SYNTHESIS AND CHARACTERISATION OF 1,2-BIS (3,4-DIMETHOXY BENZYLIDENE) HYDRAZINE

Submitted in partial fulfilment of the requirements for the award of

Master of Science in Chemistry

by

SIVATHARSINI R

(REGISTER NO: 40910011)

DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC I 12B Status by UGC I Approved by AICTE

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MAY - 2022

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DEPARTMENT OF CHEMISTRY

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of Ms. **SIVATHARSINI R (40910011)** who carried out the project entitled "**SYNTHESIS AND CHARACTERISATION OF 1,2-BIS (3,4-DIMETHOXY BENZYLIDENE) HYDRAZINE"** under my / our supervision.

Internal Guide

(Dr. J. KARTHIKEYAN)

Head of the Department (Name in Capital with Seal & Signature)

Submitted for Viva voce Examination held on_____

Internal Examiner **External Examiner**

DECLARATION

I Ms. SIVATHARSINI.R student of Sathyabama Institute of Science and Technology hereby declare that the Project Report entitled **"Synthesis and Characterization Of 1,2-Bis (3,4 –Dimethoxy Benzylidene) Hydrazine**" done by me under the guidance of Dr. J. Karthikeyan, M.Sc., Ph.D. at Sathyabama Institute of Science and Technology, Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai-600 119 is submitted in partial fulfilment of the requirements for the award of Master of Science degree in Chemistry.

DATE: **(SIVATHARSINI R)**

PLACE: **SIGNATURE OF THE CANDIDATATE**

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SIVATHARSINI R

ABSTRACT

1,2 bis (3,4-dimethoxy benzylidene) hydrazine is synthesized by condensation method. The compound is obtained by condensation of hydrazine with aldehyde. The compound comes under the category of azine where the water molecules is removed from hydrazine and aldehyde and form a N-N linkage. The compound is then characterized by different spectroscopy studies such as NMR, UV, IR, Mass spectroscopy. These spectroscopical studies confirm the compound is 1,2 bis (3,4-dimethoxy benzylidene) hydrazine.

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LIST OF ABBRIVATION

FTIR	- Fourier transform infrared spectroscopy
UV-V	- Ultraviolet Visible spectroscopy
NMR	- Nuclear magnetic resonance spectroscopy

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INTRODUCTION

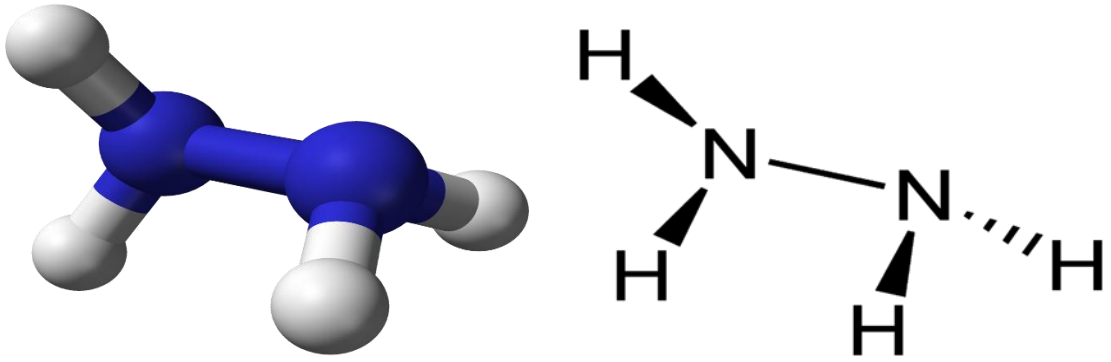
1.1 AZINE:

