublet	$\delta 134.2$

e) C_6H_{10}

a triplet	$\delta 22.9$
b triplet	$\delta 25.3$
c doublet	$\delta 127.2$

f) $C_4H_8Br_2$

a quartet	$\delta 10.9$
b triplet	$\delta 29.0$
c triplet	$\delta 35.5$
d doublet	$\delta 54.3$

10. Identify the stereoisomeric 1,3-dimethylclyobutanes on the basis of their NMR spectra.

Isomer X: singlet, $\delta 2.13, 6H$

singlet, $\delta 3.21, 4H$

IsomerY: singlet, $\delta 1.88, 6H$

doublet, $\delta 2.84, 2H$

doublet, $\delta 3.54, 2H$

doublet have equal spacing

11. When mesitylene (NMR spectrum, Fig.17.10, p. 608) is treated with HF and SbF_5 in liquid solution, the following peaks, all singlets, are observed in the NMR spectrum: $\delta 2.8, 6H$; $\delta 2.9, 3H$; $\delta 4.6, 2H$; and $\delta 7.7, 2H$ To what compound is the spectrum due?

    Of what general significance to chemical theory is such an observation?

12. What is a possible explanation for the following differences in chemical shift for the aromatic protons? Benzene $\delta 7.37$; toluene $\delta 7.17$; p-xylene $\delta 7.05$; mesitylene $\delta 6.78$.

Unit – 8

Ultra-violet and Visible Spectroscopy

This technique is Electronic Spectroscopy since it involves the promotion of electrons (σ, π, n^* electrons) from the ground state to the higher energy state. It is very useful to measure the number of conjugated double bonds and also aromatic conjuction within the various molecules. It also distinguishes between conjugated and non-conjugated systems; $\alpha, \beta -$ unsaturated carbonyl compounds from β, γ -analogues, homoannular and Heteroannular conjugated dienes etc. For visible and ultra-violet spectrum, electronic excitations occur in the range of 200-800 $m\mu$ and involves the promotion of electrons to the higher energy molecular orbital.

Since the energy levels of a molecule are quantized, the energy required to bring the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation. Clearly, if the substance is exposed to radiation of some different value of frequency, energy will not be absorbed and thus, light or radiation will not suffer any loss in intensity. If radiation of a desired or correct frequency is passed or made to fall on the sample of the substance, energy will be absorbed and electrons will be promoted to the higher energy states. Thus, light radiation on leaving the sample after absorption will be either less intense or its intensity may be completely lost.

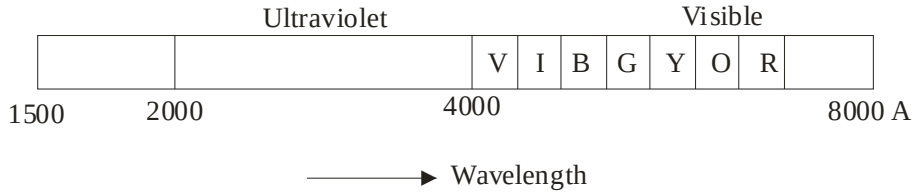


Fig. 1 The range of UV-visible Spectra

The Absorption Law

There are two laws which govern the absorption of light by the molecules. These are

(i) Lambert's Law

(ii) Beer Law

(i) **Lambert's Law:** When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

$$-\frac{dl}{dx} = kI$$

Where *I* = intensity of radiation after passing through a thickness *x*, of the medium

dI = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, *dx* of the medium.

$-\frac{dl}{dx}$ = rate of decrease of intensity of radiation with thickness of the absorbing medium.

k = proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Let I_0 be the intensity of radiation before entering the absorbing medium (*x* = 0).

Then *I*, the intensity of radiation after passing through any thickness, say *x* of the medium can be calculated as:

$$\int_{I_o}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} k dx$$

or $$\ln \frac{I}{I_o} = -kx$$

or $$\frac{I}{I_o} = e^{-kx}$$

or $$I = I_o e^{-kx}$$

The intensity of the radiation absorbed, I_{abs} is given by:

$$I_{abs} = I_o - I = I_0(1 - e^{-kx})$$

The above Lambert's law equation can also be written by changing the natural logarithm to the base 10.

$$I_{abs} = I_o 10^{-ax}$$

Where *a* = extinction coefficient of the absorbing medium

$$a = \frac{k}{2.303}$$

Note: For ultraviolet spectrum, the region from 200 mμ to 380 mμ (called quartz region) is considered. The molecular absorption in the UV-VIS region

depends mainly on the electronic structure of the molecule. Depending upon the presence of a common group, the ultraviolet spectrum of a complex compound and that of a simple compound may almost be identical.

(ii)Beer's Law: This law states that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.

Mathematically, this law is stated as

$$-\frac{dI}{dx} = k'Ic$$

Where *c* = conc. of the solution in moles litre^{-1}

k' = molar absorption coefficient and its value depends upon the nature of the absorbing substance.

Suppose I_0be the intensity of the radiation before entering the absorbing solution. (when x=a), then the intensity of radiation, *I* after passing through the thickness *x*, of the medium can be calculated:

$$\int_{I_o}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} k'cdx$$

or $$I = I_O e^{-k'cx}$$

The above equation can also be written by changing the nature of logarithm to the base 10.

$$I = I_O 10^{-a'cx}$$

Here $\frac{k'}{2.303} = a'$ where *a'* = molar extinction coefficient of the absorbing solution.

Instrumentation

A spectrophometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus, the instrument compares the intensity of the transmitted light with that of the incident light.

The modern ultra-violet visible spectrometers consist of light source, monochromator, detector, amplifier and the recording devices. The most suitable sources of light are :Tungsten Filament Lamp and hydrogen deuterium discharge lampwhich covers the whole of the UV-visible region. Tungsten Filament Lamp is particularly rich in red radiation i.e. radiations with wavelength 375 mμ , while the deuterium discharge lamp covers the region below it. The intensity of deuterium discharge lamp falls above 360 mμ . The

single source is found satisfactory over the entire UV-VIS region. Ordinary spectrometers cover a range 220-800 mμ . Better instruments cover upto a short wavelength range of 185 mμ . This spectroscopic technique is not useful below 200 mμ (inaccessible region) since oxygen absorbs strongly at 200 mμ and below. To study absorption below 200 mμ , the whole path length is evacuated. The region below 200 mμ is called vaccum ultra violet region. The low wavelength region can be extended upto 150 mμ by flushing the region with nitrogen which absorbs below 150 mμ . Most spectrophotometers are double beam instruments. The primary source of light is divided into two beams of equal intensity. Before dividing it into two beams, the incident radiation is dispersed with the help of a rotating prism.The various wavelengths of a light source are separated with a prism and then selected by slits such that the rotation of the prism causes a series of continuously increasing wavelengths to pass through the slit for recording purpose. The selected beam is monochromatic which is then divided into two beams of equal intensity. Dispersion grating can also be employed to obtain monochromatic beam of light from poly chromatic radiation (UV-VIS radiation). As the dispersion of a single beam or grating is very small, it is not possible to isolate or collimate very narrow band widths. Thus, light from the first dispersion is passed through a slit and then sent to the second dispersion. After the second dispersion, light passes through the exit slit. The main advantage of the second dispersion is that the bandwidth of the emergent light increases and the light passing through the exit slit is almost monochromatic. Also most of the stray light is suppressed.

One of the beams of selected monochromatic light (see Figure 2) is passed through the sample solution and the other beam of equal intensity is passed through the reference solvent. The solvent as well as the solution of the sample may be contained in cells made of a material which is transparent throughout the region under study. Glass cannot be used since it absorbs strongly in the ultra-violet region. Silica cells can be used. These must be properly stored and their optical surfaces should never be handled. Quartz cells also serve the purpose best. Glass can be used satisfactorily in the visible region. This type of spectrometer is called double beam spectrophotometer. Each absorbance measurement on the solution is accompanied by a simultaneous measurement on the pure solvent.

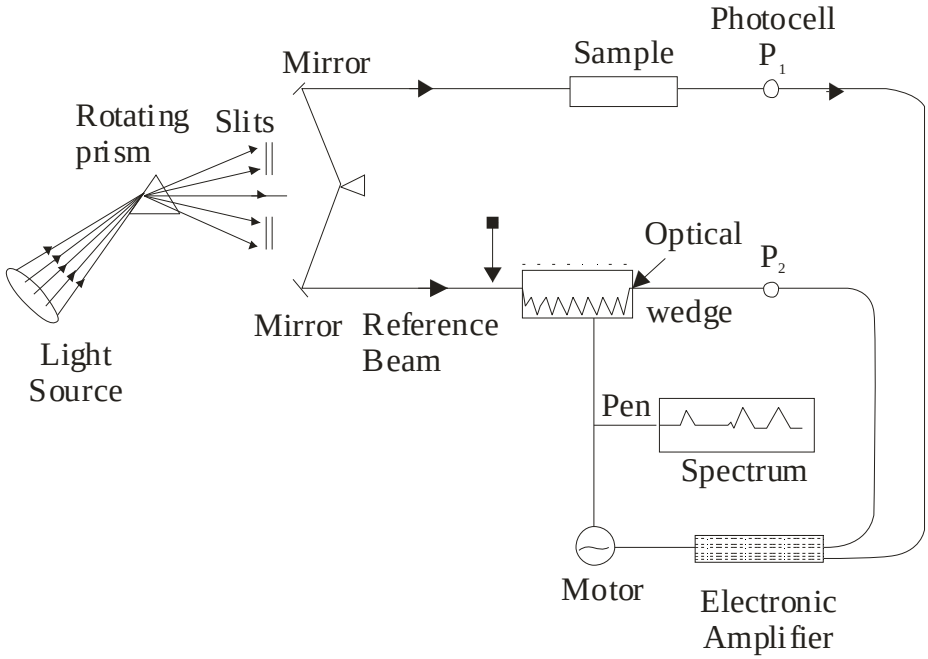


Fig. 2 Ultra-violet spectrophotometer

Usually, samples are scanned in dilute solutions. One mg of the compound under investigation (molecular weight 100-200) is accurately weighed and dissolved in a suitable solution upto 100 ml volume. A little of this solution is taken in a silica cell. The thickness of the solution in the cell should be 1 cm. Pure solvent is also taken in an exactly similar cell (Reference cell). These cells are then exposed to the monochromatic beams of equal intensity in the spectrometer. After the beams pass through the sample cell as well as the reference cell, the intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument. The spectrometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution. Hence, the effects due to the absorption of light by the solvent are minimized. In this way, the absorbance or the transmittance characteristics of the compound alone can be measured. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotted as absorbance A ($\log_{10} I_0/I$) against wavelength λ (abscissa). The plot is often represented as ε_{max} (Extinction coefficient*) against wavelength.

When the sample absorbs light, its intensity is lowered. Thus, the photoelectric cells P_1 and P_2 will receive an intense beam from the reference cell and a weak beam from the sample cell. This results in generation of pulsating or alternating currents which flow from the photoelectric cells to the electronic amplifier. The amplifier is coupled to a small servomotor which in turn, is coupled to a pen recorder. Thus, it records the absorption bands automatically. Actually, the

amplifier is coupled to a small servomotor which drives an optical wedge into the reference beam until the photoelectric cell receives light of equal intensities from the sample as well as the reference beams.

Types of Electronic Transitions

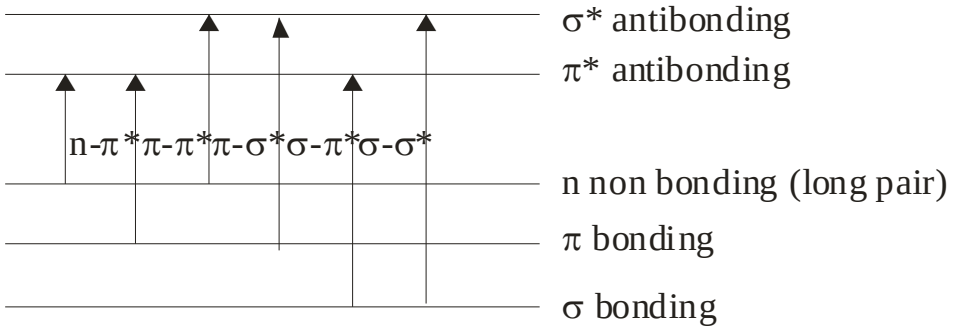
The UV radiations excite an electron from lower energy state of a molecule to a higher energy state. These higher energy states are called antibonding molecular orbitals and remain vacant in the ground state of the molecule. The antibonding molecular orbitals associated with σ (sigma) and π (pi) molecular orbitals are called σ^* (sigma star) and π^* (pi star) antibonding molecular orbitals. As the *n*(nonbonding) electrons do not form bonds, there are no antibonding orbitals associated with them. The n-electrons are promoted to either σ^* or π^* orbitals.

Different electronic transitions involved in ultraviolet and visible regions are :

(1) $\sigma \rightarrow \sigma^*$ transitions (2) $n \rightarrow \sigma^*$ transitions

(3) $\pi \rightarrow \pi^*$ transitions (4) $n \rightarrow \pi^*$ transitions

(5) $\sigma \rightarrow \pi^*$ transitions (6) $\pi \rightarrow \sigma^*$ transitions



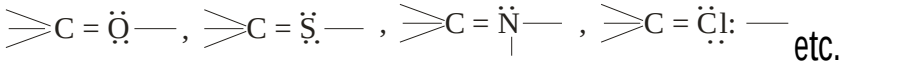
Transitions are arranged in order of increasing energy

However, most widely encountered transitions in organic compounds are as follows:

$$n-\pi^* < \pi-\pi^* < n-\sigma^* < \pi-\sigma^* < \sigma-\pi^* < \sigma-\sigma^*$$

(1) $\sigma \rightarrow \sigma^*$ **Transitions:** The $\sigma \rightarrow \sigma^*$ transitions are of very high energy and occur in far UV-region. These transitions are shown by saturated hydrocarbons containing only σ-bond viz. alkanes. It may be noted that the ultraviolet region below 200 nm is less informative and hence is not considered for practical purposes because oxygen absorbs in this region.

