SYNTHESIS AND CHARACTERISATION OF 4,4-(HYDRAZINE-1,2- DIYLIDENE BIS(METHANYLIDENE)) BIS (N,N-BIS(2- CHLOROETHYL) ANILINE

Submitted in partial fulfilment of the requirements for the award of

Master of Science in Chemistry

by

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SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

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This is to certify that this Project Report is the bonafide work of **HARSHITHA. CH (40910003)** who carried out the project entitled "**SYNTHESIS AND CHARACTERISATION OF 4,4-(HYDRAZINE-1,2- DIYLIDENE BIS (METHANYLIDENE)) BIS (N,N-BIS (2- CHLOROETHYL) ANILINE"** under our supervision from November 2021 to April 2022.

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Submitted for Viva voce Examination held on_____

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DECLARATION

I **HARSHITHA. CH (40910003),** hereby declare that the Project Report entitled **SYNTHESIS AND CHARACTERISATION OF 4,4-(HYDRAZINE-1,2-DIYLIDENE BIS (METHANYLIDENE)) BIS (N,N-BIS (2- CHLOROETHYL) ANILINE** done by me under the guidance of **Dr. J. KARTHIKEYAN, M.Sc., Ph.D.**, Associate professor, Department of Chemistry at **Sathyabama Institute of Science and Technology**, Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600119 is submitted in partial fulfillment of the requirements for the award of Master of Science degree in Chemistry.

DATE: **HARSHITHA. CH**

PLACE: **SIGNATURE OF THE CANDIDATE**

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HARSHITHA. CH

ABSTRACT

4,4-(Hydrazine-1,2-diylidene bis(methanylidene)) bis(N,N-bis(2-chloroethyl)aniline were synthesized by chemical method. The structural, morphological and optical properties of the synthesized compound were analysed by Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, proton NMR, mass spectrometry

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UV-Vis	Ultraviolet Visible
FTIR	Fourier Transform Infrared
XRD	X-Ray Diffraction

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CHAPTER-1

INTRODUCTION

1.1 AZINES

The term azine has two meanings in chemistry:

In heterocyclic chemistry, azines are aromatic six-membered rings containing one (pyridine) to six N atoms (hexazine).

In alicyclic chemistry, azines are compounds resulting from the reaction of two molecules of identical carbonyl compounds (symmetrical azines 1) or, more commonly, from the reaction of two different carbonyl compounds.

The compounds are called aldazines or ketazines depending on whether the carbonyl compound is an aldehyde or a ketone, respectively.

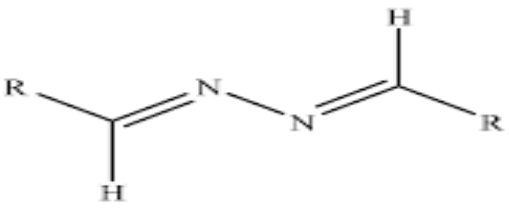

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Fig:1.1.a: 2,3 diaza

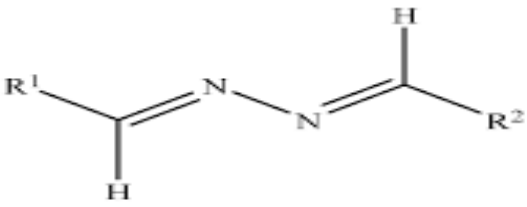

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***Fig:1.1.b: 1,3* butadiene**

Azines that are N-N-linked diimines are 2,3-diaza analogs of 1,3-butadiene. They are a class of compounds with interesting chemical properties and undergo a wide variety of chemical processes.

The two imine bonds that form the azine moiety may be considered as polar acceptor groups oriented in opposite directions, as they include an N–N bond. On the basis of their relationship to butadiene, electronic delocalization may be expected. Two resonance structures illustrating delocalization are represented by [3] and [4].

However, crystallographic data, nuclear magnetic resonance (NMR) spectroscopic studies, and theoretical calculations provide little evidence for delocalization within the azine backbone. Thus, it was concluded that an azine

bridge between two conjugated systems, termed as a “conjugation stopper”, prevents delocalization, as shown by the resonance structure [5].

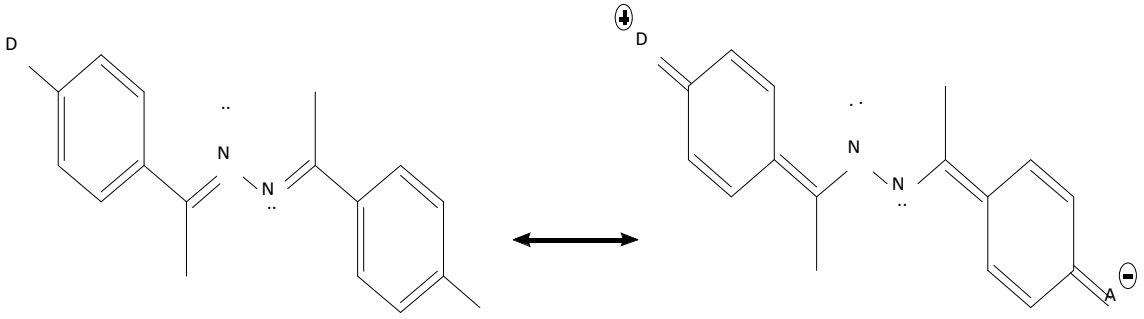


Fig:1.2: Resonance structure of azines

During the past several years, one of the active areas of organic chemistry is the study of systems containing two conjugated double bonds. Within this general classification of compounds, three types of molecules that have attracted the most attention are 1,3-dienes [6], enones [7], and 1,2-diones [8]

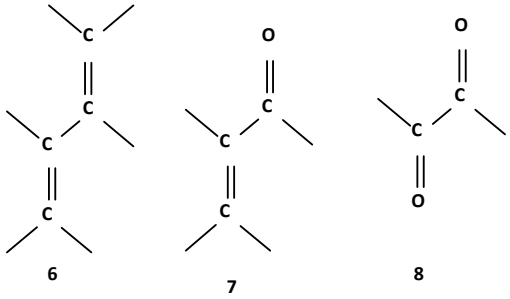


Fig:1.3: 1,3-dienes [6], enones [7], and 1,2-diones [8]

In addition to the molecules mentioned above, azines 9, enimines 10a and 10b, and 1,2-diimines 11a and 11b constitute several additional classes of compounds possessing two conjugated double bonds.

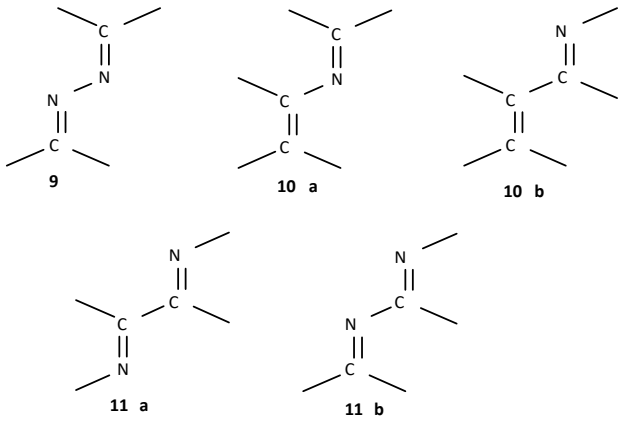


Fig:1.4: azines 9, enimines 10a and 10b, and 1,2-diimines 11a and 11b

The mechanisms of addition of hydrazines to carbonyl compounds, the bifunctionality of hydrazine results in two types of complicated scenarios:

First, the nucleophile not only can exist as a base, but also as mono- and deprotonated forms. Whereas the deprotonated form does not possess a nitrogen atom with a free electron pair, which is necessary for nucleophilic attack by amines, the monoprotonated and unprotonated forms of hydrazine can behave as nucleophiles.

Second, formation of hydrazone from the reaction between the carbonyl compound and one molecule of hydrazine may be followed by a reaction with a second molecule of the carbonyl compound. This reaction results in formation of an azine of the type ArCH=N–N=CHAr

Formaldehyde azine, the simplest azine, was prepared in 1959 by Neureiter.5 The rate of reaction of hydrazine with various carbonyl compounds decrease in the following order: aldehyde > dialkyl ketone > alkaryl ketone > diaryl ketone. Reaction of aldehydes and dialkyl ketones with hydrazine in water or alcoholic medium produce the hydrazone or azine [9].

Aldazines form more quickly than do ketazines. In fact, the reaction of hydrazones of aldehyde with a second molecule of aldehyde is faster than reaction with hydrazine itself; thus, aldazine is the normal product. On the other hand, ketazines require the presence of excess ketone together with acetic or formic acid as catalyst.

Azines are useful for the isolation, purification, and characterization of carbonyl compounds. They have several advantages as protective agents:

1) Economic advantage due to low cost (only one-half equivalent of protective group is required),

2) Easy isolation of the products due to their symmetrical structure and high melting points, and

3) Easy identification of the products due to their fully conjugated and colourful structures [11],[12] Unsymmetrical azines are particularly interesting because of their ability of their functionality to link two dissimilar groups in useful ways.

For example, they can form steroidal opiate derivatives, which show very long opioid antagonist activity. This finding suggests that a new and general method for synthesizing unsymmetrical azines may greatly facilitate the development of other useful applications.[13]

Generally, symmetrical azines are crystalline materials, facilitating their purification by recrystallization. Ease of purification and one step synthesis with quantitative yield of the desired product are two main advantages of symmetrical azines. However, crystallinity is the key limiting factor in the application of various chromophores connected via azine linkage in optoelectronic devices. Unsymmetrical azines prepared from two different carbonyl compounds are more promising from this viewpoint, as their tendency for crystallization is significantly lower.

1.2 HYDRAZINE

Hydrazine is an inorganic compound with the chemical formula N_2H_4. It is a simple pnictogen hydride, and is a colourless flammable liquid with an ammonia-like odour.