Azine are organic molecules which has the functional units of C═N-N═C which are 2,3 diaza analogues of 1,3 butadiene and it is also referred to N-N linked diimines. The first azine compound dimethylketazine is synthesized by Curtius and Thun in1891 by reaction with two molecules of acetone with hydrazine. The compound is synthesized by the condensation of hydrazine with aldehyde or ketones. The azine obtained with the synthesis of aldehyde with hydrazine are called as aldazines whereas the synthesis of ketone with hydrazine are called as ketazines. Azine are further classified as symmetrical and unsymmetrical azine. A good number of symmetrical and unsymmetrical having large contributed to the development of coordination chemistry acting as a chelating agent having the design of new molecular material with physical properties. The two imines bonds that make up the azine moiety can be considered as polar acceptor groups oriented in opposite directions because these two imines are joined by N-N bond. The presence of an azine bridge between two conjugated system prevents the delocalization of electron occurring between the two system. Azine are called as conjugation stoppers. Azine are good in heterocyclic synthesis. Mostly, azine receive more attention having to their potential bond formation reaction. Azine compound with various heterocyclic and aromatic substituents are photochromic which means the reversible transformation of a chemical species between two forms by the absorption of electromagnetic radiation. These azine compound of photochromic are widely used to make dosimeters of ultraviolet radiation, screen to protect eye and the optical devices. The unsymmetrical azines have antibacterial properties and some unsymmetrical azines are used as organic luminophores. Although the symmetrical azines system are readily synthesized by the reaction of hydrazine with an excess of an aldehyde or ketones. But the challenge part in this is the preparation of their unsymmetrical counterpart. There are two different techniques for the preparation azine. One is done by two step process which involves the first preparation of hydrazone by condensation of hydrazine with aldehyde and then it followed by

reacting the resultant hydrazone with another aldehyde derivative. Another technique is one step process by direct condensation of hydrazine with aldehyde derivate and then with ethanol solution. In this there is no intermediate of hydrazone. . The method gives a good yield at room temperature itself. The different substituted azine were yield when the aromatic aldehyde is substituted with different substituent. In the substituted azine the yield is found to be best due to one aldehyde which is electron withdrawing group and another aldehyde group is electron donating group. This reaction is carried out under solvent -free conditions and in the absence of catalyst for the good yield of azines. This reaction is environmentally friendly because there is no undesirable by products. Azine are useful for isolation, purification and characterization of carbonyl compounds. There are a number of advantages to using azines for derivatization or protection: (1) cost-effectiveness due to the low cost of only one-half of a protective group, (2) ease of isolation products with high melting points resulting from a symmetrical structure (3) easy identification of the fully conjugated and recombinant products.

HYDRAZINE:

N_2H_4 is an inorganic compound with synthetic name Hydrazine. Hydrazine is likewise called as Diamine or Diazane or Nitrogen hydride. It is strong base. It is an azane and unstable. Every subunit of H_2N-N is pyramidal and the N−N bond distance is around 1.45 Å. Diamine in its anhydrous structure, is a colorless, fuming oily liquid with smell of ammonia. It has a flash point of 99°F. On the off chance that assuming hints of air is available during the course of refining, it detonates. It is poisonous and destructive to tissues. At the point when it goes through burning, it produces poisonous oxides of nitrogen. Hydrazine is a highly poisonous and potentially unstable substance. There is little amount of ammonia because it is made up of two ammonia molecules (with H_2 loss) that are bound together. Its composition somewhat resembles the distorted hydrogen peroxide composition.



Synthesis of hydrazine:

Hydrazine was first isolated from organic compounds in 1887. The preparation is done by Raschig process. The process involves the oxidation of ammonia with sodium hypochlorite in the presence of gelatin.

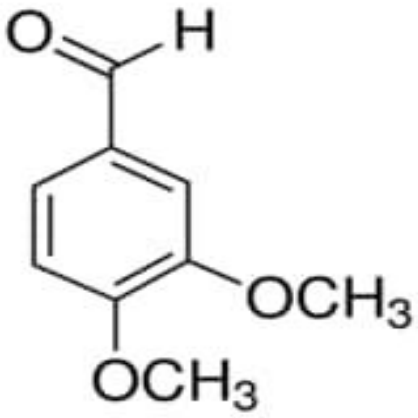
Hydrazine can also be prepared from reaction of ammonia with hydrogen peroxide in the presence of a ketone catalyst. The process is called as peroxide process. In this process the imine is first produced by condensation of ketone and ammonia, which is then oxidized by hydrogen peroxide in order to produce oxaziridine.