(2) $n \rightarrow \sigma^*$ **Transitions:** These transitions are of lower energy than $\sigma \rightarrow \sigma^*$ transitions and are shown by compounds containing oxygen, nitrogen, sulphur and halogen atoms, e.g.,


etc.

(3) $\pi \rightarrow \pi^*$ **Transitions:** The $\pi \rightarrow \pi^*$ are of lower energy than $n \rightarrow \sigma^*$ and are given by compounds having unsaturated centres e.g., >C=C<, – C= C – and $>C=\ddot{O}$ occur usually well within the region of ultraviolet spectrometer.

(4) $n \rightarrow \pi^*$ **Transitions:** The $n \rightarrow \pi^*$ transitions are of lowest energy and are given by compounds having both non bonding and π electrons eg.

$>C=\ddot{O}$, $-\overset{|}{C}=\overset{|}{C}-\ddot{O}-$ etc.

The high energy transition occurs at shorter wavelength and the lower energy transitions occur at longer wavelengths.

Chromophore and Auxochrome

Chromophore :A covalently bonded unsaturated group responsible for electronic absorption is called chromophore or chromophoric group. Examples of chromophore are:

$>C=C<$, $-C\equiv C-$, $>C=\ddot{O}$, $>C=\ddot{S}$, $-N=\ddot{O}$, $-N=N$

$>C=\ddot{N}-$, $-C\equiv\ddot{N}$, $>C=\dot{N}H$, $>C=\overset{|}{C}-\ddot{O}-$, $-N=O$ (O ↓)

Above chromophoric groups exhibit absorption in UV and visible region.

Auxochrome : A saturated group with non-bonding elections when attached to a chromophore changes both the wavelength and the intensity of the absorption band is called an auxochrome. For example:

$-\ddot{O}H$, $-\ddot{O}-R$, $-\dot{N}H_2$, $-\dot{N}HR$, $-\dot{N}R_2$, $-\ddot{S}H$, $-\ddot{S}R$

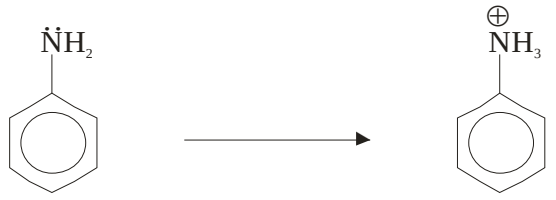
$-\ddot{C}l:$, $-\ddot{B}r:$, $-\ddot{I}:$, $-\ddot{O}-CH2-\ddot{O}-$, $-\ddot{F}:$

The absorption band usually becomes intense (ε_{max} increases) and shifts to longer wavelengths (towards visible region) due to the presence of auxochrome.

Bathochromic shift or Red shift: The shift of absorption to a longer wavelength due to substitution or solvent effect is called Bathochromic shift or Red shift. For example, benzene absorbs at 254 nm while toluene absorbs at 261nm. Thus the substitution of CH_3 group in benzene causes bathochromic shift in the absorption band of toluene. Conjugation of double bonds also causes bathochromic shift. Ethylene absorbs at 163 nm while 1,3-butadiene absorbs at 217nm.

Hypsochromic shift or Blue shift: The shift of absorption to a shorter wavelength due to substitution or solvent effect is called Hypsochromic shift or

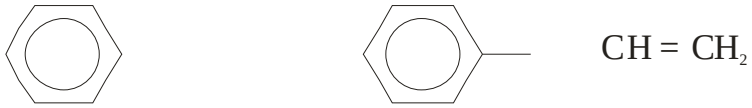
Blue shift. For example, aniline absorbs at 230 nm in neutral solvent while it absorbs at 203 nm in acidic medium.



230 nm 203 nm

The reason is that aniline gets protonated in acidic medium and hence there is no availability of lone pair of electron on nitrogen and hence absorption shifted towards shorter wavelength.

Hyperchromicshift : When a substituent group causes increase in the intensity of a band, then the effect is called Hyperchromic shift. For example the ε_{max} for benzene is 7400 while styrene has ε_{max} 14,000. Thus the substitution of vinyl (-$CH{=}CH_2$) group in benzene causes Hyperchromic shift.



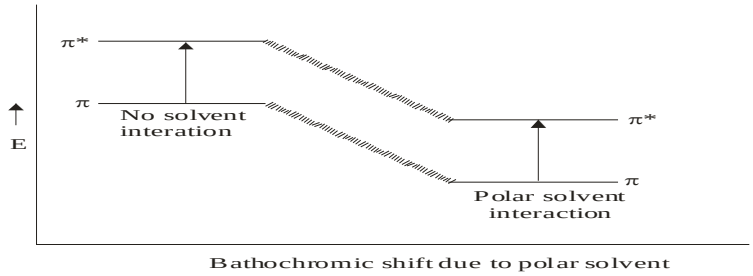
ε_{max} 7400 ε_{max} 14000

Hypochromic shift : When a particular substituent group decreases the intensity of absorption band, then the effect is called Hypochromic shift.For example, the ε_{max} for benzene is 204 for B-band while chlorobenzene has ε_{max} 190 for B-band. Thus, substitution of chloro group causes hypochromic shift.

ε_{max} 204 (B-band) ε_{max} 190

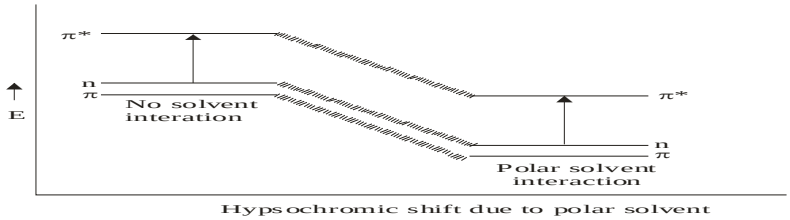
Solvent Effects on Transitions

(1) $\pi \rightarrow \pi^*$ **Transitions:** In most of $\pi \rightarrow \pi^*$transitions, the excited state is more polar than ground state. Thus a polar solvent (hydrogen bonding solvent) stabilizes the excited state more (and hence lowers its energy level) than the ground state and thus $\pi \rightarrow \pi^*$transition absorption transition shifts towards longer wave length. This shift is referred to as Bathochromic shift (or Red shift). For example, acetamide absorbs at 178 nm in hexane while in polar solvent (water) it absorbs at 220 nm.



Bathochromic shift due to polar solvent

(2) $n \rightarrow \pi^*$ **Transitions:** Non-bonding electrons of molecule are able to interact with polar solvents to greater extent in ground state than the excited state (π^*) of $\pi - \pi^*$ transition. As a result the $n - \pi^*$ transition absorption will shift towards shorter wavelength. A shift towards shorter wavelength is called Hypsochromic shift or Blue shift. For example, the absorption maximum of acetone in hexane is at 279 nm whereas in aqueous solution, the maximum is at 265 nm.



Hypsochromic shift due to polar solvent

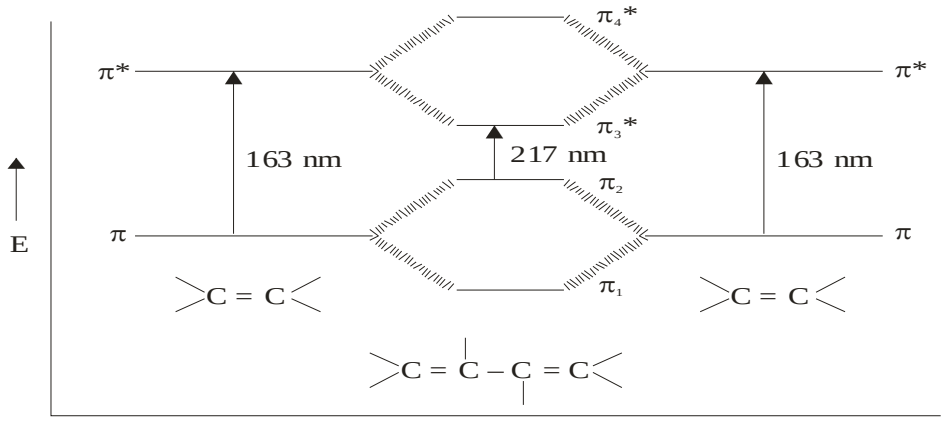
UV Spectra of Conjugated dienes

If two or more double bonds are present in a molecule and they are separated by two or more single bonds then there is a little effect on spectrum because there is little electronic interaction between isolated double bonds. However, if two double bonds are separated by only one single bond, i.e., in conjugation, a large effect on the spectrum results. In conjugated system such as C=C-C=C π-orbitals from each double bond interact to form a new set of bonding(π_1 and π_2) and antibonding (π_3^* and π_4^*) orbitals. Now there is little energy difference between $\pi_2 - \pi_3^*$ transition and hence absorption(λ_{max}) is shifted to longer wavelength (Bathochromic shift). As the conjugated system in molecule becomes larger, the energy difference between the ground state and excited state becomes further less. For example, ethene absorbs at 163 nm, 1,4-pentadiene absorbs at 185 nm and conjugated 1,3-butadiene absorbs at 217 nm. Therefore, it can be inferedthat :

(i) $\lambda_{max} \alpha$ number of conjugated double bonds. The λ_{max} increasing the number of conjugated double bonds.

(ii) ε_{max} is also related to conjugation. It also increases with increasing number of conjugated double bonds.

The compounds containing a number of conjugated double bonds will appear coloured to the eye if they absorb above 400 nm. If the compound appears coloured it will contain not less than four and usually five or more conjugated double bonds. β – Carotene having eleven double bonds is red in colour and absorbs at 448 nm.



Presentation of UV Spectra

An ultraviolet spectrum is a plot of the wavelength *versus* the absorption intensity(transmittance or absorbance). The data are frequently shown as a graphical plot of wavelength *versus* molar absorptivity ε_{max} or log ε_{max}. The use of molar absorptivity as the unit of absorption intensity has the advantage that all intensity values refers to the same number of absorbing species.

The ultraviolet spectrum of an organic compound is measured from its very dilute solution, e.g. 1-mg of the compound is dissolved in a solved (which must be transparent within the wavelength range being examined) and made up to say 100 ml. A part of this solution is transferred to a cell which is placed in the spectrophotometer along with a matched cell with pure solvent. Two equal beams of UV light are passed, one through the solution of the compound and other through the solvent. The intensities of the transmitted beams are now compared over the entire wavelength of the instrument.

The UV spectrum of isoprene (Fig. 3) displays a broad absorption band in the region 200-240 nm. The absorption is at its maximum at 222.5 nm. In addition to this wavelength of maximum absorption (λ_{max}), the intensity of the absorption (molar absorptivity, ε_{max}) is also reported.

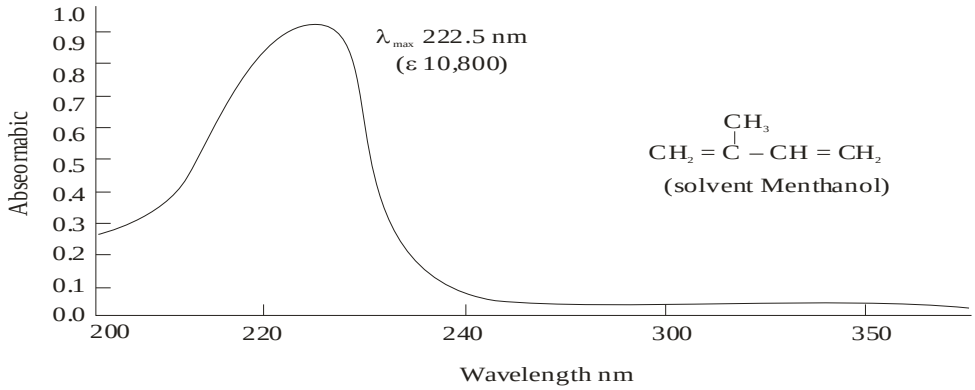


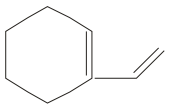
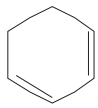
Fig. 3 UV spectrum

Interpretation of the spectra

UV Correlation Table

Table

Woodward rules for the UV adsorption maxima of dienes

Acyclic diene	Hetero annular diene	Homo annular diene
e.g. 	e.g. 	e.g. 
Values	λ_{max} (nm)	
Values	λ_{max} (nm)	
For parent acyclic diene	214 nm	
For parent hetero annular diene	214 nm	
For parent homoannulardiane	253 nm	
Increments to be added		
If an additional double bond Extends conjugation	30 nm	
If one of the diene double bond is exocyclic	.5	
Increments to be added for auxochrome(Substituents)		
Alkyl group	5 nm	
Ring residue	5 nm	
Halogen (CI, Br)	5 nm	
Alkoxy group (OR)	6 nm	
Acyloxy group (OCOR)	0 nm	

Alkyl thio coup (SR)	30 nm
Dialkyl amino group (NR)	60 nm

The application of these rules is best illustrated with the following examples which only predict the lowest $\pi -> \pi *$ transition.