Hydrazine is highly toxic unless handled in solution as, for example, hydrazine hydrate ($NH_2NH_2 \cdot xH_2O$)

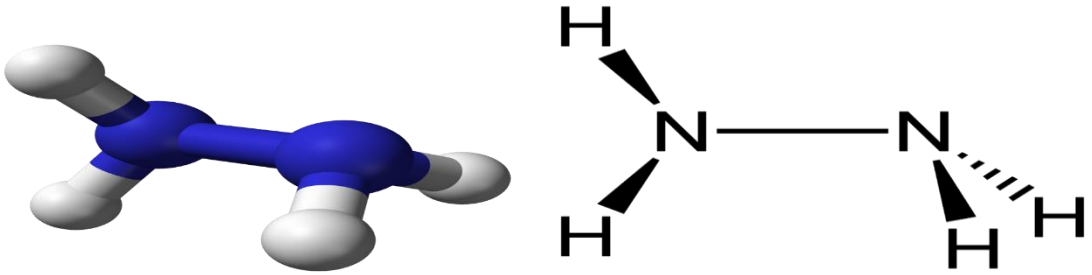


Fig:1.5: Hydrazine

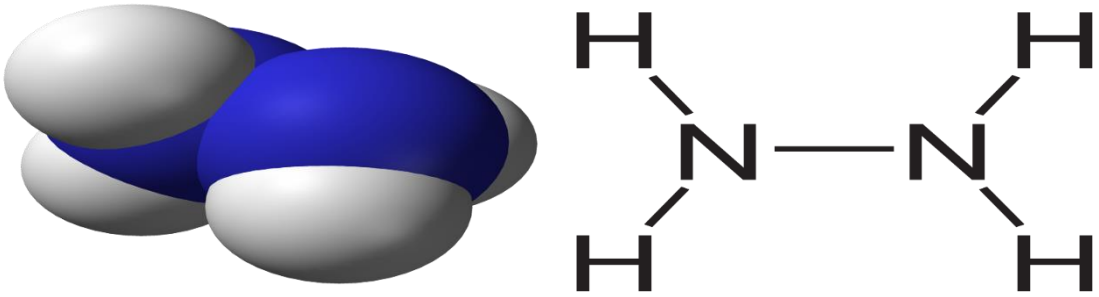


Fig:1.6: Hydrazine

Hydrazine was first used as a component in rocket fuels during World War II. A 30% mix by weight with 57% methanol (named M-Stoff in the German Luftwaffe) and 13% water was called C-Stoff by the Germans.[14]

The mixture was used to power the Messerschmitt Me 163B rocket-powered fighter plane, in which the German high test peroxide *T-Stoff* was used as an oxidizer. Unmixed hydrazine was referred to as B-Stoff by the Germans, a designation also used later for the ethanol/water fuel for the V-2 missile.[15]

Hydrazine is used as a low-power monopropellant for the maneuvering thrusters of spacecraft, and was used to power the Space Shuttle's auxiliary power units (APUs). In addition, mono-propellant hydrazine-fuelled rocket engines are often used in terminal descent of spacecraft. Such engines were used on the Viking program landers in the 1970s as well as the Mars landers Phoenix (May 2008), Curiosity (August 2012) and Perseverance (February 2021).

A mixture of hydrazine and red fuming nitric acid was used in the Soviet space program where it was known as devil's venom due to its dangerous nature

In all hydrazine mono-propellant engines, the hydrazine is passed over a catalyst such as iridium metal supported by high-surface-area alumina (aluminium oxide), which causes it to decompose into ammonia, nitrogen gas, and hydrogen gas.

1.3 HYDRAZINES

Hydrazines ($R_2N{-}NR_2$) are a class of chemical compounds with two nitrogen atoms linked via a covalent bond and which carry from one up to four alkyl or aryl substituents. Hydrazines can be considered as derivatives of the inorganic hydrazine ($H_2N{-}NH_2$), in which one or more hydrogen atoms have been replaced by hydrocarbons

Production

- 1,1-Dimethylhydrazine is produced by the reduction of *N*-nitrosodimethylamine.
- The reduction of benzenediazonium chloride with tin(II) chloride and hydrochloric acid provides phenylhydrazine.
- 2,4-Dinitrophenylhydrazine is produced by the reaction of 1-chloro-2,4-dinitrobenzene with hydrazine.
- Tetraphenylhydrazine is formed by the oxidation of diphenylamine with potassium permanganate in acetone.

1.3.1 CLASSIFICATION OF HYDRAZINES

Hydrazines can be divided into three groups according to the degree of substitution. Hydrazines belonging to the same group behave similarly in their chemical properties. Monosubstituted hydrazines and so-called asymmetrically disubstituted hydrazines, where (only) two hydrocarbon groups are bonded to the same nitrogen atom are colourless liquids.

Aliphatic monosubstituted and asymmetrically disubstituted hydrazines are very water soluble, strongly alkaline and good reducing agents. Aromatic monosubstituted and asymmetrically disubstituted hydrazines are poorly soluble in water, less basic and weaker reducing agents.

For the preparation of aliphatic hydrazines, the reaction of hydrazine with alkylating compounds such as alkyl halides is used, or by reduction of nitroso derivatives. Aromatic hydrazines are prepared by reducing aromatic diazonium salts.

In symmetric disubstituted hydrazines, a hydrocarbon group is bonded to each of the hydrazine nitrogen atoms. Like asymmetrically disubstituted hydrazines, they are liquids, but their boiling points are typically higher. In particular, the aliphatic compounds are basic and reducing agents and are soluble in water. Aromatic symmetric disubstituted hydrazines are not soluble in water. Symmetrically disubstituted hydrazines are prepared by reducing nitro compounds under basic conditions or by reducing the azines.

Tri- or tetrasubstituted aliphatic hydrazines are water-insoluble weakly basic compounds. The corresponding arylhydrazines are solid colourless substances which are insoluble in water and substantially not basic. They react with concentrated sulfuric acid to form a violet or dark blue compounds

ALKYL HYDRAZINES

1,1-dimethylhydrazine is a chemical compound with the formula $H_2NN(CH_3)_2$ that is used as a rocket propellant. It is a colourless liquid, with a sharp, fishy, ammonia-like smell typical for organic amines. Samples turn yellowish on exposure to air and absorb oxygen and carbon dioxide. It is miscible with water, ethanol, and kerosene. In concentration between 2.5% and 95% in air, its vapours are flammable. It is not sensitive to shock. Symmetrical dimethylhydrazine, 1,2-dimethylhydrazine is also known but is not as useful.

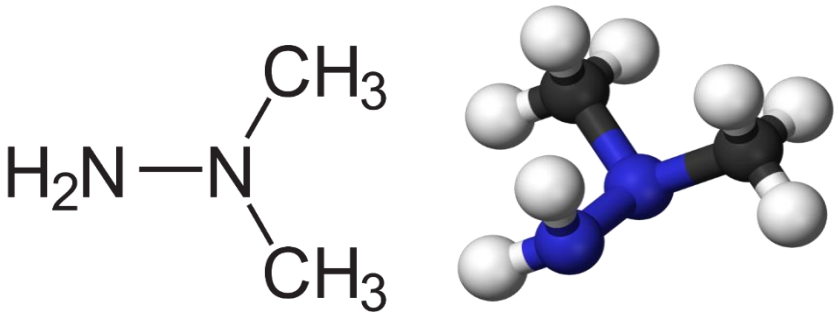


Fig 1.7 : 1,1-Dimethyl hydrazine

ARYL HYDRAZINES

Phenylhydrazine is the chemical compound with the formula $C_6H_5NHNH_2$. It is often abbreviated as $PhNHNH_2$. It is also found in edible mushrooms.

Phenylhydrazine forms monoclinic prisms that melt to an oil around room temperature which may turn yellow to dark red upon exposure to air. Phenylhydrazine is miscible with ethanol, diethyl ether, chloroform and benzene. It is sparingly soluble in water.

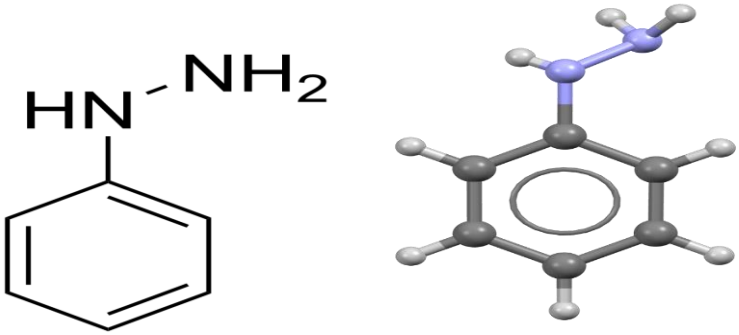


Fig 1.8: Phenyl hydrazine

2,4-Dinitrophenylhydrazine (2,4-DNPH) is the organic compound $C_6H_3(NO_2)_2NHNH_2$. Dinitrophenylhydrazine is a red to orange solid. It is a substituted hydrazine.

The solid is relatively sensitive to shock and friction. For this reason, dinitrophenylhydrazine is usually handled as a wet powder. DNPH is a precursor to the drug Sivifene

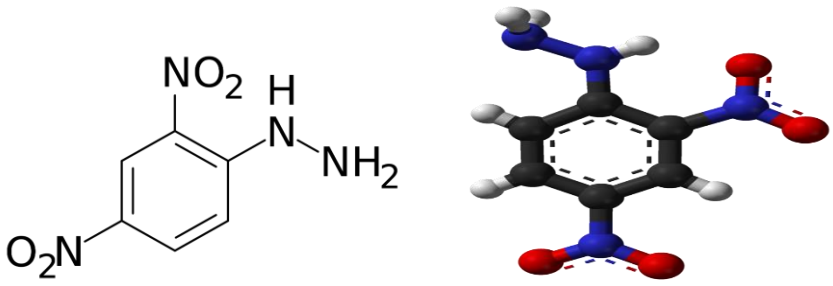


Fig 1.9: 2,4-Dinitrophenylhydrazine (2,4-DNPH)

Hydrazobenzene (1,2-diphenylhydrazine) is an aromatic organic compound consisting of two aniline groups joined via their nitrogen atoms. It is an important industrial chemical used in the manufacture of dyes, pharmaceuticals, and hydrogen peroxide.