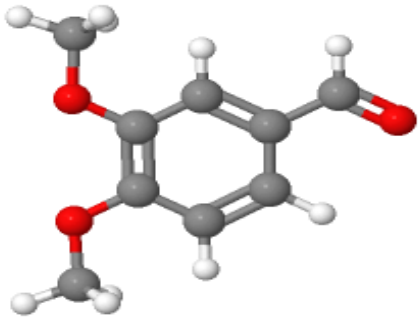
Hydrazine is used as pharmaceuticals and pesticides. Hydrazine is majorly used as a blowing agent. It is used as component of rocket fuel in World War II. It also used as precursor to polymerization catalyst.

3,4 dimethoxy benzaldehyde:

3,4 dimethoxy benzaldehyde is also known as veratraldehyde. It is an organic compound which is widely used as a flavouring and odorant. The compound is structurally related to benzaldehyde. In 3,4 dimethoxybenzaldehyde one of the methoxy C atoms deviated from the plane of the aromatic ring by 0.337Å. Crystallisation was hindered by oiling out in various solvents. The crystal contains neither hydrogen nor aromatic π-π stacking. The veratraldehyde is commercially available because it has pleasant woody fragrance. It is derivative of vanillin, from which it is prepared by methylation. It is white to brown or blue-gray needle crystal

(crystallization in ether); sweet woody fragrance, fragrant grass aroma and strong flavours of vanilla blue; oxidized into odourless 3,4-dimethoxybenzoic acid (veratric acid) in the air; Melting point 43~45℃; Insoluble in cold water; soluble in hot water, ethanol and oil.





Synthesis and crystallization of 3,4 dimethoxy benzaldehyde:

Commercial 3,4-dimethoxybenzaldehyde (close to 100% unadulterated, Aldrich) was utilized for the precious crystallization. A crystal of the commercial powder was added to an aqueous saturated solution of 3,4-dimethoxybenzaldehyde at room temperature. Hence, the temperature was cycled somewhere in the range of 298 and 303 K. Following fourteen days colorless needles were grown, appropriate for single-gem X-ray diffraction.

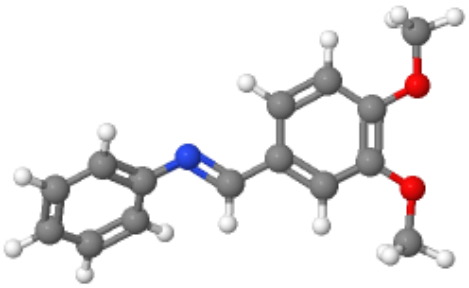
Uses of 3,4 dimethoxy benzaldehyde:

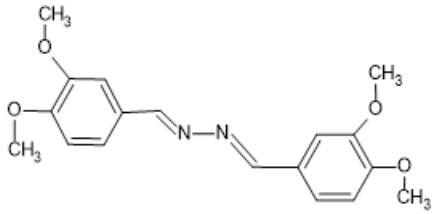
Veratraldehyde was used in the preparation of 4-chloromethyl-2-(dimethoxyphenyl)-1,3-dioxolane. It was used in the synthesis of (+)-lithospheric acid, having anti-HIV activity. It forms 1:1 inclusion complex with cyclodextrins. It reacts with 3-acetyl-2,5-dimethythiophene to yield chalcone dye, (2E)-3-(3,4-Dimethoxyphenyl)-1-(2,5-dimethylthiophen-3-yl) prop-2-en-1-one.

3,4 dimethoxy benzylidene:

The 3,4 dimethoxy benzylidene which comes under the imines The reaction of aliphatic or aromatic primary amines with aldehydes or ketones produces imine compounds (also referred to as Schiff bases). They're aldehyde nitrogen analogues.

A ketone in which the carbonyl group (CO) has been replaced with a hydrogen atom an imine group Schiff bases are a popular type of organic compound that has a wide range of applications. biological, inorganic, and analytical chemistry are just a few examples of the many applications. The basic units are among them. They are used as liquid crystals and in certain dyes. Bases Schiff appear to be important intermediates in a number of enzymatic reactions involving an enzyme's interaction with a substrate's amino or carbonyl group.