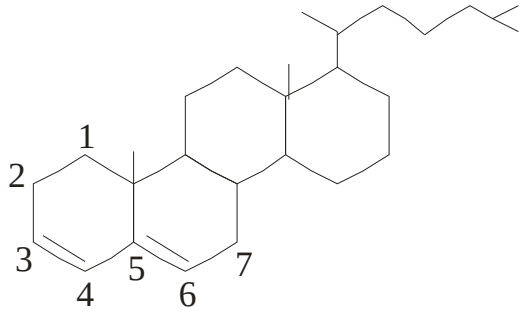
1. Calculation of λ_{max} of conjugated diemes

Example: Cholesta - 3, 5-diene

Parent (heteroannular) diene = 214 nm

Substituents:

2-3 bond (ring residue)	5 nm
6-7 bond (ring residue)	5 nm
5-10 bond (ring residue)	5 nm
exocyclic double bond	5 nm
calculated λ_{max}	234 nm



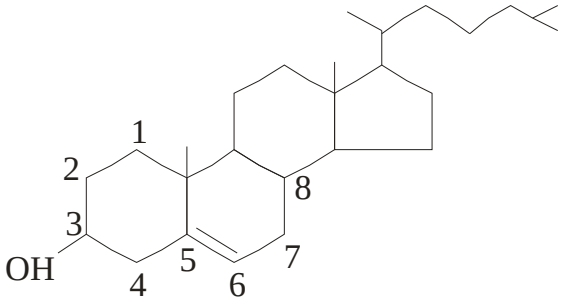
The observed value is λ_{max} = 235 nm

Example - 2 :Cholesta - 5,7 – diene -1,3 diol

Parent (homoannular) diane = 253 nm.

Substituent:

4-5 bond (ring residue)	5nm
8-9 bond (ring residue)	5nm
5-10bond (ring residue)	5nm
6-14bond(ring residue)	5nm
calculated λ_{max}	= 273 nm.



The observed value is λ_{max} = 272 nm

II. Calculation of λ_{max} of $\alpha,\beta-$ unsaturated ketones

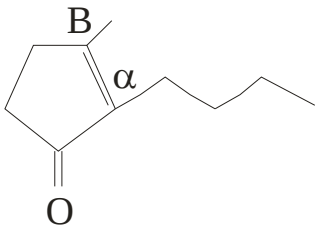
Example -3 :Dihydrojasmone

Parent $\alpha,\beta-$ unsaturated

Five ring Ketone	=202 nm
α Substituents : alkyl groups	10 nm
β Substituents **:**	
alkyl group	12 nm
ring residue	12nm

calculated λ_{max} (ε tOH) 236 nm.

The observed value is λ_{max} = 237 nm.



Example 4: Rotundifolene

Example:

Parent $\alpha,\beta-$ unsaturated acyclic Ketone	= 215 nm
α Substituents: ring resolve	= 10 nm
β Substituents: two alkyl groups	= 24 nm
Exocyclic double bond	= 5 nm
Calculated λ_{max} (ε tOH)	= 254 nm

The observed value is λ_{max} = 260 nm.

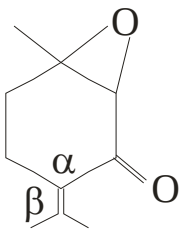
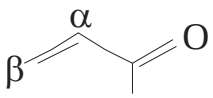
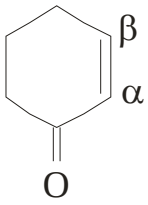
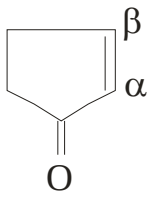


Table Woodward rules for UV adsorption maxima of $\alpha,\beta-$ unsaturated ketones in ethanol.

Acyclic	Six membered ring	Five membered ring
		
Values		λ max (nm)

Values	λ_{max} **(nm)**
For parent acyclic $\alpha,\beta-$ unsaturated ketone	215 nm
For parent six membered ring $\alpha,\beta-$ unsaturated ketone	215 nm
For parent five membered ring $\alpha,\beta-$ unsaturated ketone	202 nm

Increments to be added

If an additional double bond extends, conjugation

If one of the double bonds is exocyclic 5 nm

Increments to be added for α - Substituents (auxochromes)

Alkyl group	10nm
Ring Residue	10nm
Hydroxyl group (OH)	35nm
Alkoxy group (OR)	35nm
Acyloxy coup (OCoR)	6nm
Chloro group (Cl)	15nm
Bromo Substituents (Br)	25nm

Increment to be added for $\beta-$ Substituents **(auxochromes)**

Alkyl group	12nm
Ring Residue	12nm

Hydroxyl group (OH)	30nm
Alkoxy group (OR)	30nm
Acyloxy coup (OCoR)	6nm
Chloro group (Cl)	12nm
Bromo Substituents (Br)	30nm
Alkylthio group (SR)	85nm
Dialkylamino group (NR_2)	95nm

Table : Solvent correction for UV absorption spectra of $\alpha,\beta-$ unsaturated ketone

1) Using the table (5.3) calculate the expected λ_{max} in ethanol for $\alpha,\beta-$ unsaturated ketone and

2) Subtract the solvent correction factor for the solvents given below:

Table

Solvent	**Correction Factor(nm)**
Water	-8 nm
Methanol	0 nm
Hexane	11 nm
Chloroform	1 nm

Interpretation of the spectra

Unlike IR and NMR, the UV spectra are simple which show band or bands characterized by and values are mainly helpful in distinguishing the conjugation system from other

Types of unsaturation based on certain additive rules.

The empirical rules first formulated by R.B.Woodward in 194l and subsequently modified by L.F. Fieser are known as Woodward Fieser rules which enable to predict the λ_{max} values for conjugated dienes and $\alpha,\beta-$ unsaturated carbonyl compounds. The rules were further developed by A.I. Scott in one of the classic works on UV spectroscopy, interpretation of the ultraviolet spectra of natural products published in 1964.

The rules assign a λ_{max} values to the $\pi-\pi*$ k transition of the parent chromophore and tabulate increment for the effect of added substituent called auxochromes. The simplest type of auxochromes are alkylgroups which cause a small (5-10nm) bathochromic shift when attached to a chromophore similarly

other groups OR, OCOR, SR, NR_2 and halogen all act as auxochromes which cause bathochromic shift. The addition of extra unsaturation in the form of another double or triple bond causes a much longer shift to longer wave length.The rules mentioned in the correlation tables have been used to calculate the λ_{max} values of conjugated dienes and $\alpha,\beta-$unsaturated ketones, illusuated in the examples.

Aromatic compounds

Ultraviolet absorption spectra of aromatic, heteroaromatic and nonbenzenoid aromatic compound can be interpreted and their presence confirmed following certain guide lines, though there are no simple quantitative rules for predicting their electronic spectra.

Benzene in hexane solution shows three absorption bonds λ_1,λ_2 and λ_3 at 184 nm (ε, 60,000), 204 nm(ε 7400) and 254 nm(ε 204) respectively which are due to the allowed $\pi->\pi*$ transitions.

Absorption characteristics of aromatic systems and their substituted derivatives:

1. In monosubstituted, benzenes, conjugating substituent such as CH=CH ; COR which extend the Chromophore increases both the wavelength and intensity of the absorption.
2. Alkyl substituents have a small bathochromic effect.
3. Substituent with lone pair of electrons interacts with the aromatic π system and cause bathochromic shift. The effect of the donor substituents decrease in the order NH_2>OH>Cl.

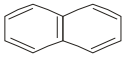
   4. In polysubstituted benzenes, the combined effect of the substituent may be greater than the expected on the basis of individual effect of each substituent. As an example 4-methoxy benzaldehyde with the two substituents electro releasing –OCH_3(methoxy) group and the electron withdrawing substituent -CHO(aldehyde) in the para position are complementary which extend the chromophore as a result of conjugation and the observed λ_{max} is greater than would be expected from the individual effects of the groups

Complementary substitution in 4-methoxy benzaldehyde

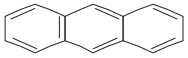
When the groups are meta or ortho related the effect on the chromophore is much less and the observed λ_{max} values are much closer to those expected from the individual effects of the substituents. Similarly if the two substituents are non-complementary, in other words both are electron releasing or electron withdrawing the chromophore is not affected to the same extent.

5. Bicyclic and polycyclic both linear and angular aromatic systems absorb at much longer wavelengths than monocyclic systems. The greater the number of the rings the more pronounced the bathochromic shift. Thus naphthalene and anthracene are colourless, but naphthalene is yellow and pentacene is blue.

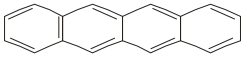
Aromatic hydrocarbons



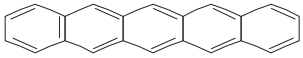
Naphthalene
(Colourless)



Anthracene
(Colourless)

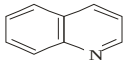


Naphthacence
(Yellow)

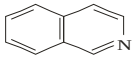


Pentacene
(blue)

Pyridene



Quinoline



Isoquinoline

Heterocyclic Systems:

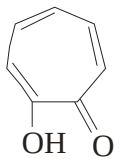
Tbe UV Spectra of simple heterocyclic aromatic compounds generally resemble the spectra of benzenoid compounds in that they consists of an absorption and of relatively large extinction coefficient (ε 5000 -15000) at short wavelength (λ_{max} 190 - 240 nm) and a series of fine structure bands of lower intensity (ε 1-400) at longer wave length(λ_{max} 240 -300 nm).

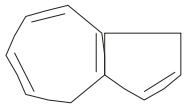
Pyridine exhibits an absorption spectrum similar to that of benzene with an additional adsorption band at 270 nm, assigned to the transition involving the nitrogen loan pair ($n->\pi*$ transition). Similarly UV spectra of quinolone and isoquinoline resemble with that of naphthalene

Nonbenzenoid aromatic hydrocarbons

Measurements of the UV absorption spectra is one of the critention to detemine and confirm the aromaticity of nonbenzenoid aromatic hydrocarbons as there is a close resemblance between the UV spectra of nonbenzenoid hydrocarbons and benzene.

Thus tropolone and its derivatives which show absorption in the region 220 - 250 nm (ε30,000) and 340-375 nm(ε8,000) are characterized as aromatic compound as these values closely resemble the bonds of the aromatic systems (Fig.) Azulene and its derivatives are blue coloured compounds which give a number of intense bonds in the UV region (upto 360 nm) and a number of relatively weak bond in the visible region(500 - 700 nm) are characterized as typical aromatic compound.





Azulene

Identification of phenols and amines

UV spectra are extremely useful to identify phenols and amines.

Phenol: The interaction of the phenolic oxygen with the π - system increases considerably in the phenolate anion since there are two nonbonding pairs of electrons and there is a large bathochromic shift in the absorption maximum. Hence the UV spectrum of a phenol changes if a base is added to the sample to deprotonate the phenolic - OH.

The effect is illustrated in Fig.4 which shows the UV spectrum of 4-nitrophenol run in ethanol and the changes that take place on adding Sodium hydroxide to the solution.

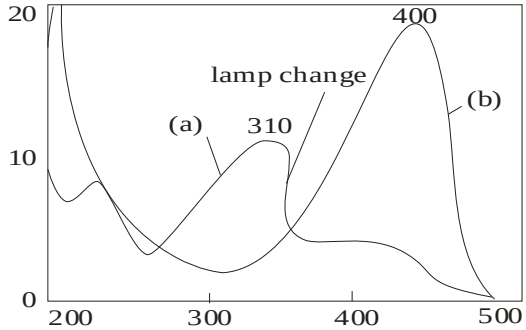


Fig. 4 UV absorption spectrum of 4-nitrophenol in alkaline solution

On adding base the λ_{max} value increases from 310 nm to 400 nm. The intensity of absorption also increases. The original dilute ethanol solution of 4-nitrophenol is very faintly yellow, but the colourdeepers considerably when a drop of sodium hydroxide solution is added.

Anilines: The nitrogen lone pair because of its greater donor ability over oxygen, has a greater interaction with the π system. However this interaction can be removed by protonating the nitrogen. The resulting aniliumcation no longer has nonbonding electrons to interact with the aromatic system and therefore shows a hypochromic shift in the UV spectrum. Hence the UV spectrum of aniline should change if an acid is added to the solution to protonate the NH_2 group. This effect is illustrated in Figure 5 which shows the UV spectrum of-methoxyaniline in ethanol and the changes which occur on addition of hydrochloric acid.

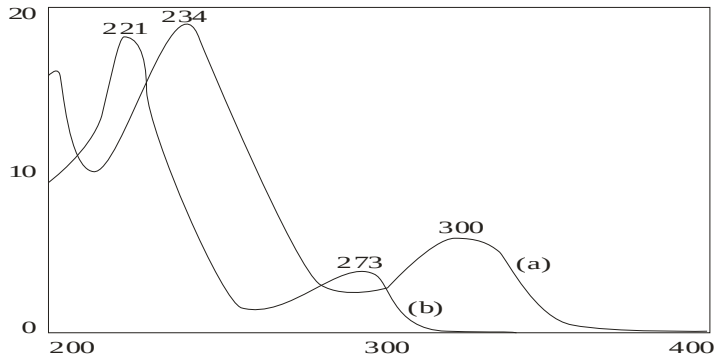


Fig. 5 :-UV spectra of 4-methoxyaniline in ethanol with added hydrochloride

The long wavelength absorption at 300 nm shifts to 273 nm with a decrease in intensity on addition of the acid. Such simple experiments are very useful in the identification of these functional groups.

Heterocyclic compounds

The ultra-violet spectrum of five-membered heterocyclic aromatic compounds can be compared with cyclopentadiene. It has been observed that in these compounds, a forbidden band(R-band) due to $n->\pi*$ transition is also observed with very 1ow value of ε_{max}. For example, in furan, we observe a band at 252 mμ ε_{max} 10,000. The chromophoric or auxochromic substitution brings about bathochromic as well as hyper chromic shift.

Table: Heterocyclic compounds

Compound	λ_{max} (mμ)	Intensity ε_{max}
Furan	200	10,000
	252	1
2-Nitro furan	225	3,400

	315	8,100
Pyrrole	183	-
	211	15,000
Pyrrole 2-aldehyde	252	5,000
	290	16,500
Thiophene	231	7,100
2-Bromothiophene	236	9,100

In six-membered heterocyclic compounds, the ultra-violet spectrum of pyridine can be distinguished from that of benxene as its B-band is more intense than that of benzene. Moreover B-band in pyridine shows a marked increase in intensity with the increase in polarity of the solvent (UV spectrum of pyridine is shown in figure 6). On the other hand, this band for benzene is little effected in position as well as intensity. The presence of substitution in pyridine usually brings hyper chromic effect. For example, the B-band for pyridine at 275 m μ ε_{max} 2750 is shifted to 262 m μ ε_{max} 3560 for 2 methyl pyridine and to 263 m μ ε_{max} 3560 for 2 chloro pyridine.