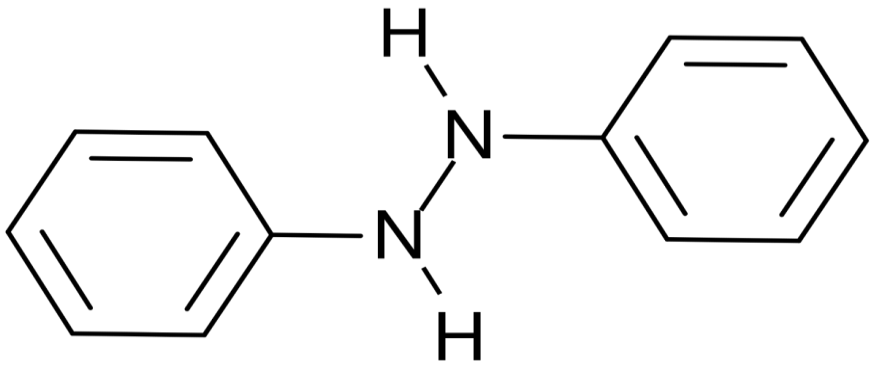


Fig 1.10: 1,2-Diphenyl hydrazine

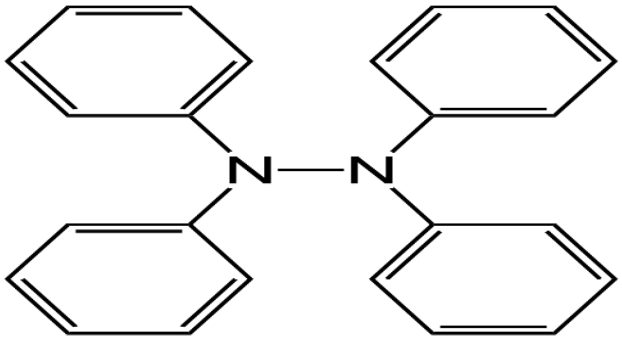


Fig 1.11: Tetra Phenyl hydrazine

Phenylhydrazine and 2,4-dinitrophenylhydrazine have were used historically in analytical chemistry to detect and identify compounds with carbonyl groups.

Phenylhydrazine was used to study the structure of carbohydrates, because the reaction of the sugar's aldehyde groups lead to well crystallizing phenylhydrazones or osazones.

1.3.2 EXAMPLES

Organo hydrazines and their derivatives are numerous, especially when hydrazones are included.

- monomethyl hydrazine, where one of the hydrogen atoms on the hydrazine molecule has been replaced with a methyl group (CH_3). Due to the symmetry of the hydrazine molecule, it does not matter which hydrogen atom is replaced. It is sometimes used as a rocket fuel.
- 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) and 1,2-dimethylhydrazine (symmetrical dimethylhydrazine) are hydrazines where two hydrogen atoms are replaced by methyl groups. UDMH is the easier of the two to manufacture and is a fairly common rocket fuel.
- Gyromitrin and agaritine are hydrazine derivatives found in the commercially produced mushroom species *Agaricus bisporus*. Gyromitrin is metabolized into monomethyl hydrazine.
- Isoniazid, iproniazid, hydralazine,
  and phenelzine are medications whose molecules contain hydrazine-like structures.
- 2,4-dinitrophenylhydrazine (2,4-DNPH) is commonly used to test for ketones and aldehydes in organic and clinical chemistry.
- Phenyl lhydrazine, $C_6H_5NHNH_2$, the first hydrazine to be discovered.

1.3.3 IMPORTANCE OF HYDRAZINES

Hydrazine is mainly used as a foaming agent in preparing polymer foams, but applications also include its uses as a precursor to polymerization catalysts, pharmaceuticals, and agrochemicals, as well as a long-term storable propellant for in-space spacecraft propulsion.

Although it is toxic to us directly, hydrazine rapidly breaks down in oxygen, making release into the environment low risk. It could even be an environmentally friendly fuel. In some types of hydrogen fuel cell, hydrazine breaks down to make nitrogen and water and gives out energy in an exothermic reaction.

1.4 HYDRAZINE HYDRATE

As a water-based solution, Hydrazine Hydrate and its Derivatives are supplied by Arkema to be widely used as reducing agent, blowing agent, corrosion inhibitor, oxygen scavenger or intermediate of synthesis.

It is a colourless liquid base $N_2H_4.H_2O$ made usually by reaction of sodium hypochlorite and ammonia or urea and used for the same purposes as hydrazine.

Currently, most hydrazine is produced by the ketazine process, which is a variation of the Raschig process. Ammonia is oxidized by chlorine or chloramine in the presence of an aliphatic ketone, usually acetone. The resulting ketazine is then hydrolyzed to hydrazine

CHAPTER-2

LITERATURE SURVEY

2.1 Acetophenone Azine

Naida Raison et al (2021) Acetophenone azine (CAS 729-43-1) has recently been identified as a powerful allergen in shin pads and footwear made of the foam elastomer ethyl vinyl acetate. The molecule is most likely the consequence of interactions between other chemicals that occur throughout the production process, rather than being purposely added to ethyl vinyl acetate. A 0.1 percent concentration in acetone or petrolatum is advised for patch testing. Patch testing shoes, as well as plastics and glues, should include acetophenone azine. The chemical is currently unavailable from patch testing materials vendors, but this is expected to change soon. Acetophenone azine (CAS 729-43-1) has recently been identified as a powerful allergen in shin pads and footwear made of the foam elastomer ethyl vinyl acetate.

2.2 Azine-N-oxides as effective controlling groups for Rh-catalyzed intermolecular alkyne hydroacylation

Danial F Moseley et al (2021) In metal-catalyzed hydroacylation chemistry, heterocycle-derived aldehydes are difficult substrates. We show that azine N-oxide substituted aldehydes have high reactivity and are excellent substrates for intermolecular hydroacylation of alkynes. Using a Rh(i)-catalyst, we develop a moderate and scalable aldehyde C-H activation that allows for good yields and high regioselectivities (up to >20: 1 l:b) when coupled with unactuated terminal alkynes. Both substrates are capable of tolerating a wide range of functional groups. Diazine aldehydes with a free N-lone pair can also be used in this process. A one-pot hydroacylation/deoxygenation sequence is used to convert the hydroacylation products to the appropriate azine. The synthesis of a bidentate pyrrolyl ligand is also achieved using a one-pot hydroacylation/cyclisation utilising N-Boc propargylamine.

2.3 Azine Steric Hindrances Switch Halogen Bonding to N-Arylation upon Interplay with σ-Hole Donating Haloarenenitriles

Sergey V Baykov et al (2021) Depending on the steric and electronic effects of the heterocycles, an interaction between 4-bromo- and 4-iodo-5-

nitrophthalonitriles (XNPN, X=Br or I) and any of the azines (pyridine 1, 4-dimethylaminopyridine 2, isoquinoline 3, 4-cyanopyridine 4, 2-methylpyridine 5, 2-aminopyridine 6, quinoline 7, 1-methylisoquinoline 8, and 2,2'-bipyr N-arylation of sterically unrestricted azines 1-3 yielded the matching azinium salts (as determined by 1 H and 13 CH NMR and high-resolution ESI-MS). Azines 4-9 with sterically hindered N atoms or an electron-withdrawing substituent, on the other hand, create stable co-crystals with XNPN in which two interacting molecules are bound by halogen bonding. XN structure-directed halogen bonds were identified in all co-crystals and theoretically analysed using DFT calculations (PBE0-D3/def2-TZVP level of theory), QTAIM analysis, molecule electrostatic potential surfaces, and noncovalent halogen bonds.

2.4 Deoxygenative Amination of Azine- *N*-oxides with Acyl Azides via [3 + 2] Cycloaddition

Dongeun Kim et al (2020) The reaction of azine-N-oxides with acyl azides is described as a transition-metal-free deoxygenative C-H amination process. The aminated azine derivative can be produced via a [3 + 2] dipolar cycloaddition of polar N-oxide fragments after the initial production of an isocyanate from the starting acyl azide via a Curtius rearrangement. The late-stage and sequential amination reactions of complex bioactive chemicals, such as quinidine and fasudil, demonstrate the method's usefulness. Furthermore, the relevance of this newly discovered approach is demonstrated by the direct transformation of aminated azines into different bioactive N-heterocycles.

2.5 Base-induced multi-state fluorescence of a trefoil-shaped salicylaldehyde azine derivative

Nariho Tanguchi et al (2021) Base-induced multi-state luminescence is observed in a trefoil-shaped salicylaldehyde azine derivative with numerous acidic protons. 1,3,5-triformylphloroglucinol was combined with 4-methoxysalicylaldehyde hydrazone to make the azine. The azine existed in solution at room temperature as an equilibrium mixture of two geometric isomers, according to 1H NMR spectroscopy. Using 1H NMR, UV-vis absorption, and emission spectroscopy, the three-step deprotonation (four-state change) of the azine in solution was confirmed.

CHAPTER-3

AIM AND SCOPE

3.1 AIM

- To synthesis an azine from hydrogen hydrate and 4-bis-(2-Chloroethylamino) benzaldehyde under basic conditions.

- To characterize the compounds using FT-IR, UV-Vis spectroscopy, ^{1}H NMR and Mass spectroscopy.

- To study the molecular structure of the compound using single crystal X-ray diffraction studies.

3.2 SCOPE

The detailed spectroscopic studies of the synthesized compounds were carried out. The detailed spectral assignments were made.

CHAPTER-4

MATERIALS AND METHODS

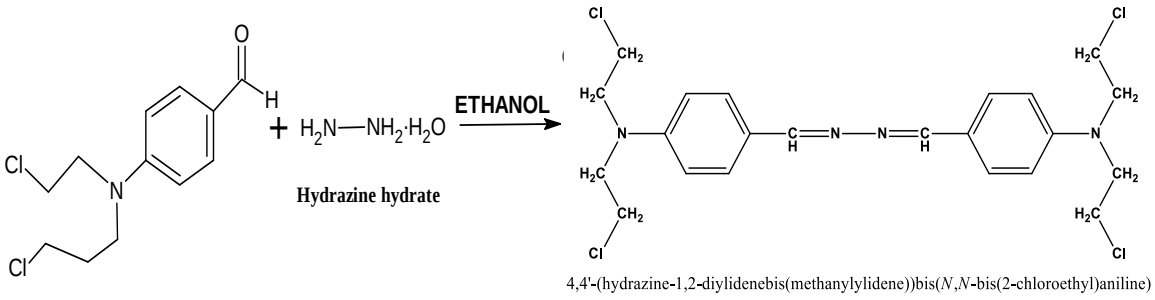
4.1 MATERIALS

In this chemical synthesis we are used hydrogen hydrate,4-bis-(2-Chloroethylamino) benzaldehyde, ethanol, triethyl amine these chemicals are used for further purification.