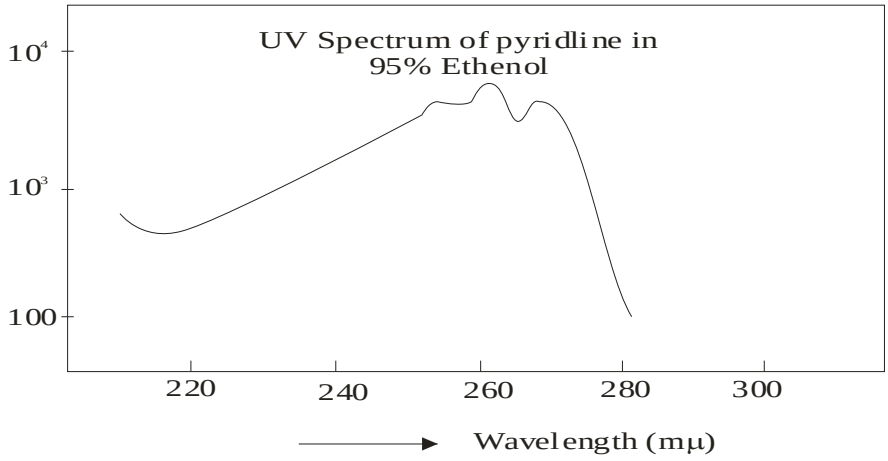
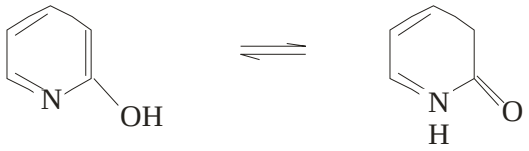


Fig. 6: UV spectrum of pyridine in 95% ethanol

In some cases, like hydroxyl pyridines, hypochromic shifts are also observed. Sometimes, a change in pH brings about a marked change in the Absorption maximum of the substance which is clearly due to the change in the chromophore. The change in chromophore is explained as the shifting of equilibrium to one of the tautomeric forms with the change in pH. Thus, a

substance existing in tautomeric forms can be carefully diagnosed for the preference of one form over the other by this technique. For example, 2-hydroxy pyridine and Pyridine-2 exist in tautomeric equilibrium.



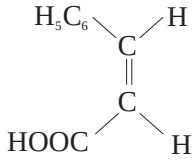
2 Hydroxy Pyridline Pyridone

The spectra of these compounds were shown to favour pyridine-2 which is an $\alpha,\beta-$ unsaturated ketone. Clearly, the equilibrium is shifted towards right.

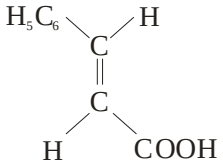
Steric hindrance and coplanarity

Woodward rules give reliable results only for those compounds in which there is no strain around the chromophore. We know that in case of extended conjugation, the position of absorption depends upon the length of conjugated system. Longer the conjugated system, higher will be the absorption maxima and larger will be the value of extinction coefficient. If in a structure, the π electron system is prevented from achieving coplanarity, there is a marked shift in the absorption maximum and extinction coefficient. The departure in the value of absorption maximum calculated from the empirical rules is due to steric crowding which distorts the geometry of the chromophore. Thus, the conjugation is reduced by reduction in the π orbital overlap. Consider the cases of biphenyl and substituted biphenyl. The $\pi->\pi^*$ transitions for diphenyl which readily achieves coplanarity absorbs at 250 mμ ε_{max} 19,000 but in 2-methyl diphenyl, $\pi->\pi^*$transitions undergoes blue shift and diminished intensity as the two rings remain no longer coplanar. The absorption maximum for 2-methyl diphenyl is 237 mμ ε_{max} 10250. Also nitro benzene absorbs at 252 mμ ε_{max} 5950 due to reduction in coplanarity.

If the compound containing alkene chromophore is capable of existing as geometrical isomers, the trans-isomer is found to absorb at longer wavelength with higher value of extinction coefficient as compared to *cis* isomer. It is due to more effective π orbital overlap possible in the trans-isomer which, thus, achieves coplanarity of π electron system more readily. Consider the case of cinnamic acid. It exists in two isomers:



(Cis)



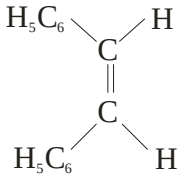
(Trans)

Due to greater crowding in cis-form (both bulky groups are on the same side), the geometry of the alkene chromophore is distorted and departure from coplanarity results. Thus, $\pi -> \pi^*$ transition in cis-cinnamic acid takes place at lower wave-length with lower extinction coefficient.

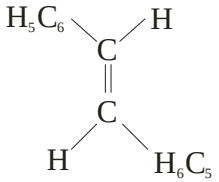
(i) Trans-cinnamic acid absorbs at 272 mμ ε_{max} 15900.

(ii) Cis-cinnamic acid absorbs at 268 mμ ε_{max} 10700.

Slight steric hindrance to coplanarity about a single bond has a very little effect on the position and intensity of the absorption maximum. If the steric hindrance to coplanarity about a single bond is more, then, there is a marked decrease in intensity and may accompany a red or blue shift. The absorption maximum of 2,5 dimethyl *p*-nitro aniline occurs at 385 mμ ε_{max} 4840 showing a red shift and marked decrease in the intensity as compared to *p*-nitro aniline which absorbs at 375 μ ε_{max} 16000. A blue shift is observed in case of 2,4,6 trimethylacetophenone which absorbs at 242 mμ ε_{max} 3200 as compared to *p*-methyl acetophenone at 252 mμ ε_{max} 15000. Out of cis- and trans-stilbenes, a distortion in coplanarity in cis-stilbene is due to steric hindrance. This results in lowering the value of absorption maximum at lower extinction coefficient. Thus, a band which appears at 295 mμ ε_{max} 25000 in trans-stilbenes has a value 283 mμ ε_{max} 12300 in cis-stilbene.



(Cis-stilbene)



(Trans-stilbene)

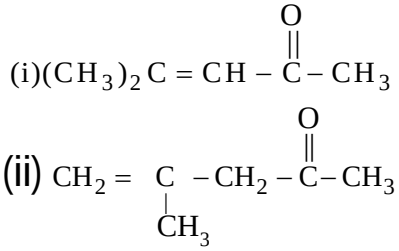
Applications of Ultra-Violet Spectroscopy

Ultra-violet spectroscopy has been mainly applied for the detection of functional groups (chromophore), the extent of conjugation, detection of polynuclear compounds by comparison, etc. Some important applications of ultra-violet spectroscopy are as follows:

(a) **Detection of functional groups:** The technique is applied to detect the presence or absence of the chromophore. The absence of a band at a particular wavelength may be regarded as an evidence for the absence of a particular group in the compound. A little information can be drawn from the UV spectrum if the molecule is very complicated. If the spectrum is transparent above 200 mμ, it shows the absence of (i) conjugation (ii) a carbonyl group (aldehydes and ketones) (iii) benzene or aromatic compounds and also (iv) bromo or iodo atoms. An isolated double bond or some other atoms or groups may be present. It means that no definite conclusions can be drawn if the molecule absorbs below 200 mμ.

(b) **Extent of conjugation :** The extent of conjugation in polyenes R-$(CH=CH)_n$-R can be estimated. Addition in unsaturation with the increase in the number of double bonds (increase in the value of *n*) shifts the absorption to longer wavelength. It is found that the absorption occurs in the visible region, i.e., at about 420, mμ, if n = 8 in the above polyene. Such an alkene appears coloured to the human eye.

(c) **Distinction in conjugated and non-conjugated compounds.** It also distinguishes between a conjugated and a non-conjugated compound. The following isomers can be readily distinguished since one is conjugated and the other is not.



The forbidden $n->\pi^*$ band for the carbonyl group in the compound (i) will appear at longer wavelength compared to that for compound (ii)

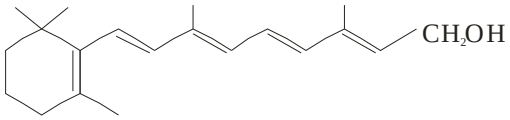
The alkyl substitution in an alkene causes a bathochromic shift. The technique is not much useful for the identification of individual alkenes.

(d) **Identification of an unknown compound.** An unknown compound can be identified by comparing its spectrum with the known spectra. If the two spectra coincide, the two compounds must be identical. If the two spectra do not coincide, then the expected structure is different from known compound.

(e) **Examination of Polynuclear hydrocarbons.** Benzene and Polynuclear hydrocarbons have characteristic spectra in the ultra-violet and visible region. Thus, the identification of the polynuclear hydrocarbons can be made by comparison with the spectra of known polynuclear compounds. The presence of substituents on the ring, generally, shifts the absorption maximum to longer wavelength.

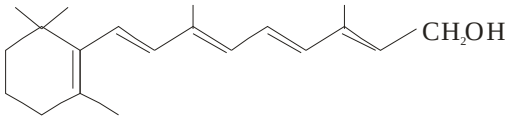
(f) **Elucidation of the structure of vitamins A and K.** It is useful for the elucidation of the structures of vitamin $K_1$and $K_2$and also those of A_1 and A_2. The ultraviolet spectra of vitamins K_1 and K_2 are due to the presence of the same chromophore i.e. 2,3 dimethyl naptha-quinone. The absorption maxima of this compound are 243, 249, 260, 269 and 330 mμ.

The elucidation of the structures of vitamin A_1 and A_2 are possible by this technique. Vitamin A_1 absorbs at 325 mμ and absorption maxima for vitamin A_2 appears at 287 and 351 mμ. The absorption maxima appear at longer wavelength for vitamin A_2 due to the presence of additional ethylene bond.



λ_{max} = 325 mμ

Vitamine A_1



λ_{max} = 325 mμ and 351 mμ

Vitamine A_2

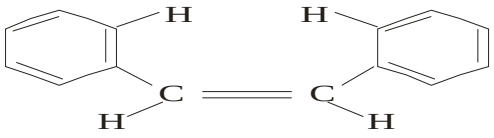
(g) **Preference over two Tautomeric forms.** If a molecule exists in two tautomeric forms, preference of one over the other can be detected by ultra-violet spectroscopy. Consider 2-hydroxy pyridine which exists in equilibrium with its tautomeric form, pyridine-2

2 Hydroxy Pyridline ⇌ Pyridone-2

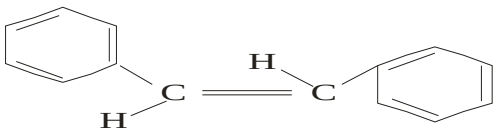
The spectra of these two compounds were found to favour pyridine-2 which is an $\alpha,\beta-$unsaturated ketone and clearly, the equilibrium is shifted towards the right i.e. Pyridone-2.

(h) **Identification of a compound in different solvents.** Sometimes, the structure of the compound changes with the change in the solvent. Chloral hydrate shows an absorption maxima at 290 mμ in hexane while the absorption disappears in the aqueous solution. Clearly, the compound contains a carbonyl group in hexane solution and its structure is $CCl_3.CHO.H_2O$ whereas in aqueous solution it is present as $CCl_3.CH(OH)_2$.

(i) **Determination of configurations of Geometrical isomers.** The results of absorption show that cis-alkenes absorb at different wavelengths as



Cis-stilbene

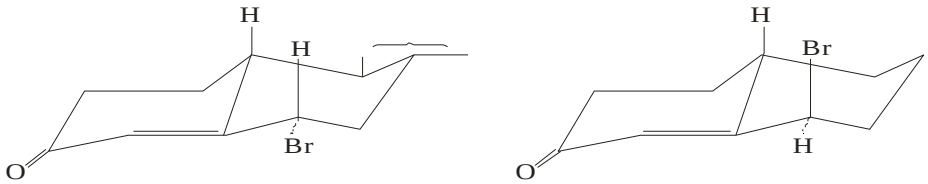


$\lambda_{max} = 295.5$ mμ

Trans-Stilbene

Compared to their corresponding trans isomers. The distinction becomes possible when one of the isomers is forced to be non-coplanar by steric hindrance. Thus, cis forms suffer distortion and absorption occurs at lower wavelength. For example, consider the spectra of cis- and transstilbenes as shown above.

(j) **Distinguishes between equatorial and axial conformations.** This technique also distinguishes between equatorial and axial conformations. Consider the following conformations.



The $n->\pi^*$(R bond) which appears at longer wavelength in α,β-unsaturated ketones is influenced by the presence of polar group in the γ position. It has been noted that the effect of an axial substituent to displace the R-bond to longer wavelength is greater compared to that observed in its equatorial isomer.

Unit – 9

Carbon-13 NMR (CMR) spectroscopy

Among the atoms, like the proton, give rise to NMR spectra is one of the isotopes of carbon. ^{13}C. The ^{13}C NMR (CMR) spectrum is generated in the same fundamental way as the proton NMR spectrum (PMR), and the same basic principles that we learned before apply here, too. Practically, however, obtaining a useable spectrum is more difficult for CMR than for proton NMR, and requires more sophisticated instrumentation. Such instrumentation methods have been developed in the years since about 1970, and today CMR spectroscopy is used routinely to complement proton NMR spectroscopy.To distinguish these two kinds of nuclear magnetic resonance, we shall generally use the terms "CMR" and "proton NMR". When used alone, "NMR" should be taken to mean "proton NMR".

The isotope ^{13}C makes up only 1.1% of naturally occurring carbon, but the sensitivity of modern spectrometers makes this level adequate for the measurement of CMR spectra. Indeed, as we shall see in the following section, this low natural abundance is actually an advantage.

The CMR spectrum gives much the same kinds of information as proton NMR, but now the information is directly about the carbon skeleton- not just the protons attached to it.

(a) The *number of signal*s tells us how many different carbons - or different sets of equivalent carbons - there are in a molecule.

(b) The *splitting of signals* tells us how many types of hydrogen are attached to each carbon.

(c) The *chemical shift* tells us the hybridization (sp^3, sp^2, sp) of each carbon.

(d) The *chemical shift* tells us about the electronic environment of each carbon with respect to other, nearby carbons or functional groups.

CMR Splitting: One of the major practical problems in CMR spectroscopy is the splitting of signals: too much splitting, potentially, and hence spectra that would be too complicated to interpret easily.

Part of the problem is already solved for us by the low natural abundance of ^{13}C. Only occasionally is a ^{13}C near enough to another ^{13}C for ^{13}C -^{13}C spin – spin coupling to occur. As a result CMR *spectra do not ordinarily show*

carbon-carbon splitting, and are thus enormously simplified. (An equal blessing: proton spectra do not show splitting by ^{13}C!)

But there remains splitting of ^{13}C signals by protons. In a CMR spectrum we cannot see the absorption by protons because these signals are far off the scale. But we can see splitting of carbon signal by protons: protons on the carbon itself and on more distant carbons as well. Unless something is done about this, the spectrum will consist of many overlapping multiplets very difficult to interpret.

Unwanted splitting is removed by decoupling the ^{13}C spin from that of the proton. This decoupling can be done in either of two principal ways, depending upon the frequency of the radiation used in the double resonance.

One method of decoupling gives a completely proton-decoupledspectrum. This spectrum shows *no splitting at all*; it consists of a set of single peaks, one for each carbon - or each set of equivalent carbons - in the molecule. Even for very complicated molecules, such a spectrum is amazingly simple.

Look, for example, at Fig.1 which shows the proton-decoupled spectrum of *sec*-butyl bromide. There are four carbons in this molecule, all different – that is, non-equivalent.

$\overset{a}{C}H_3-\overset{c}{C}H_2-\overset{d}{C}H(Br)-\overset{b}{C}H_3$ 4 CMR signals

sec-Butyl bromide

In the spectrum we see four peaks, one for each of these four carbons.

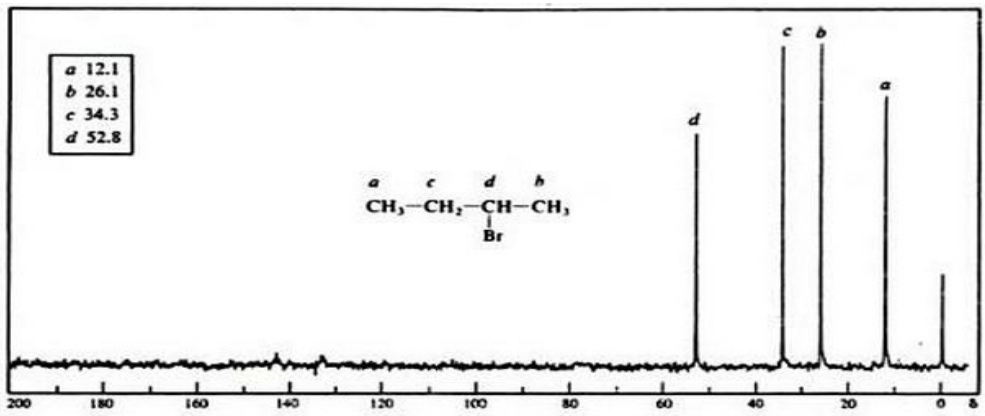


Fig. 1 : Proton decoupled CMR spectrum of *sec*-butyl bromide

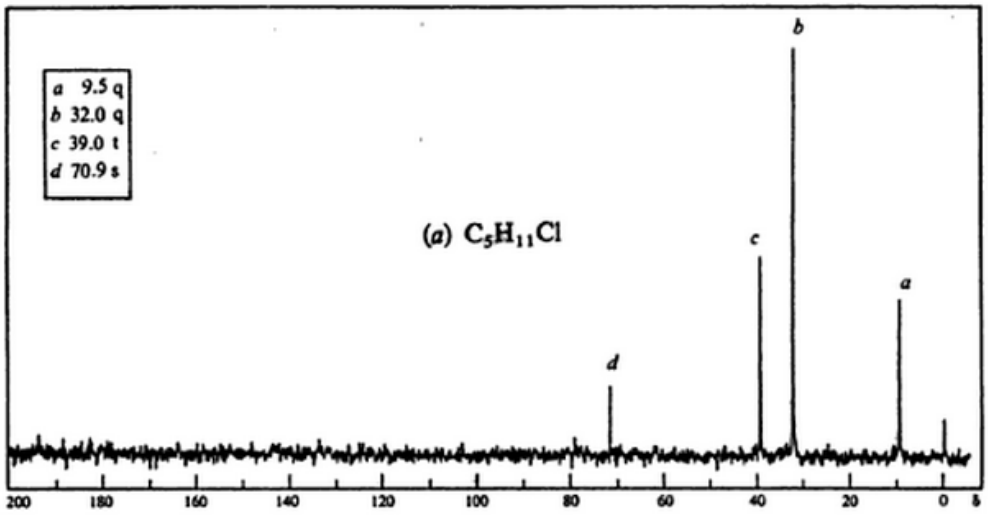
We judge the equivalence or non-equivalence of carbons in the same way that we dealt with protons. We must not forget that, to be chemically equivalent, carbons, like protons, must be *stereo* chemically equivalent: in an achiral medium diastaerotopic carbons will give different signal, and enantiotopic carbons will not.

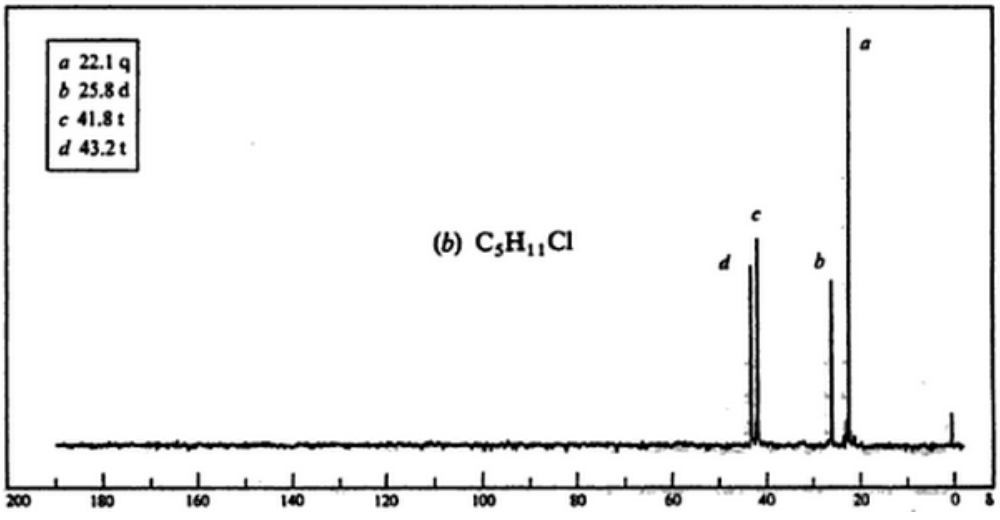
A second method of decoupling (called *off-resonance*) gives a spectrum which shows splitting of the carbon signal only by protons attached to that carbon itself. That is, we see only ^{13}C -H coupling and not ^{13}C -C-H or ^{13}C –C-C-H coupling. We shall refer to this kind of spectrum as **a** proton-coupled spectrum.

For each carbon, then, the multiplicity of the signal depends upon how many protons are attached to it:

no protons one proton two protons three protons

Singlet Doublet Triplet Quartet





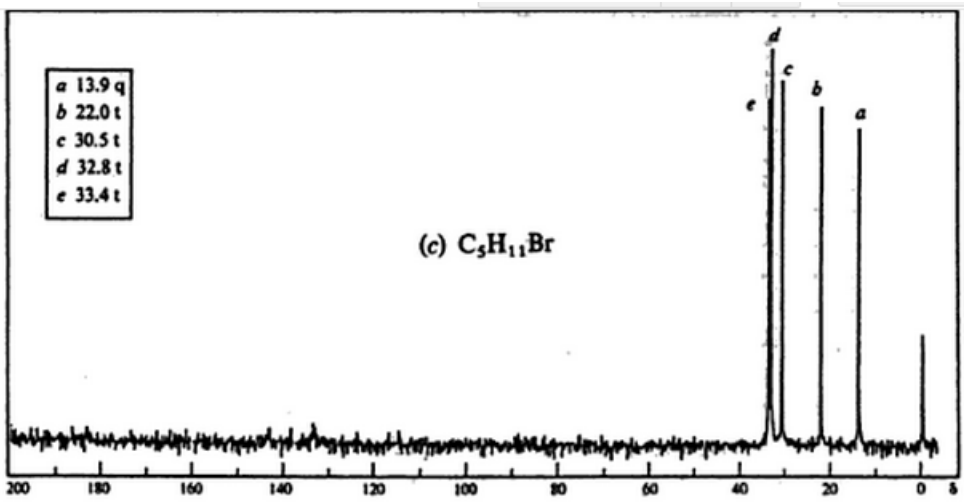


FIGURE 2 CMR spectra for Problem

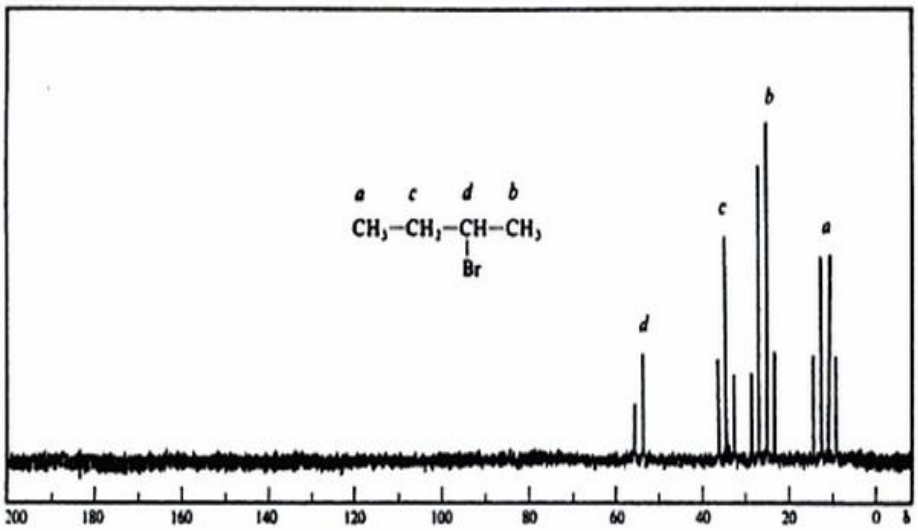


FIGURE 3 Proton coupled CMR spectrum of *sec*-butyl bromide.

In Fig. 3, for example, we see again a CMR spectrum of sec-butyl bromide, but this time proton-coupled. Now each peak is a multiplet: we see a doublet, a triplet, and two quartets.

$$\overset{q}{C}H_3-\overset{t}{C}H_2-\overset{d}{C}H(Br)-\overset{q}{C}H_3$$

sec-Butyl bromide

So now, we have two kinds of CMR spectra which give us two kinds of information about the structure of a molecule. The photon-decoupled spectrum tells us how many different carbons there are (and much besides), and the proton coupled spectrum tells us how many protons are attached to each of these carbons. Together, these spectra give us a remarkably detailed picture of the molecule.

Most of the CMR spectra in this book will *display* the proton-decouple spectrum, and will list the multiplicity of the peaks in the upper left-hand corner (See, for example, Fig. 2). We shall thus have both kinds of information give within a single frame.

CMR Chemical shift: Chemical shift in the CMR spectrum arise in basically the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied field strength. But the shifts in CMR differ in several ways from those in proton NMR.

To begin with, chemical shift are much larger in CMR than in proton NMR. Figure 4 summarizes shifts for carbons of various "kinds". As we see, the scale extends from δ 0 to beyond δ 200, more than 30 times as wide as in NMR.