4.2 METHODS

EXPERIMENTAL SYNTHESIS

A mixture of hydrazine (0.06 ml) was added to 4-bis (2-chloro ethyl amino) benzaldehyde (0.049 g) was dissolved in 10 ml of ethanol in a 50 ml round bottomed flask.



4,4'-(hydrazine-1,2-diylidenebis(methanylylidene))bis(*N*,*N*-bis(2-chloroethyl)aniline)

To this mixture 5 ml of triethylamine was added drop wise to the mixture, the reaction mixture was monitored by TLC, the reaction was maintained in room temperature and the mixture is kept under magnetic stirrer for 4 hours and then filtered the sample by using whattmann filter paper then collect the product from the filter paper.

The obtained solid product was washed with triethyl acetate and used for further studies (UV-Vis spectroscopy, FTIR, SEM,^{1}H NMR).

4.3 CHARACTERISTIC TECHNIQUES

4.3.1 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared (FTIR) spectroscopy is a very efficient non-destructive characterization technique for surface characterization of nanoparticles' surfaces, providing a specific setup is connected to the spectrometer.

It is used to determine the functional groups. The chemical structure of the nanoparticles' surface and the surface reactive sites responsible for surface reactivity can be determined under particular conditions.

The structure and bands of the synthesised nanoparticles, FTIR may be used to test a variety of components, including bulk or thin films, liquids, solids, pastes, powders, fibres, and other materials. FTIR analysis may be used for quantitative (amount) analysis as well as qualitative (identification) analysis of materials where appropriate criteria are used. FTIR can test samples up to 11 mm in diameter and weigh in bulk or the top 1 mm of the sample.

The difficulty in FTIR characterization is mainly because of high degree of overlapping of the IR absorption bands which makes difficult for the attribution of certain functional groups, despite the fact that up-to-date computer-searchable databases are available.

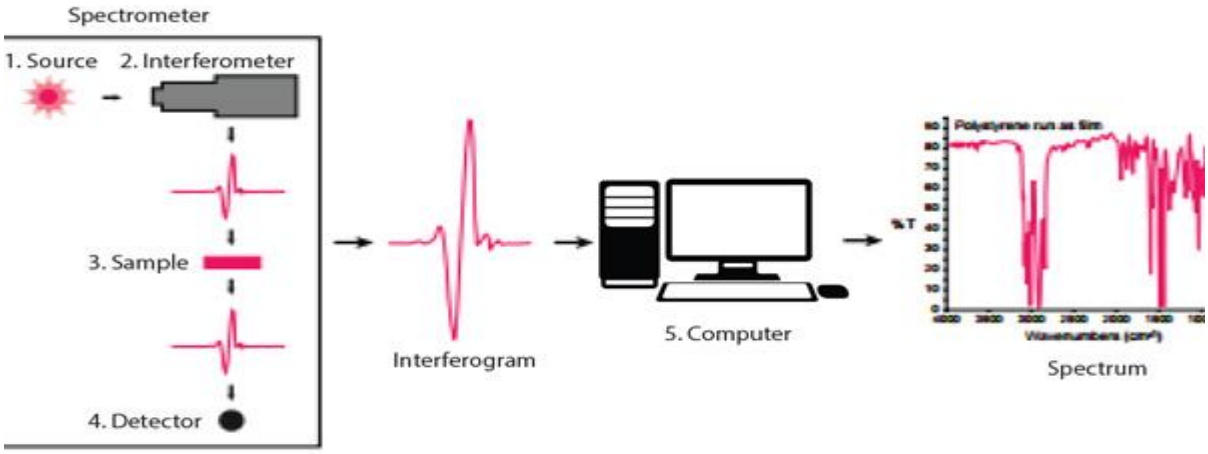


Fig 4.1: Schematic representation of FTIR

4.3.2 UV-VISIBLE SPECTROSCOPY

UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample.

Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions of electrons from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals.

The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. There are four possible types of transitions (π–π*, n–π*, σ–σ*, and n–σ*), and they can be ordered as follows :σ–σ* > n–σ* > π–π* > n–π*

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes or sample, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

- All diluted inorganic solutions are uv active
- Solutions of transition metal ions can be coloured (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another.
- The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue;

adding ammonia intensifies the colour and changes the wavelength of maximum absorption (λ_{max}).

- While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

The Beer–Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward–Fieser rules, for instance, are a set of empirical observations used to predict λ_{max}, the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample.

The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer–Lambert law:

where A = absorbance

I = intensity of the incident is the transmitted intensity,

L = the path length

c= concentration of absorbing species

ε = molar absorptivity coefficient.

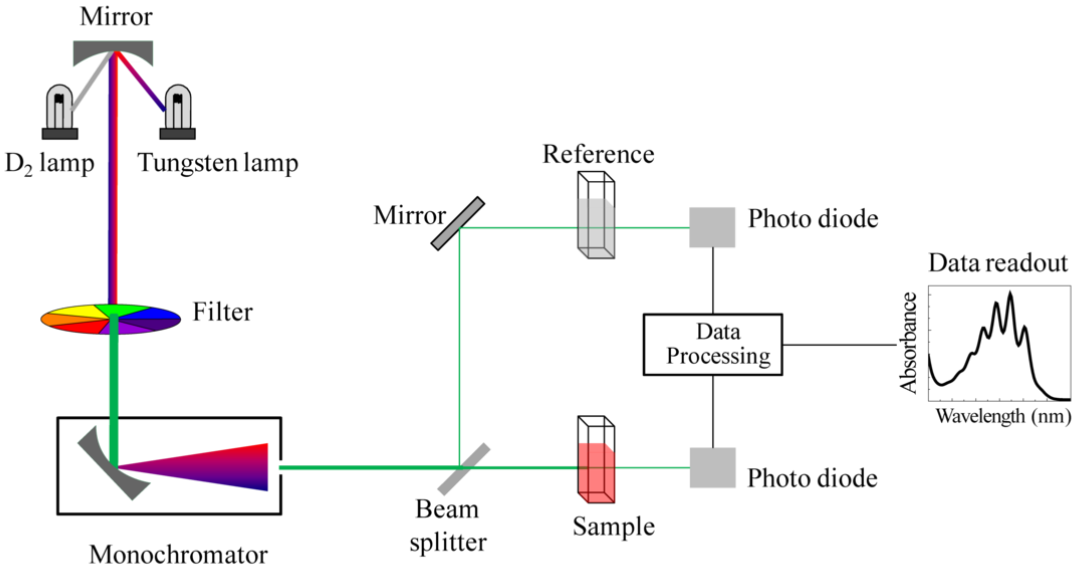


Fig 4.2: Schematic representation of UV-visible spectroscopy

4.3.3 ^{1}H NMR (PROTON NUCLEAR MAGNETIC RESONANCE)

It is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a substance, in order to determine the structure of its molecules[18].In samples where natural hydrogen (H) is used, practically all the hydrogen consists of the isotope ^{1}H (hydrogen-1; i.e. having a proton for a nucleus).

Simple NMR spectra are recorded in solution, and solvent protons must not be allowed to interfere. Deuterated (deuterium = ^{2}H, often symbolized as D) solvents especially for use in NMR are preferred, e.g. deuterated water, D_2O, deuterated acetone, $(CD_3)_2CO$, deuterated methanol, CD_3OD, deuterated dimethyl sulfoxide, $(CD_3)_2SO$, and deuterated chloroform, $CDCl_3$. However, a solvent without hydrogen, such as carbon tetrachloride, CCl_4 or carbon di sulfide, CS_2, may also be used.

Historically, deuterated solvents were supplied with a small amount (typically 0.1%) of tetra methyl silane (TMS) as an internal standard for calibrating the chemical shifts of each analyte proton. TMS is a tetrahedral molecule, with all protons being chemically equivalent, giving one single signal, used to define a chemical shift = 0 ppm. [2] It is volatile, making sample recovery easy as well.

Modern spectrometers are able to reference spectra based on the residual proton in the solvent (e.g., the $CHCl_3$, 0.01% in 99.99% $CDCl_3$). Deuterated solvents are now commonly supplied without TMS.

Deuterated solvents permit the use of deuterium frequency-field lock (also known as deuterium lock or field lock) to offset the effect of the natural drift of the NMR's magnetic field . In order to provide deuterium lock, the NMR constantly monitors the deuterium signal resonance frequency from the solvent and makes changes to the to keep the resonance frequency constant.[3] Additionally, the deuterium signal may be used to accurately define 0 ppm as the resonant frequency of the lock solvent and the difference between the lock solvent and 0 ppm (TMS) are well known.

Proton NMR spectra of most organic compounds are characterized by chemical shifts in the range +14 to -4 ppm and by spin-spin coupling between protons. The integration curve for each proton reflects the abundance of the individual protons.

Simple molecules have simple spectra. The spectrum of ethyl chloride consists of a triplet at 1.5 ppm and a quartet at 3.5 ppm in a 3:2 ratio. The spectrum of benzene consists of a single peak at 7.2 ppm due to the diamagnetic ring current.

4.3.3.1 Chemical Shifts

Chemical shift values, symbolized by **δ**, are not precise, but typical - they are to be therefore regarded mainly as a reference. Deviations are in ±0.2 ppm range, sometimes more. The exact value of chemical shift depends on molecular structure and the solvent, temperature, magnetic field in which the spectrum is being recorded and other neighbouring functional groups.