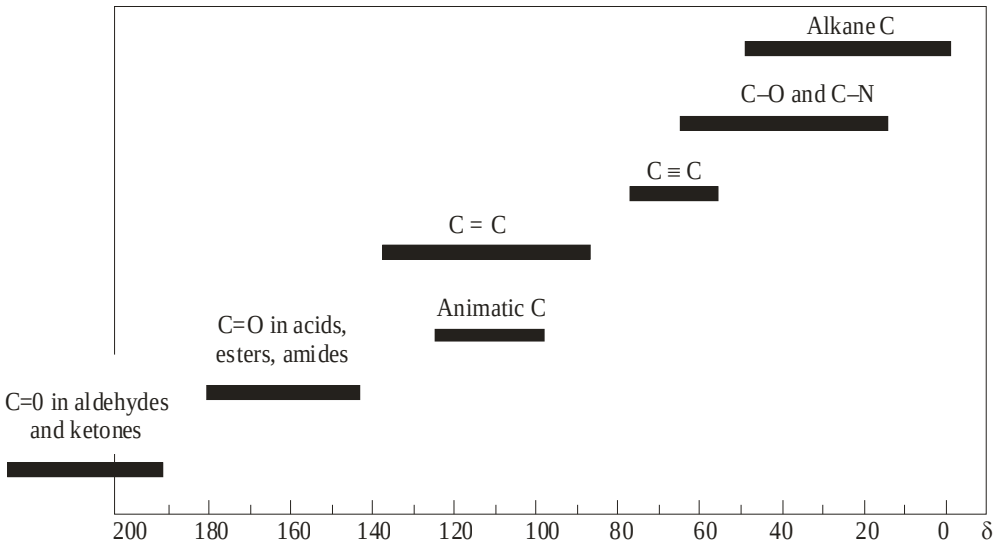


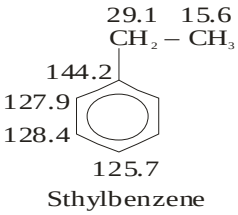
FIGURE 4 Chemical shifts for ^{13}C in various kinds of compounds

Of these shifts, the biggest and most important are determined by the hybridization of the carbon : something that, of course, is not a factor for the proton. Look, for example, at the spectrum of 1-octene (Fig. 17.29). We see the peaks for the sp^3-hybridized carbons upfield, between δ 14.1 and δ 34.0, and for the sp^2-hybridized carbons over 100 ppm downfield from them, at δ 113 and δ 140!

$$\overset{14.1}{CH_3}-\overset{22.9}{CH_2}-\overset{32.1}{CH_2}-\overset{29.3}{CH_2}-\overset{29.1}{CH_2}-\overset{34.1}{CH_2}-\overset{139}{CH}-\overset{114}{CH_2}$$

Aromatic carbons are also sp^2-hybridized, and also absorb downfield, in much the same region as alkene carbons do. In the spectrum of ethylbenzene (Fig.) we again see two widely separated sets of peaks: upfield, a set from the side-

chain (sp^3-hybridized) carbons, and downfield, after a 100-ppm gap, a set from the ring (sp^2-hybridized) carbons.



Sthylbenzene

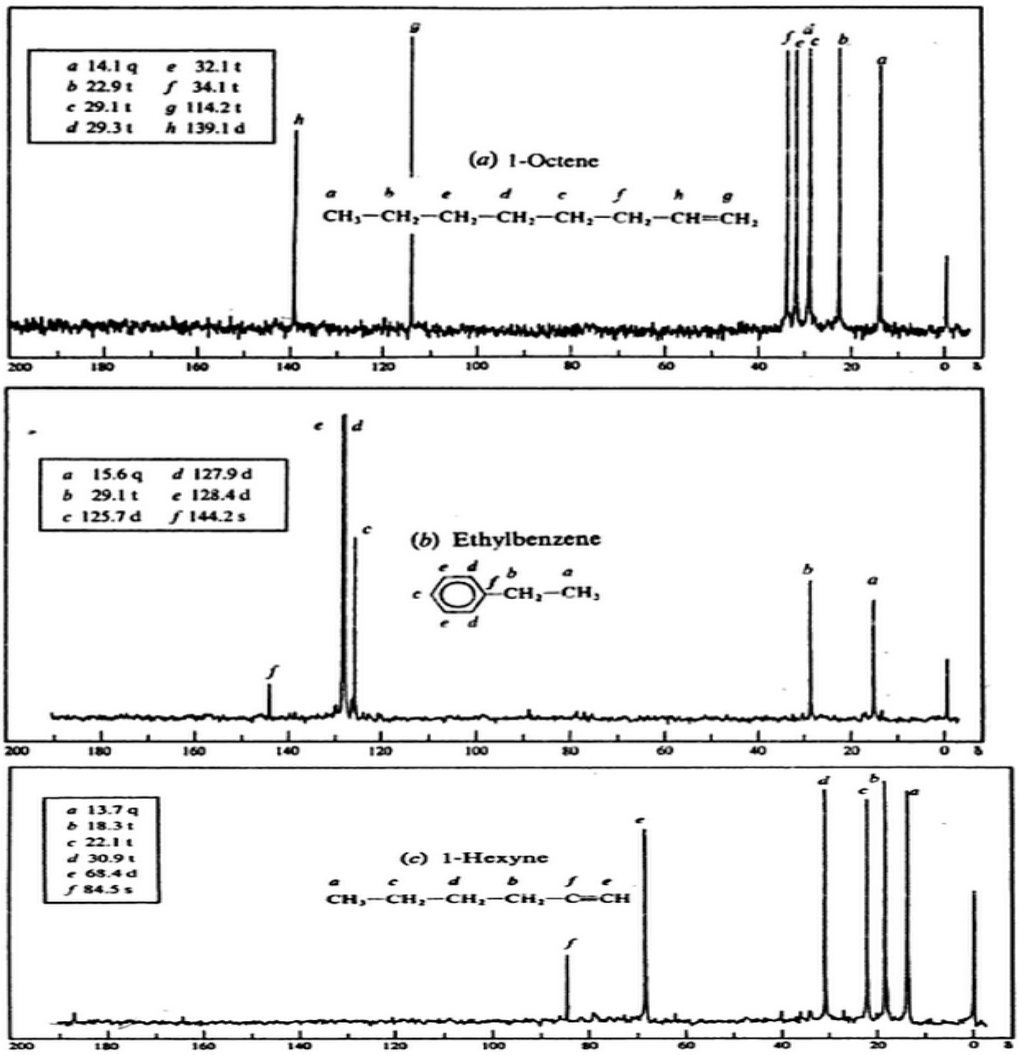


FIGURE 5: CMR spectra – Chemical shift (a) 1-Octene; (b) ethylbenzene; (c) 1-hexyene

Absorption by triply bonded (*sp*- hybridized) carbon falls between the regions for sp^3-hybridized and sp^2-hybridized carbons, as shown for l-hexyne.

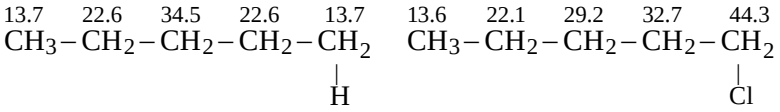
13.7 22.1 30.9 18.3 84.5 68.4
$CH_3 - CH_2 - CH_2 - CH_2 - C \equiv CH$

l-Hexyne

In relating structure to chemical shift then, we begin with the hybridization of carbon.

Next, we consider the effects of substituents, which are superimposed on the hybridization effects. As in proton NMR, most substituents in most positions deshield the nucleus, and shift the signal downfield. But with carbon these effects are bigger, are felt from farther away, and fall into different patterns. To get some idea ofwhat these patterns are like, let us examine the effects of several substituents on absorption by sp^3-hybridized carbons.

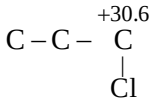
Let us look first at the effects of chlorine on the absorption by various carbons of a saturated chain. The spectra of *n*-pentane and 1-chloropentane, for example, give data that we can summarize like this:



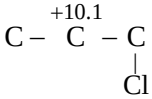
l-Chloropentane

Let us compare, carbon by carbon, the δ values for the two compounds.

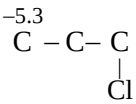
In the signal for C-l, chlorine causes a very large downfield shift, from δ 13.7 to δ 44.3, a difference of +30.6 ppm. Such a shift, *for the carbon bearing the substituent*, is called anα effect**.**

Anα effect. 

In the signal for C-2, chlorine again exerts a downfield shift from δ 22.6 to δ 32.7, a difference of + 10.1 ppm. Such a shift, *for the carbon once removed from the carbon bearing the substituent*, is called aβ effect**.**

Anβ effect. 

At C-3 we see a reversal of the substituent effect. Absorption here is shifted *upfield*, from δ 34.5 to δ 29.2, a difference of - 5.3 ppm. Such a shift, *for the carbon twice removed from the carbon bearing the substituent,* is called aγ effect**.**

Anγ effect. 

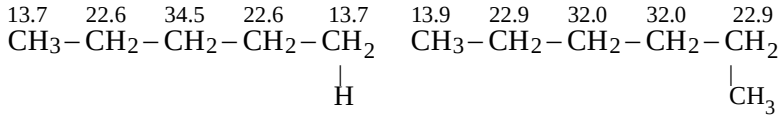
Beyond the γ-carbon, we see, the effect of chlorine, like that of other substituents, is very small.

Each substituent chlorine exerts effects of about these same sizes on absorption by saturated carbon in a wide variety of compounds.

Nearly all substituent effects on absorption by sp^3-hybridized carbon follow the same pattern as those for chlorine: α- and β-effects downfield, with α greater

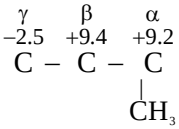
than β; and γ -effects still smaller, and *upfield*. And for most of these substituents, the sizes of the effects are, like those of chlorine, quite large. Consider, for example, the α-effects exerted by these substituents attached to C-I of pentane: F, +70.1 ppm; Br, +19.3ppm; NH2, +29.7ppm; OH, +48.3ppm; NO_2, + 64.5 ppm.

Alkyl groups exert smaller effects than other substituents, and follow a somewhat different pattern. Let us look, for example, at the effects of a methyl group, using data from the spectra of *n*-pentane and *n*-hexane. If we display the δ values as before, considering *n*-hexane to be *n*-pentane with a methyl substituent on C-I,



n-Pentane n-Hexane

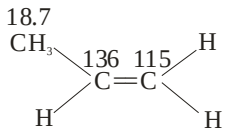
We can calculate the following substituent effects of methyl:



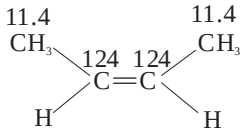
These effects are typical of alkyl groups acting on the absorption by saturated carbon: α- and β-effects downfield, and of about the same size; and γ-effects smaller and up field.

What we have discussed so far are substituent effects on chemical shifts for sp^3-hybridized carbon. For absorption by sp^2-hybridized carbons - in alkenes and aromatic rings--the pattern of effects is somewhat different. Many substituents exert alternating effects, which we shall not go into, but which will be evident in some of the spectra we shall encounter.

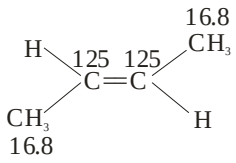
The presence of a carbon-carbon double bond in a molecule can introduce a new factor, *geometric isomerism*, which has important effects on the absorption by sp^3-hybridized carbons. To see how this stereo chemical factor works, let us compare the absorption data for propylene with the data for *cis*- and *trans*-2-butene.



Propylene



cis2-Butene



trans-2-Butene

Interpretation of ^{13}C Spectra (Peak Assignments)

How are specific peaks assigned in a noise decoupled ^{13}C spectrum, such as Figure 1b? First, we do have reference material and empirical relationships to correlate chemical shift with structure. However, we lack coupling information because of noise decoupling of protons, and we cannot depend on peak integrations for the following reasons.

Repetitive scan (continuous wave) H spectrometry usually results in a satisfactory relationship between integrated peak areas and the number of nuclei under those areas because there is sufficient time between irradiations of an individual proton for relaxation to occur. Satisfactory integrations would also result for most ^{13}C spectra under these conditions, but the time needed for the number of scans required is prohibitive for routine work.

In routine Fourier Transform runs, the repetitive pulses are spaced at intervals of 0.1-1 second (acquisition time) during which the signal is averaged and stored. Under these conditions, ^{13}C nuclei, whose relaxation times (T_1) vary over a wide range, are not equally relaxed between pulses, and the resulting peak areas do not integrate to give the correct number of carbon atoms. Very long pulse delays (following the acquisition period) can be used, but the time required limits this technique to special situations. Furthermore, there is another complication: the Nuclear Over-hauser Enhancement (see above) is not the same for all nuclei, and this result in further loss of quantitation.

However, one advantage does result. It is usually possible by "eyeballing" a ^{13}C spectrum to recognize nuclei that do not bear protons by their low intensity. The common spin lattice relaxation mechanism for ^{13}C results from dipole-dipole interaction with directly attached protons. Thus, non-protonated carbon atoms often have longer relaxation times and give small peaks. It is therefore often possible readily to detect carbonyl groups (except formyl), nitriles, non-protonated olefinic and acetylenic carbon atoms, and other quaternary carbon atoms. However, care must be taken to allow a sufficient number of pulses or a long enough interval between pulses (to compensate for the long T_1) so that these weak signals are not completely lost in the baseline noise.

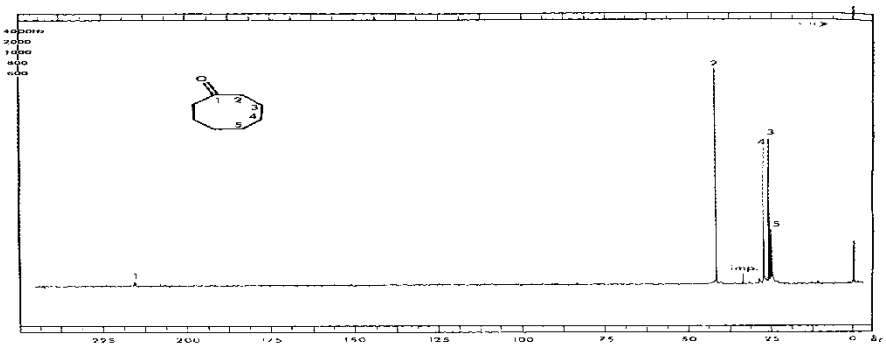
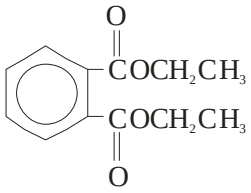


Figure :6- ^{13}C NMR spectrum of cyclooctanone with proton coupling completely removed by noise decoupling. CDCl3 solvent, 20 MHz, sweepwidth 3500 Hz.

The most useful techniques for assigning peaks, in addition to structure-shift correlations, are off resonance decoupling, selective proton decoupling, the use of chemical shift reagents, and deuterium substitution. The concept of chemical shift equivalence should always be kept in mind. The use of spin relaxation times is beyond the scope of this chapter.

In the noise decoupled spectrum of diethyl phthalate (Figure 1b),



we can assign the very small peak at 167.75 ppm to the 2 equivalent C=O groups, the very small peak at 132.85 ppm to the equivalent substituted aromatic carbons, the large peaks at 131.33 ppm and 129.19 ppm to the remaining aromatic carbons, the medium peaks at 61.63 ppm to the 2 equivalent CH_2 groups, and the medium peak at 14.15 ppm to the 2 equivalent CH_3 groups. These assignments can be made on the basis of Appendices B and C and on the assumption that the quaternary carbon atoms are responsible for the weak peaks. Their relative intensity can be increased by inserting a pulse decay (an interval between the acquisition period and the next pulse) as in Figure 1c.

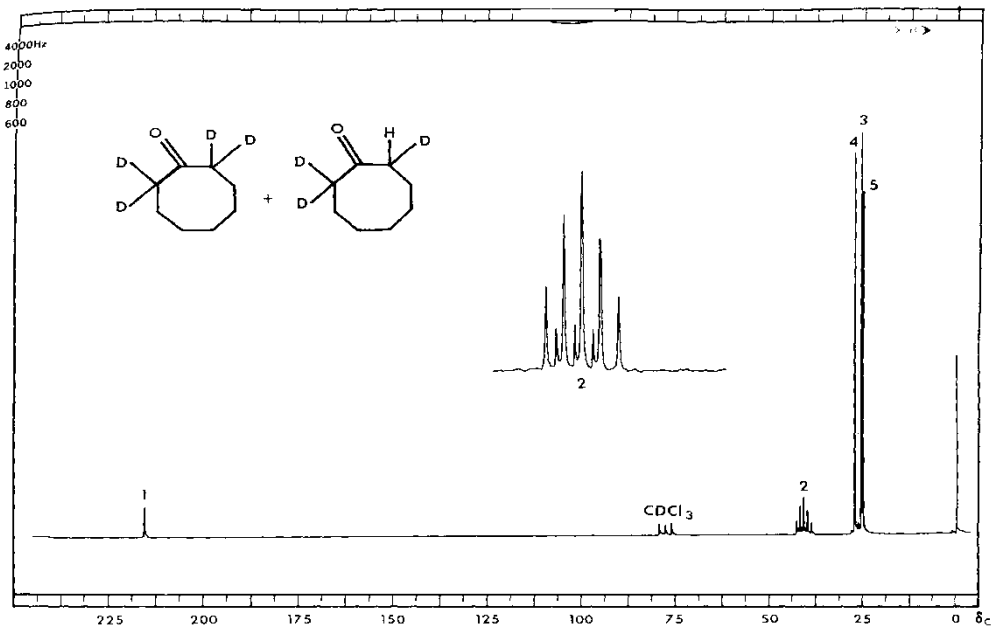


Figure :7- Non decoupled ^{13}C NMR spectrum of tetradeuterated (major component) and trideuterated (minor component) cyclooctanone. $CDCl_3$ solvent, 20 MHz, sweepwidth 3500 Hz.For insert, sweepwidth 1000 Hz.

Note that the 10-second pulse delay nearly equalizes the intensities of all the peaks except for those representing the quaternary carbons.

Off-Resonance Decoupling: We have seen that proton noise decoupling simplifies the spectrum and increases peak heights, but with the loss of coupling information. Off-resonance decoupling gives a simplified spectrum yet retains "residual" ^{13}C-H coupling (J^T) information. Off-resonance decoupling is achieved by offsetting the high-power proton decoupled by about 1000-2000 Hz upfield or about 2000 3000 Hz downfield from the proton frequency of TMS without using the noise generator; that is, we irradiate upfield or downfield of the usual (1000 Hz sweepwidth) proton spectrum. This results in residual coupling from protons directly bonded to the ^{13}C atoms, while long range coupling is usually lost. The observed residual coupling (J^T), which is determined by the amount of offset and the power of the decoupler, is smaller than the true coupling J.

$$J^T \approx \frac{2\pi J \Delta\nu}{\gamma H_2}$$

where γ is the magnetogyric ratio for protons, $\Delta\nu$ is the difference between the resonance frequency of the proton of interest and the decoupled frequency, and H_2 is the strength of the rotating magnetic field generated by the decoupled frequency. Thus, the multiplicities of the ^{13}C bands can be readily observed, usually without overlap with other ^{13}C bands.

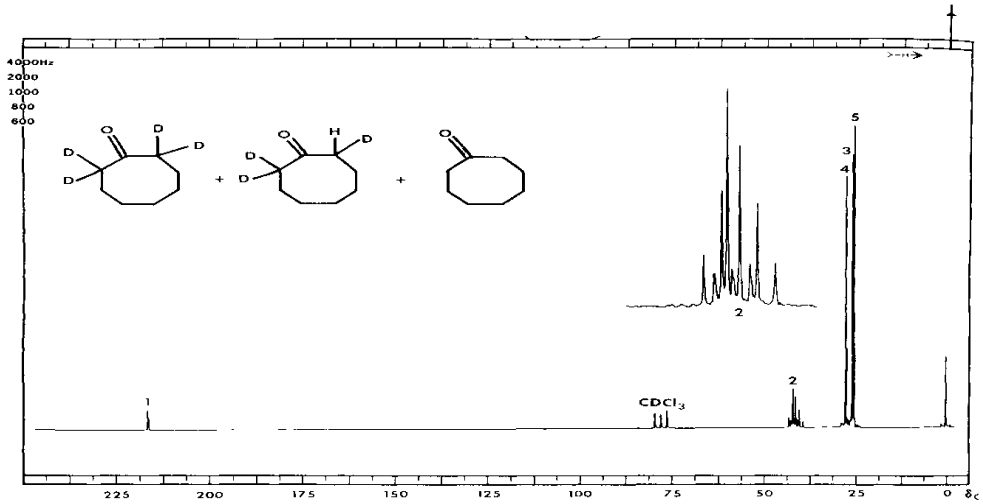


Figure :8- Noise-decoupled 13C spectrum of deuterated sample undeuteratedcyclooctanone, $CDCl_3$ solvent, 20 MHz, sweep width 5000Hz. For insert, sweepwidth 1000 Hz.

Methyl carbon atoms appear as quartets,methylenes as triplets (or as pair of doublets if the protons are not equivalent and their coupling constants are sufficiently different), methines as doublets, and quaternary carbon atoms as singlets. The procedure, of course, also gives a proton count to corroborate the proton spectrum. A discrepancy between the number of protons obtained from the off resonance decoupled ^{13}C spectrum and the molecular formula obtained from the mass spectrum results from elements of symmetry whose presence can be correlated with molecular structure .

In Figure ,only the doublets of peaks 3 and 4 overlap. The residual couplings become slightly larger as the frequency increases; in this case, the irradiation is upfield of the proton frequency of TMS. It is convenient to superimpose the off-resonance decoupled spectrum on the noise-decoupled spectrum on a light-table. Thus, we can see that the quaternary carbons (singlets) and the center peak of the CH_2 triplets are superimposed on the corresponding noise-decoupled singlets, whereas the CH doublet and CH3 quartets "straddle" the corresponding noise-decoupled peaks.

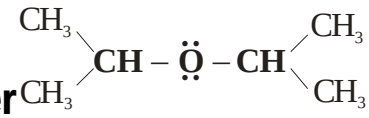
A second-order effect is discussed in Section VI and the use of off-resonance decoupling to correlate a particular ^{13}C peak with the shift position of its attached proton is discussed in Section V.

The off-resonance decoupled spectrum of diethyl phthalate (Figure 1d) allows us to confirm the assignments made on the basis of chemical shifts and peak heights. The multiplicity of peak1 is unchanged. Peak 2 is buried under peak 3a. Peaks 3 and 4 are overlapping doublets. Peak 5 is a triplet, and peak 6 a quartet. We count 6 carbon atoms and 7 protons, which, given an element of

symmetry, corroborates the molecular formula $C_{12}H_{14}O_4$ and the ortho substitution. For this simple molecule, the nondecoupled spectrum (Figure 1a) presents no problem, but in more complex molecules, overlapping multiplets are often difficult to interpret.

Structure Elucidation Of Simple Organic Compounds Using UV, IRand NMR Spectroscopic Techniqques

Problem

Problem1: spectra di-isopropyl ether 

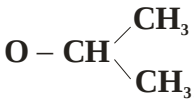
UV spectrum: it does not display any absorption band in UV-VS region indicating the absence of unsaturation, conjugation or the presence of aromatic system in the molecule.

IR spectrum: It exhibits no characteristic OH or C=O peak but the presence of a strong band at $100 cm^{-1}$ indicative of C-O bonds.

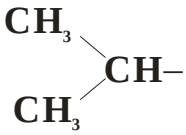
NMR spectrum: It NMR spectrum displays following data:

Position (δ)	Multiplicity	Number of protons
3.7	Septet	1
1.1	Doublet	12

(i) Septet at $\delta 3.7$ **:** Its multiplicity and chemical shift reveal the presence of

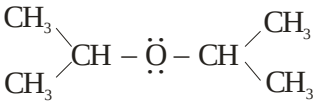

Structural moicty

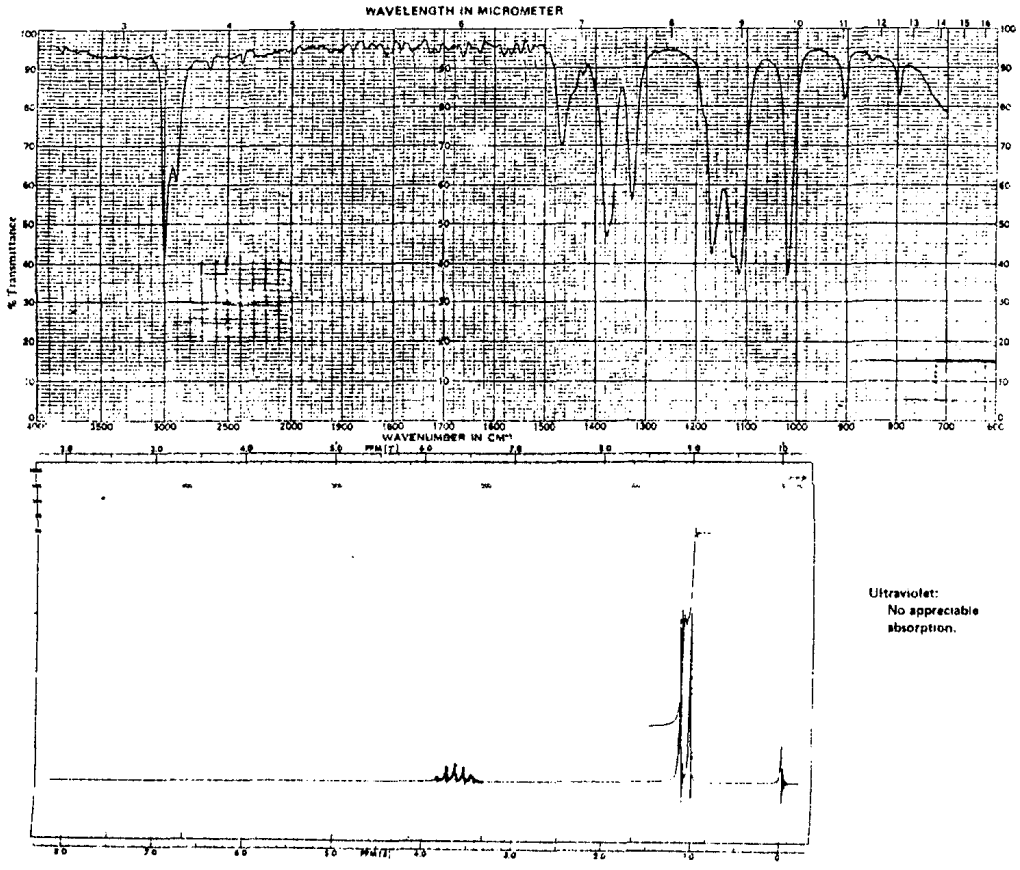
(iii) **Doublet at** $\delta 1.1$ **:** The position and multiplicity of the doublet are indicative of



The J values identical to that of the septet at thus these groups must be coupled. The fragment present must be

Number of hydrogen atoms indicated the compound has the structure:





PROBLEM 1 :H-NMR and IR-spectra of di-isopropyl enther

Problems 2: spectra of diethyl malonate,

Uv spectrum: the lack of any significant absorption UV-VS region climinates the possibility of conjugated system.