Hydrogen nuclei are sensitive to the hybridization of the atom to which the hydrogen atom is attached and to electronic effects. Nuclei tend to be deshielded by groups which withdraw electron density. Deshielded nuclei resonate at higher δ values, whereas shielded nuclei resonate at lower δ values.

Examples of electron withdrawing substituents are -OH, -OCOR, -OR, -NO_2 and halogens. These cause a downfield shift of approximately 2–4 ppm for H atoms on C_α and of less than 1–2 ppm for H atoms on C_β. C_α is

an aliphatic C atom directly bonded to the substituent in question, and C_β is an aliphatic C atom bonded to C_α. Carbonyl groups, olefinic fragments and aromatic rings contribute sp^2 hybridized carbon atoms to an aliphatic chain. This causes a downfield shift of 1–2 ppm at C_α.

FUNCTIONAL GROUP	CH3	CH2	CH
CH_2R	0.8	1.3	1.6
C=C	1.6	2.0	2.6
C≡C	1.7	2.2	2.8
C_6H_5	2.3	2.6	2.9
F	4.3	4.4	4.8
Cl	3.0	3.4	4.0
Br	2.7	3.4	4.1
I	2.2	3.2	4.2
OH	3.3	3.5	3.8
OR	3.3	3.4	3.7
OC_6H_5	3.8	4.0	4.3
OCOR	3.6	4.1	5.0
$OCOC_6H_5$	3.9	4.2	5.1
$OCOCF_3$	4.0	4.4	—
CHO	2.2	2.4	2.5
COR	2.1	2.2	2.6
COOH	2.1	2.3	2.6
COOR	2.0	2.3	2.5
$CONR_2$	2.0	2.1	2.4
CN	2.1	2.5	3.0
NH_2	2.5	2.7	3.0
NR_2	2.2	2.4	2.8
NRC_6H_5	2.6	3.0	3.6

4.3.3.2 Signal Intensity

The integrated intensities of NMR signals are, ideally, proportional to the ratio of the nuclei within the molecule [19]. Together with chemical shift and coupling

constants, the integrated intensities allow structural assignments. For mixtures, the signal intensities can be used to determine molar ratios. These considerations are valid only when sufficient time is allowed for full relaxation of the affected signals, as determined by their T_1 values. A further complication arises from the difficulty of integrating signals of very different line shapes

4.3.3.3 Spin-Spin Couplings

In addition to chemical shift, NMR spectra allow structural assignments by virtue of spin-spin coupling (and integrated intensities). Because nuclei themselves possess a small magnetic field, they influence each other, changing the energy and hence frequency of nearby nuclei as they resonate—this is known as spin-spin coupling. The most important type in basic NMR is *scalar coupling*. This interaction between two nuclei occurs through chemical bonds, and can typically be seen up to three bonds away (3-J coupling), although it can occasionally be visible over four to five bonds, though these tend to be considerably weaker.

The effect of scalar coupling can be understood by examination of a proton which has a signal at 1 ppm. This proton is in a hypothetical molecule where three bonds away exists another proton (in a CH-CH group for instance), the neighbouring group (a magnetic field) causes the signal at 1 ppm to split into two, with one peak being a few hertz higher than 1 ppm and the other peak being the same number of hertz lower than 1 ppm. These peaks each have half the area of the former **singlet** peak. The magnitude of this splitting (difference in frequency between peaks) is known as the coupling constant. A typical coupling constant value for aliphatic protons would be 7 Hz.

The coupling constant is independent of magnetic field strength because it is caused by the magnetic field of another nucleus, not the spectrometer magnet. Therefore, it is quoted in hertz (frequency) and not ppm (chemical shift).

In another molecule a proton resonates at 2.5 ppm and that proton would also be split into two by the proton at 1 ppm. Because the magnitude of interaction is the same the splitting would have the same coupling constant 7 Hz apart. The spectrum would have two signals, each being a **doublet**. Each doublet will have the same area because both doublets are produced by one proton each.

This can be extended to any CH_n group. When the CH_2-CH group is changed to CH_3-CH_2, keeping the chemical shift and coupling constants identical, the following changes are observed:

- The relative areas between the CH_3 and CH_2 subunits will be 3:2.
- The CH_3 is coupled to two protons into a 1:2:1 triplet around 1 ppm.
- The CH_2 is coupled to *three* protons

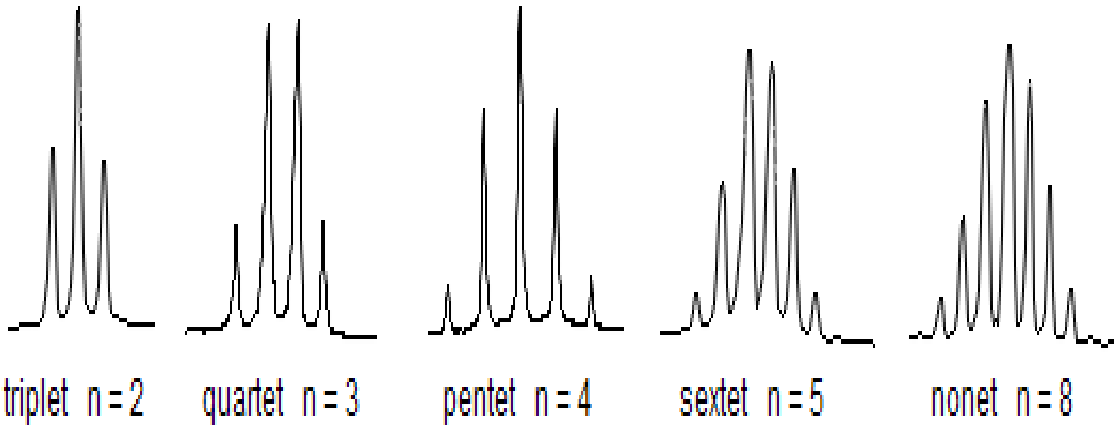
Something split by three identical protons takes a shape known as a quartet, each peak having relative intensities of 1:3:3:1.

A peak is split by *n* identical protons into components whose sizes are in the ratio of the *n*th row of **Pascal's triangle:**

n	**Name**	**Row**
0	Singlet	1
1	Doublet	1 1
2	Triplet	1 2 1
3	Quartet	1 3 3 1
4	Quintet	1 4 6 4 1
5	Sextet	1 5 10 10 5 1
s6	Septet	1 6 15 20 15 6 1
7	Octet	1 7 21 35 35 21 7 1
8	Nonet	1 8 28 56 70 56 28 8 1

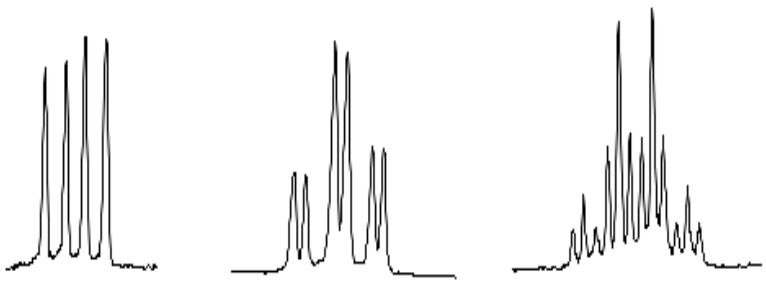
Because the *n*th row has *n*+1 components, this type of splitting is said to follow the "*n*+1 rule": a proton with *n* neighbours appears as a cluster of *n*+1 peaks.

With 2-methylpropane, $(CH_3)_3CH$, as another example: the CH proton is attached to three identical methyl groups containing a total of 9 identical protons. The C-H signal in the spectrum would be split into ten peaks according to the (n + 1) rule of multiplicity. Below are NMR signals corresponding to several simple multiplets of this type.



When a proton is coupled to two different protons, then the coupling constants are likely to be different, and instead of a triplet, a doublet of doublets will be seen. Similarly, if a proton is coupled to two other protons of one type, and a third of another type with a different, smaller coupling constant, then a triplet of doublets is seen. In the example below, the triplet coupling constant is larger than the doublet one.

By convention the pattern created by the largest coupling constant is indicated first and the splitting patterns of smaller constants are named in turn. In the case below it would be erroneous to refer to the quartet of triplets as a triplet of quartets.



Doublet of doublets Triplet of doublets Quartet of triplets

NMR SPECTROSCOPY BY ISOTOPES

- **^{1}H**
- **^{2}H**
- **^{3}He**
- **^{11}B**
- **^{13}C**
- **^{15}N**
- **^{17}O**
- **^{19}F**
- **^{29}Si**
- **^{31}P**
- **^{51}V**
- **^{57}Fe**
- **^{59}Co**
- **^{77}Se**
- **^{195}Pt**
- **^{199}Hg**
- **^{207}Pb**

4.3.4 MASS SPECTROMETRY

Mass spectrometry (MS) is an analytical technique that is used to measure the mass-to-charge ratio of ions. The results are presented as a mass spectrum, a plot of intensity as a function of the mass-to-charge ratio. Mass spectrometry is used in many different fields and is applied to pure samples as well as complex mixtures.

A mass spectrum is a type of plot of the ion signal as a function of the mass-to-charge ratio. These spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to elucidate the chemical identity or structure of molecules and other chemical compounds.

In a typical MS procedure, a sample, which may be solid, liquid, or gaseous, is ionized, for example by bombarding it with a beam of electrons. This may cause some of the sample's molecules to break up into positively charged fragments or simply become positively charged without fragmenting.

These ions (fragments) are then separated according to their mass-to-charge ratio, for example by accelerating them and subjecting them to an electric or magnetic field: ions of the same mass-to-charge ratio will undergo the same amount of deflection [20]. The ions are detected by a mechanism capable of detecting charged particles, such as an electron multiplier. Results are displayed as spectra of the signal intensity of detected ions as a function of the mass-to-charge ratio. The atoms or molecules in the sample can be identified by correlating known masses (e.g., an entire molecule) to the identified masses or through a characteristic fragmentation pattern

4.3.4.1 PARTS OF MASS SPECTROMETRY

A mass spectrometer consists of three components: an ion source, a mass analyser, and a detector. The ionizer converts a portion of the sample into ions. There is a wide variety of ionization techniques, depending on the phase (solid, liquid, gas) of the sample and the efficiency of various ionization mechanisms for the unknown species.