IR spectrum: presence of a strong band at $1750cm^{-1}$ is indicative of ester.

$$\begin{array}{l} \mathrm{O} \\ \| \\ \mathrm{C-O-}\text{function.} \end{array}$$

NMR spectrum: It gives following data:

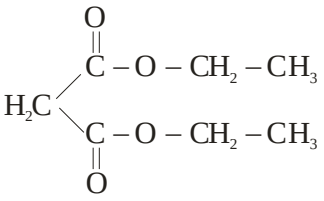
Position (δ)	Multiplicity	Number of protons
4.2	quartet	4H
3.3	Singlet	2H
1.3	triplet	6H

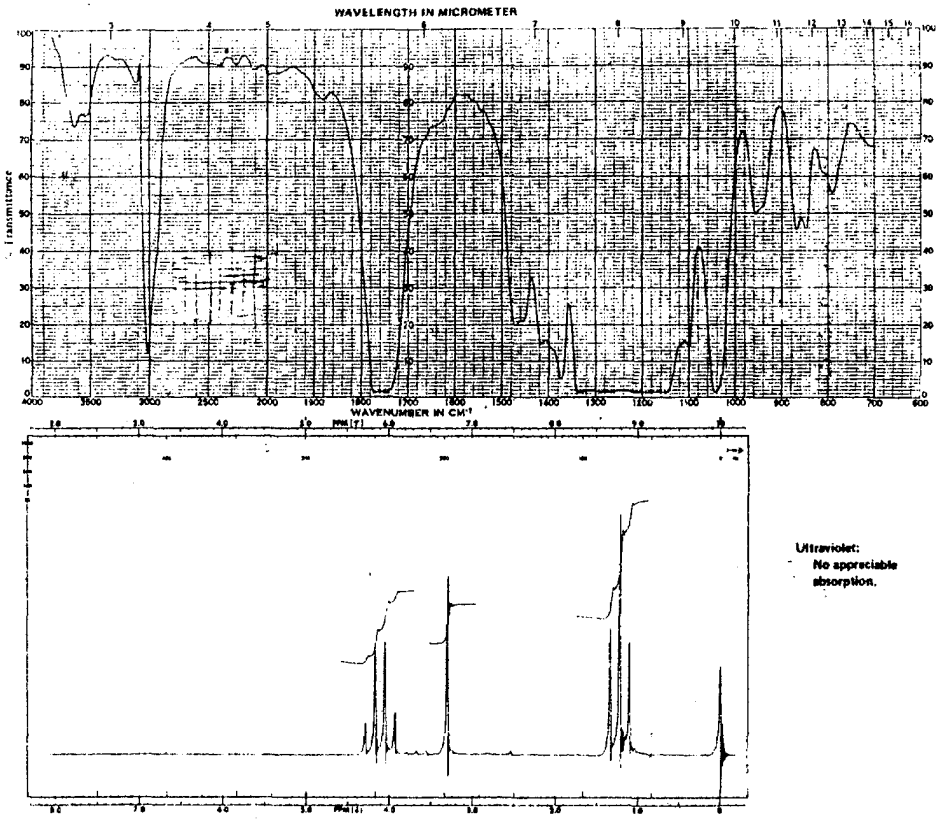
(i) **Quartet at** $\delta 4.2$: Its multiplicity indicates $-CH_2-CH_3$ protons. The position of the quartet indicates $O-CH_2-CH_3$

(ii) **Singlet at** $\delta 3.3$: Its multiplicity revels the absence of hydrogen atoms on adjacent carbon atoms. The position indicates that electron withdrawing groups are attached to the carbon, but the electron withdrawing groups must not be oxygen (oxygen would shift absorption further downfield).

(iii) **Triplet at** $\delta 1.3$ **:** The multiplicity and position are indicative of $CH_3 - CH_2 -$ protons. The J value is similar to that of the quartet at $\delta 4.2$, thus these two groups must be coupled. The fragment present must be $CH_3 - CH_2 - O$.

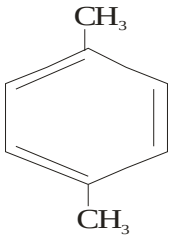
Above data lead to the following structure:





PROBLEM 2 :M-NMR and IR-spectra of diethyl malonale

Problem 3: Spectra of p-xylene.



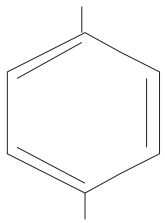
UV Spectrum: presence of multiple absorption bands in the region λ_{max} 250-270 nm indicates an aromatic system.

IR Spectrum: It indicates the lack of OH and C=O groups. The absorption bands at 1529 and 800 cm^{-1} indicate the presence of an aromatic system.

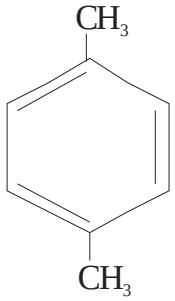
NMR spectrum: Its MR spectrum displays following data:

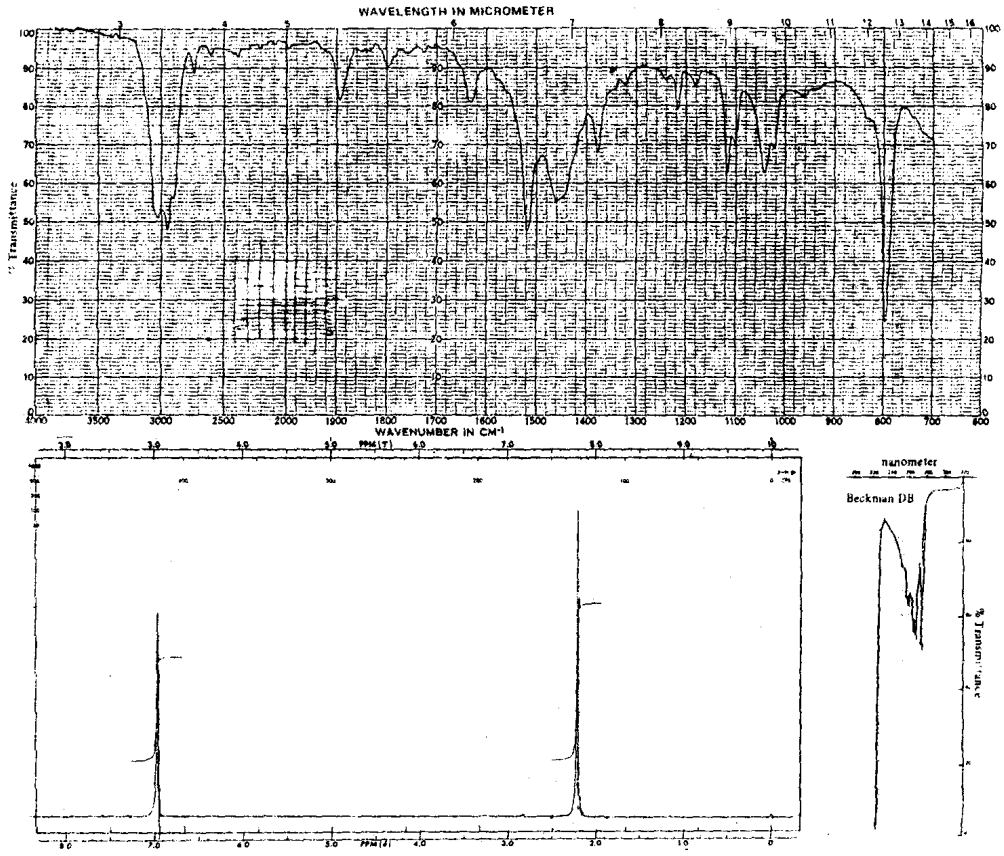
(i) **Singlet at $\delta 7.0$:** The position of the peak is indicative of aromatic protons. The number of protons (4) is indicative of a disubstitues ring. The singlet nature of the peak is indicative of a symmetrical-para substitution with identical substituents.

(ii) **Singlet at $\delta 2.2$:** The six protons singlet is indicative of groups. These methyl groups are symmetrically substituted, thus the fragment must be:



From above spectral data the compound has the structure:





PROBLEM 3: H-NMR, IR and UV-spectra of *p*-xylene

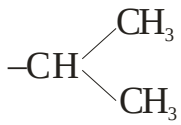
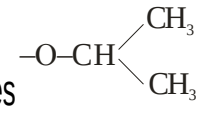
Problem 4: Spectra of isopropyl acctate $CH_3CH(CH_3)-O-C(=O)-CH_3$

UV spectrum: It does not exhibit any absorption in UV-VS region indicating the absence of unsaturation, as well as the conjugation in the molecule.

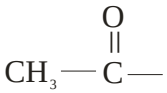
IR spectrum: It displays a strong band at $1750 cm^{-1}$ indicating the presence of an ester $\left(-C(=O)-O-\right)$ function.

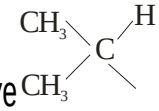
NMR Spectrum: It gives the following data:

Position (δ)	Multiplicity	Number of protons
5.0	Septet	1
1.9	Singlet	3
1.2	doublet	6

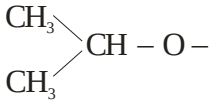
(i) Septet at $\delta 5.0$: Its multiplicity indicates proton.  The position of the septet indicates  functionality.

(ii) Singlet at $\delta 1.9$: Its multiplicity indicates the absence of hydrogen atoms on adjacent carbon. The position indicates a weak electron withdrawing group attached to the methyl group. The position is appropriate for following moiety:

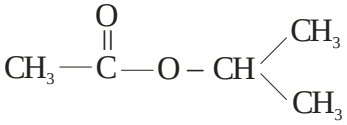


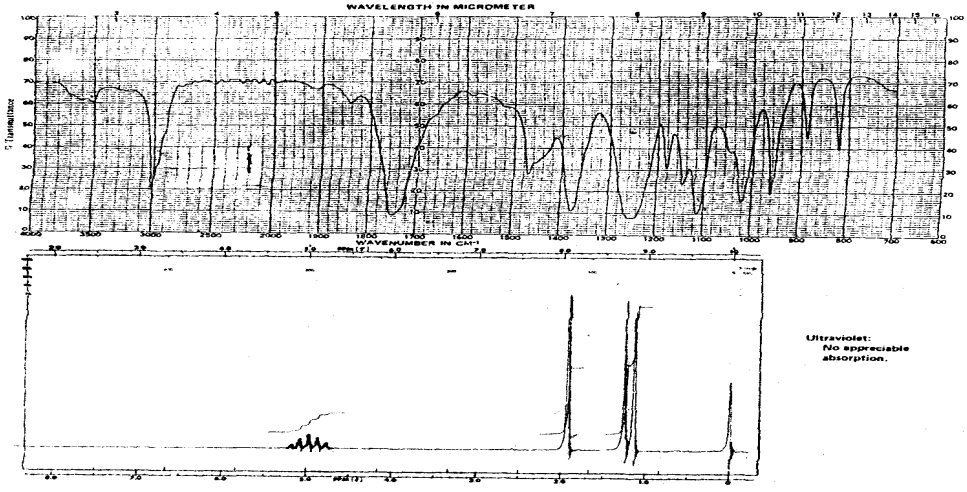
(iii) Doublet at $\delta 1.2$: The position and multiplicity of the peak are indicative  of species.

The J value is identical to that of the septet at $\delta 5.0$, thus these two groups must be coupled. The fragment present must be.



From above spectral analysis the compound has the structure:





PROBLEM 4 : H-NMR and IR spectra of isopropyl acetate

Problem 5: Spectra of ethylacctoacctate, $CH_3COCH_2COOCH_2CH_3$

UV spectrum: It shows absorption band at λ_{max} 250mn indicating the presence of unsaturatuion.

IR spectrum: It displays band at 1720 and $1750 cm^{-1}$ indicating the presence of $-\overset{O}{\overset{\|}{C}}-$ and $-\overset{O}{\overset{\|}{C}}-O-$ groups respectively.

NMR spectrum: It givcs the following data:

Position (δ)	Multiplicity	Integration curve height	Number of protons
4.1	quartet	4.0	2
3.5	Singlet	3.5	2
2.2	Singlet	5.4	3
1.2	triplet	5.9	3

(i) Quartet at $\delta 4.0$: Its multiplicity indicates $CH_2 - CH_3$ protons. The chemical shift of the quartet indicates $-O - CH_2 - CH_3$ fragment.

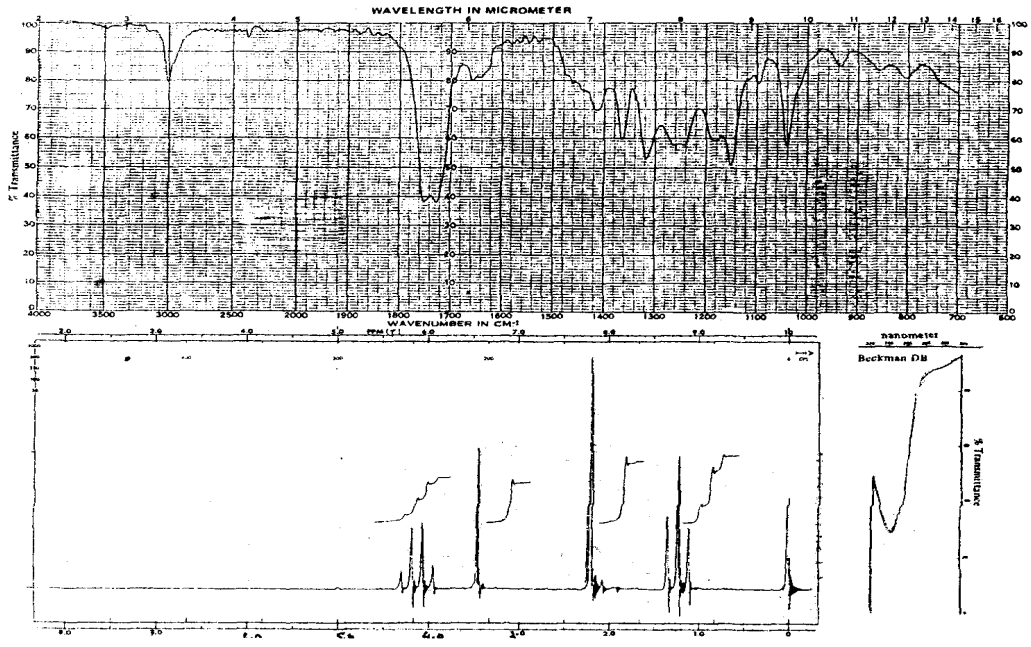
(ii) Singlet at $\delta 3.5$: multiplicity indicates the absence of hydrogen atoms on adjacent carbons. The position of chemical shift shows that electron withdrawing groups are attached to the carbon, but the electron withdrawing groups must not be oxygen (oxygen would shift absorption further downfield),

(iii) Singlet at $\delta 2.2$: Its multiplicity indicates the absence of hydrogen atoms on adjacent carbon. The position indicates a weak electron withdrawing group attached to the methyl protons. The position is appropriate for

$$CH_3-\overset{O}{\overset{\|}{C}}-$$

(iv) Triplet at $\delta 1.2$: The multiplicity and position are indicative of .the J value is identical to that of the quartet at $\delta 4.1$, thus, these two groups must be coupled. The fragment present must be $CH_3 - CH_2 - O -$. From above spectral data the compound has the following structure:

$$CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - \overset{O}{\overset{\|}{C}} - O - CH_2 - CH_3$$



PROBLEM 5 :H-NMR, IR and UV-spectra of ethylacetoacetate