An extraction system removes ions from the sample, which are then targeted through the mass analyser and into the detector. The differences in masses of the fragments allows the mass analyser to sort the ions by their mass-to-charge ratio. The detector measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present. Some detectors also give spatial information, e.g., a multichannel plate

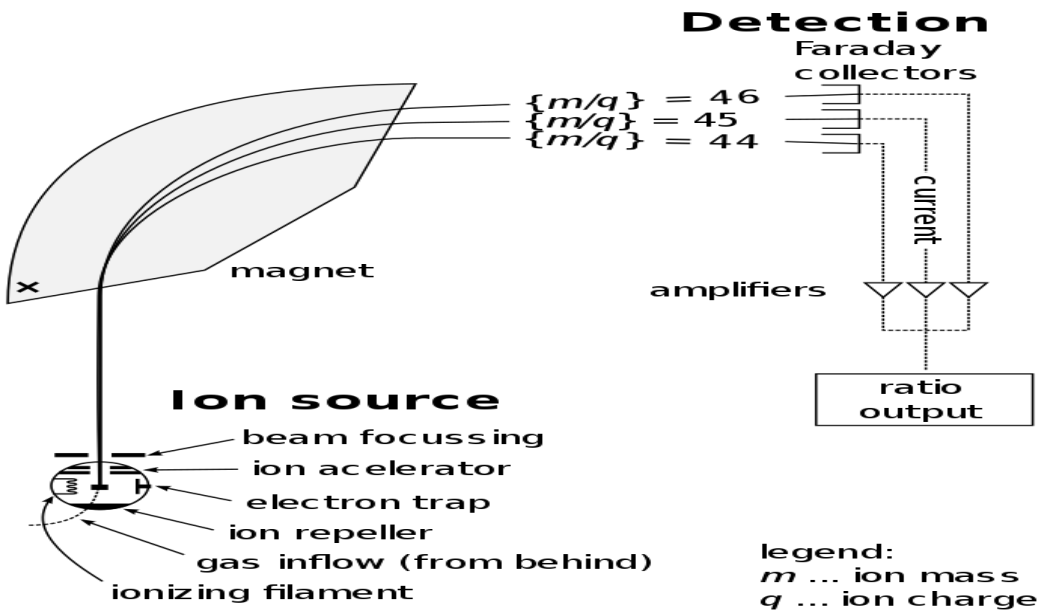


Fig 4.3: Parts of mass spectrometry

4.3.5 DATA AND ANALYSIS

4.3.5.1 DATA REPRESENTATION

Mass spectrometry produces various types of data. The most common data representation is the mass spectrum.

Certain types of mass spectrometry data are best represented as a mass chromatogram. Types of chromatograms include selected ion monitoring (SIM), total ion current (TIC), and selected reaction monitoring (SRM), among many others.

Other types of mass spectrometry data are well represented as a three-dimensional contour map. In this form, the mass-to-charge, *m/z* is on the *x*-axis, intensity the *y*-axis, and an additional experimental parameter, such as time, is recorded on the *z*-axis.

4.3.5.2 DATA ANALYSIS

Mass spectrometry data analysis is specific to the type of experiment producing the data. General subdivisions of data are fundamental to understanding any data.

Many mass spectrometers work in either negative ion mode or positive ion mode. It is very important to know whether the observed ions are negatively or positively

charged. This is often important in determining the neutral mass but it also indicates something about the nature of the molecules.

Different types of ion source result in different arrays of fragments produced from the original molecules. An electron ionization source produces many fragments and mostly single-charged (1-) radicals (odd number of electrons), whereas an electrospray source usually produces non-radical quasimolecular ions that are frequently multiply charged. Tandem mass spectrometry purposely produces fragment ions post-source and can drastically change the sort of data achieved by an experiment.

Knowledge of the origin of a sample can provide insight into the component molecules of the sample and their fragmentations. A sample from a synthesis/manufacturing process will probably contain impurities chemically related to the target component. A crudely prepared biological sample will probably contain a certain amount of salt, which may form adducts with the analyte molecules in certain analyses.

Results can also depend heavily on sample preparation and how it was run/introduced. An important example is the issue of which matrix is used for MALDI spotting, since much of the energetics of the desorption/ionization event is controlled by the matrix rather than the laser power. Sometimes samples are spiked with sodium or another ion-carrying species to produce adducts rather than a protonated species.

Mass spectrometry can measure molar mass, molecular structure, and sample purity. Each of these questions requires a different experimental procedure; therefore, adequate definition of the experimental goal is a prerequisite for collecting the proper data and successfully interpreting it.

4.3.5.3 INTERPRETATION OF MASS SPECTRA

The precise structure or peptide sequence of a molecule is deciphered through the set of fragment masses, the interpretation of mass spectra requires combined use of various techniques. Usually, the first strategy for identifying an unknown compound is to compare its experimental mass spectrum against a library of mass

spectra. If no matches result from the search, then manual interpretation] or software assisted interpretation of mass spectra must be performed.

Computer simulation of ionization and fragmentation processes occurring in mass spectrometer is the primary tool for assigning structure or peptide sequence to a molecule. An a priori structural information is fragmented in silico and the resulting pattern is compared with observed spectrum. Such simulation is often supported by a fragmentation library[44] that contains published patterns of known decomposition reactions. Software taking advantage of this idea has been developed for both small molecules and proteins.

Analysis of mass spectra can also be spectra with accurate mass. A mass-to-charge ratio value (m/z) with only integer precision can represent an immense number of theoretically possible ion structures; however, more precise mass figures significantly reduce the number of candidate molecular formulas. A computer algorithm called formula generator calculates all molecular formulas that theoretically fit a given mass with specified tolerance.

A recent technique for structure elucidation in mass spectrometry, called precursor ion fingerprinting, identifies individual pieces of structural information by conducting a search of the tandem spectra of the molecule under investigation against a library of the product-ion spectra of structurally characterized precursor ions.

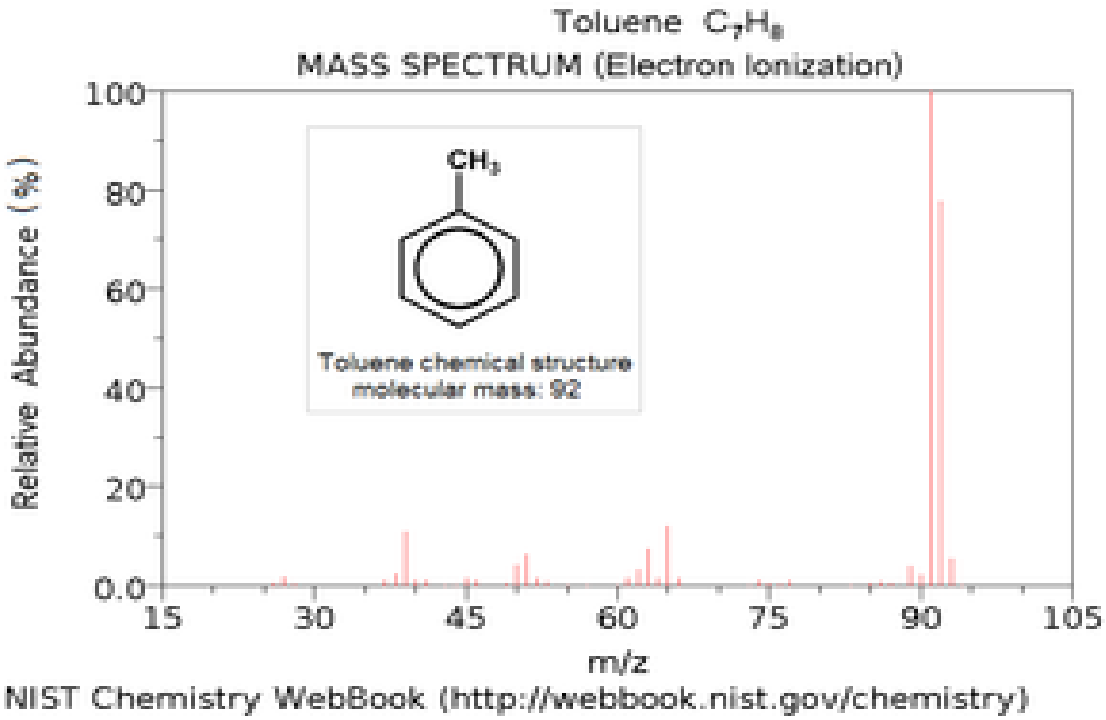


Fig 4.4: Mass spectrum

4.3.5.4 APPLICATIONS

Mass spectrometry has both qualitative and quantitative uses. These include identifying unknown compounds, determining the isotopic composition of elements in a molecule, and determining the structure of a compound by observing its fragmentation. Other uses include quantifying the amount of a compound in a sample or studying the fundamentals of gas phase ion chemistry (the chemistry of ions and neutrals in a vacuum). MS is now commonly used in analytical laboratories that study physical, chemical, or biological properties of a great variety of compounds.

As an analytical technique it possesses distinct advantages such as: Increased sensitivity over most other analytical techniques because the analyser, as a mass-charge filter, reduces background interference, Excellent specificity from characteristic fragmentation patterns to identify unknowns or confirm the presence of suspected compounds, Information about molecular weight, Information about the isotopic abundance of elements, temporally resolved chemical data.

A few of the disadvantages of the method is that it often fails to distinguish between optical and geometrical isomers and the positions of substituent in o-, m- and p-

positions in an aromatic ring. Also, its scope is limited in identifying hydrocarbons that produce similar fragmented ions.

4.3.5.5 ISOTOPE RATIO OF MASS SPECTROMETRY

Mass spectrometry is also used to determine the isotopic composition of elements within a sample. Differences in mass among isotopes of an element are very small, and the less abundant isotopes of an element are typically very rare, so a very sensitive instrument is required.

These instruments, sometimes referred to as isotope ratio mass spectrometers (IR-MS), usually use a single magnet to bend a beam of ionized particles towards a series of Faraday cups which convert particle impacts to electric current. A fast on-line analysis of deuterium content of water can be done using flowing afterglow mass spectrometry, FA-MS.

Probably the most sensitive and accurate mass spectrometer for this purpose is the accelerator mass spectrometer (AMS).

CHAPETR-5

RESULTS AND DISCUSSION

Structural composition, mass of the synthesized compound, types of protons present and functional group analysis of the given nanocomposite have been confirmed by characteristic techniques like, UV-Vis spectroscopy, mass spectrometry,^{1}H NMR, FTIR.

5.1 UV-Vis SPECTROSCOPY

Ultraviolet-visible (UV-Vis) spectroscopy is a widely used technique in many areas of science ranging from bacterial culturing, drug identification and nucleic acid purity checks and quantitation, to quality control in the beverage industry and chemical research.

It is a quantitative technique used to measure how much a chemical substance absorbs light. This is done by measuring the intensity of light that passes through a sample with respect to the intensity of light through a reference sample or blank.

This spectroscopy technique is also used to determine the absorption of the given polymer under neutral condition.

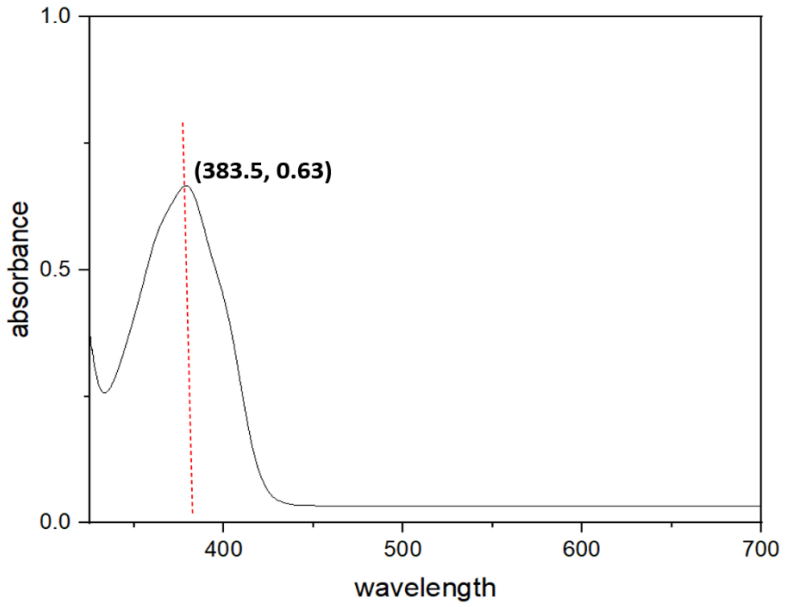


Fig 5.1: Spectrum of UV

S.NO	WAVELENGTH	ABSORBANCE
1	422.5	0.077
2	422	0.081
3	421.5	0.085
4	420.5	0.093
5	419.5	0.103
6	419	0.108
7	418.5	0.114
8	418	0.121
9	417.5	0.127
10	417	0.134
11	416	0.148
12	415.5	0.156
13	415	0.164
14	414.5	0.173
15	414	0.181
16	413.5	0.191
17	413	0.201
18	412.5	0.21
19	412	0.219
20	411.5	0.229

Table 5.1 Spectral data of UV

5.2 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

This spectroscopic technique is used to determine the functional groups present in the compound at different frequency levels.

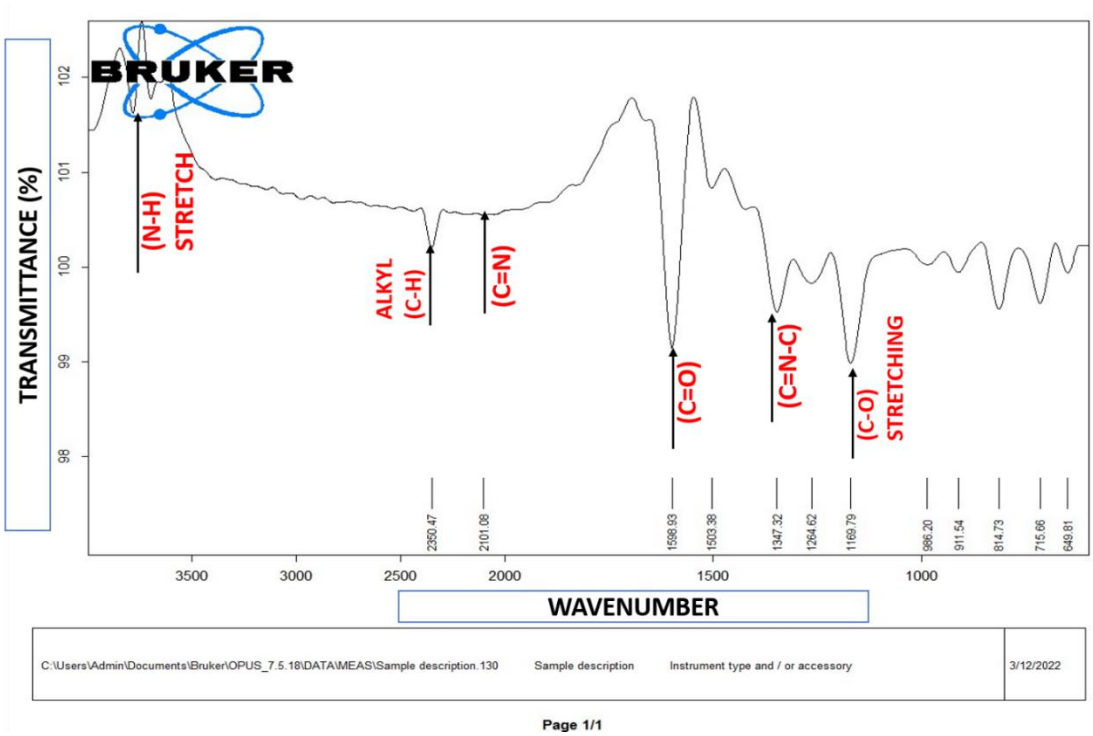


Fig 5.2: FTIR Analysis Of Azine

S.NO	FUNCTIONAL GROUP	WAVENUMBER (CM^{-1})
1	N-H	3680
2	C-H	2350.47
3	C=N	2101.08
4	C=O	1568.93
5	C=N-C	1347.32
6	C-O	1169.79

Table 5.2 Spectral data of FTIR

The above data given the result of different functional observed at different wavenumbers i.e., the functional group (N-H) is observed at 3680 $cm^{-1,\ then}$ alky (C-H) was observed at 2350.47 $cm^{-1,\ after}$ this (C=N) was observed at 2101.08 $cm^{-1,\ then}$ (C=O) peak was observed at 1568.93 $cm^{-1,}$ after this (C=N-C) functional group was found at 1347.32 and finally (C-O) frequency was observed at 1169.79 cm^{-1}.

5.3 ^{1}H NMR

This technique is used to determine the type of protons present in the compound, this technique applicable only when the compound having hydrogen atoms as proton.

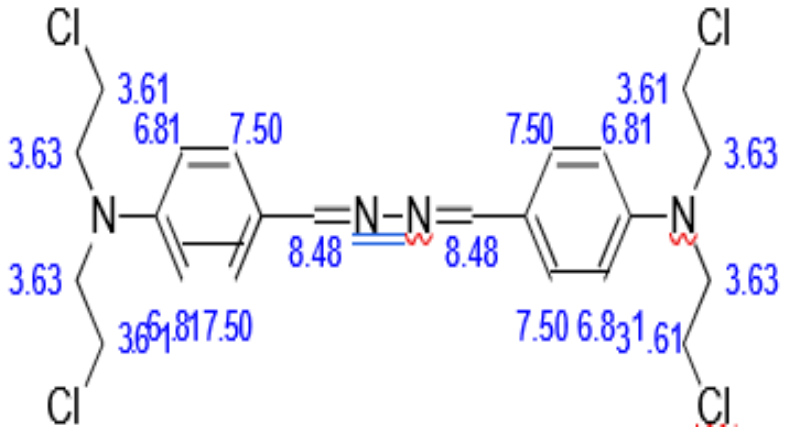


Fig 5.3: Structural analysis of NMR

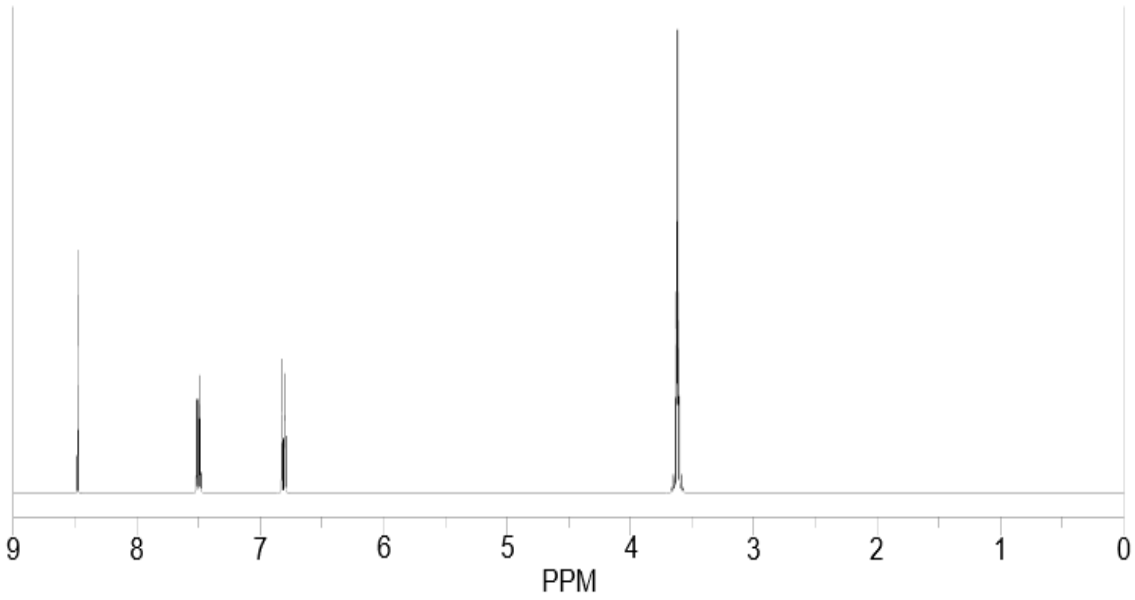


Fig 5.4: Spectral data of NMR

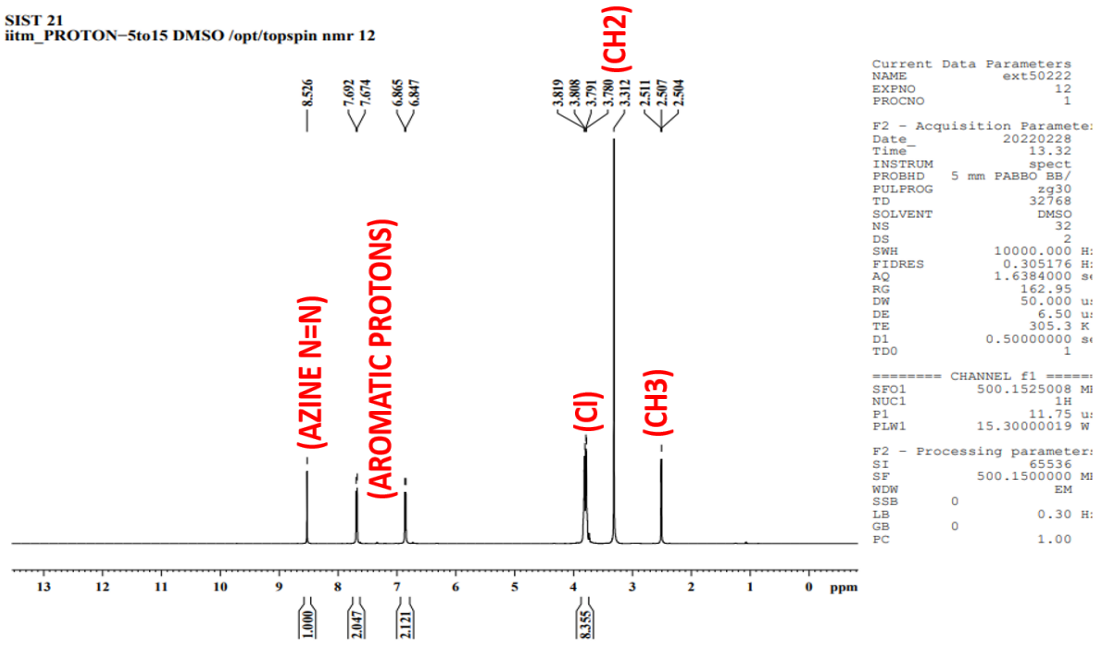


Fig 5.5:Spectrum of ^{1}H NMR

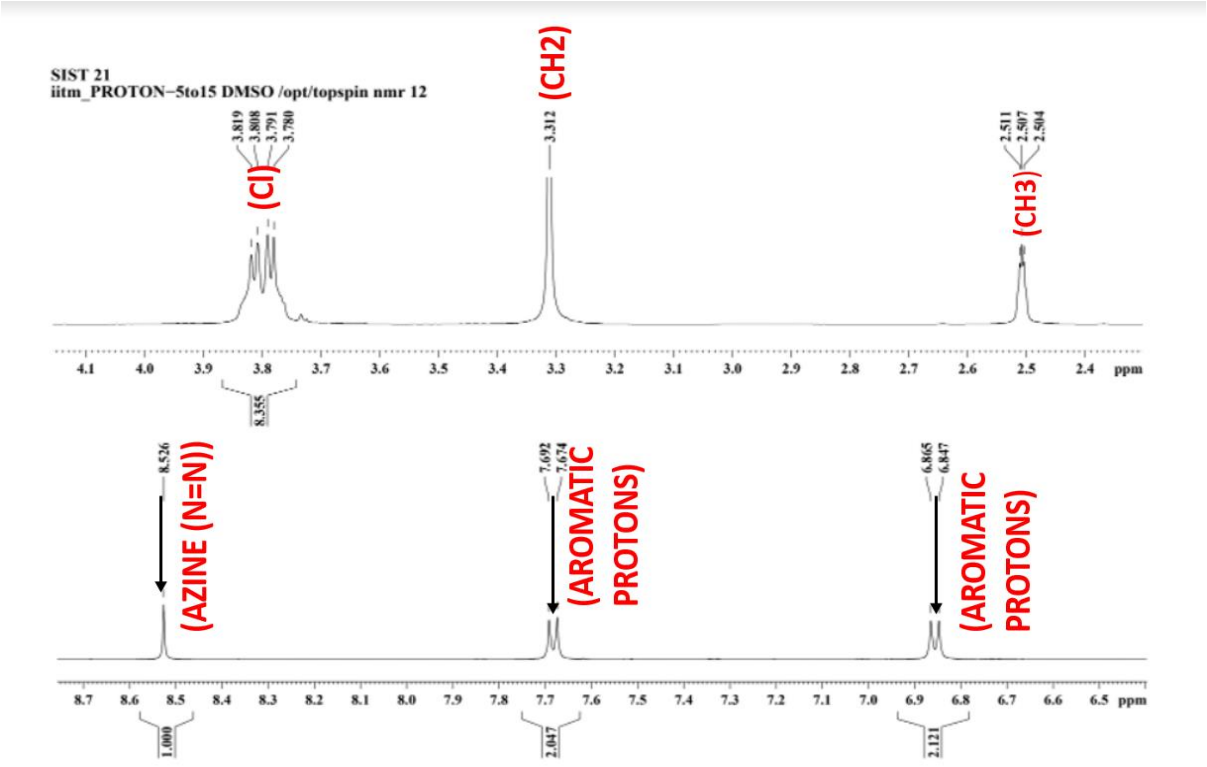


Fig 5.6:Spectrum of ^{1}H NMR

S.NO	TYPE OF PROTONS	CHEMICAL SHIFT
1	AZINE (N=N)	8.526
2	AROMATIC PROTONS	7.692
		7.674
3	Cl	3.819
		3.808
		3.791
		3.780
4	CH2	3.312
5	CH3	2.511
		2.507
		2.504

Table 5.3 Spectral data of ^{1}H NMR

5.4 MASS SPECTROMETRY

This technique is used to determine the different molecular ion peaks with different molecular weights.

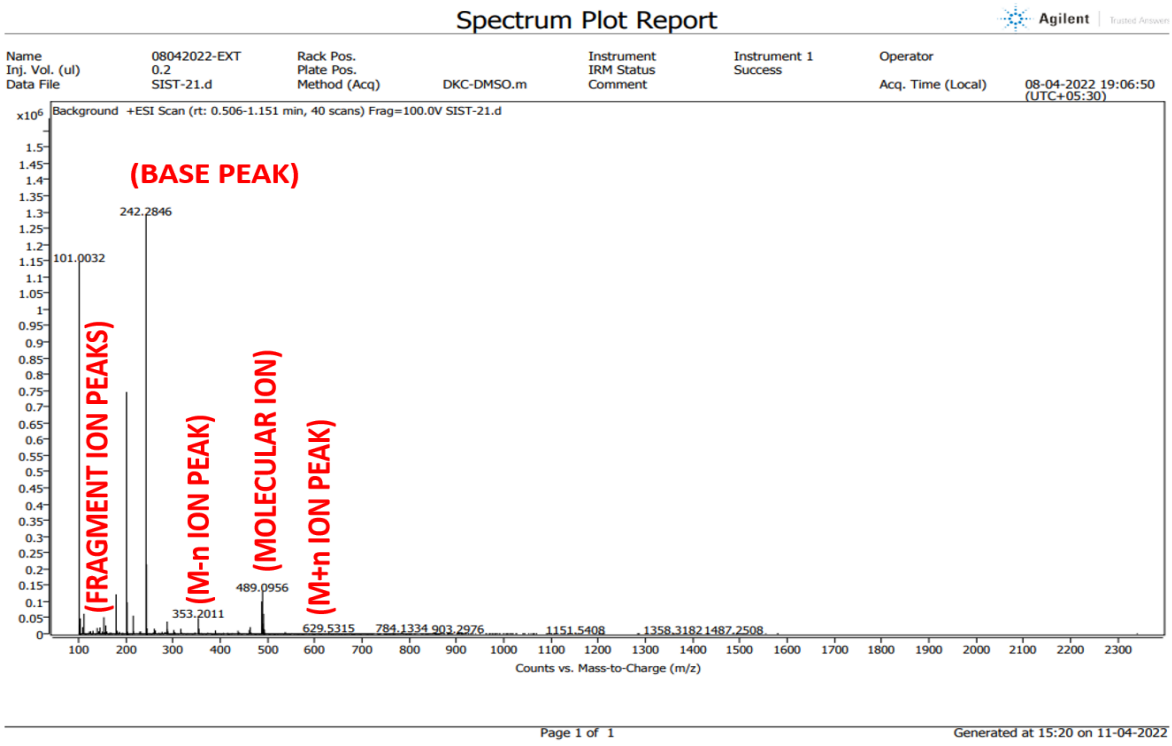


Fig 5.7: Spectrum of mass

S.NO	TYPE OF PEAK	MASS TO CHARGE (M/Z)
1	Fragment ion	101.0032
2	Base peak	242.2846
3	M-n ion peak	353.2011
4	Molecular ion	489.0956
5	M+n ion peak	629.5315

Table 5.4 Spectral data of mass

The above data gives the brief information about founded organic compound, from this data we come to know that fragment ion observed at 101.0032 then base peak we observed at 242.2846 after this M-n ion peak observed at 353.2011 then molecular ion peak observed at 489.0956 and finally M+n ion peak observed at 629.5315 mass to charge ratio.

CHAPTER 6

CONCLUSION

In the present study, azines derivatives were synthesized by reacting hydrazine hydrate with 4- bis-(2-chloroethylamine)benzaldehyde under basic condition and characterized by spectroscopy techniques. Vibrational properties were studied by FTIR. Analysis of functional groups present in 1,2-diylidenebis(methanylydene)bis(N,N-bis(2-chloroethyl)anline). Molecular weight of sample was studied by mass spectroscopy.

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