1,2-bis(3,4-dimethoxybenzylidene)hydrazine

CHAPTER-2

LITRATURE SURVEY

2.1 Highly Efficient Practical Procedure for the Synthesis of Azine Derivatives Under Solvent-Free Conditions

J. Safari & S. Gandomi-Ravandi et al (2011) It was developed a broad and practical method for the synthesis of azines of aromatic aldehydes and ketones in high yields. To obtain good yields of the required azines, this reaction is carried out without the use of solvents and without the use of a catalyst. The reaction is also environmentally beneficial, as it produces no unwanted by-products, and it outperforms previously described processes. The typical processes were used to classify the products (infrared, 1H NMR, and 13C NMR).

2.2 Rapid, Chemo selective and Facile Synthesis of Azines by Hydrazine/I_2

H.M. Nanjundaswamy & M. A. Pasha et al (2007), We describe a reaction of hydrazine hydrate with carbonyl compounds at 0–10°C in the presence of molecular iodine that gives symmetrical azines in excellent yields in 1–4 minutes with no adverse effects on other substituents. The reactions are fast and chemo selective, with high purity products and great yields. The workup is non-hazardous to the environment and does not require solvent extraction

2.3 An Azine-Linked Covalent Organic Framework: Synthesis, Characterization and Efficient Gas Storage

Yongefeng Zhi et al (2015) For the first time, an azine-linked covalent organic framework, COF-JLU2, was developed and synthesised under solvothermal conditions by condensation of hydrazine hydrate and 1,3,5-triformylphloroglucinol. Permanent micropores, excellent crystallinity, good thermal and chemical durability, and abundant heteroatom activated sites in the skeleton are all features of the novel covalent organic framework material. COF-JLU2 has a pore volume of 0.56 cm3 g1 and a moderate BET surface area of over 410 m2 g1. At 273 K and 1 pressure, COF-JLU2 exhibits significant carbon dioxide (up to 217 mg g1) and methane (38 mg g1) uptake, as well as excellent CO2/N2 (77) selectivity. We also point out that it has a higher hydrogen storage capacity (16 mg g1) than previously reported COFs at 77 K and 1 bar

2.4 Solvent- and catalyst-free synthesis of an azine-linked covalent organic framework and the induced tautomerization in the adsorption of U(VI) and Hg(II)

Xing Li et al (2019) During the first time, a green and simple solvent- and catalyst-free technique was presented to synthesis an azine-linked covalent organic framework (ACOF) with excellent efficiency without inert gas protection and/or mechanical grinding. The as-synthesised ACOF has a high crystallinity and superior physical and chemical stability, as well as good adsorption performance for both radioactive heavy metal U(VI) and ordinary heavy metal Hg (II), with adsorption capacities of 169 mg g1 for U(VI) and 175 mg g1 for Hg (II), making it a potential adsorbent material for heavy metal removal and uranium recycling. Tautomerization of the enol and keto forms was confirmed in the structure of the ACOF, which can be produced by metal ion adsorption and can also impact adsorption.

2.5 An azine-containing bispillar [5] arene-based multi-stimuli responsive supramolecular pseudopolyrotaxane gel for effective adsorption ofrhodamine B

Li-Hua Qi et al (2019) An azine-containing bispillar [5] arene was designed and synthesized by the reaction of aldehyde functionalized-pillar [5] arene and hydrazine. Then, a novel bispillar [5] arene-based supramolecular pseudopolyrotaxane has been successfully prepared via host-guest interaction. Interestingly, by taking advantage of the host-guest interactions, π-π stacking interactions and hydrogen bonding interactions, the multi-stimuli-responsive gel-sol phase transitions of such a supramolecular pseudopolyrotaxane gel were successfully realized under different stimuli, such as acid, temperature, concentration, and competitive guests. Moreover, this supramolecular system could effectively adsorb dye molecule rhodamine B. It is worth noting that this supramolecular pseudopolyrotaxane gel prepared in cyclohexanol solution (BP5·G·C) could be used as an adsorbent material for adsorbing rhodamine B with adsorption efficiency of 98.4%. Meanwhile, the adsorption efficiency was 97.6% for supramolecular pseudopolyrotaxane gel prepared in DMSO-H2O (v: v, 8: 2) binary solution (BP5·G·D), also indicating the superior adsorption effect of BP5·G·D toward the dye molecule rhodamine B.

2.6 Design, synthesis and biological evaluation of symmetrical azine derivatives as novel tyrosinase inhibitors

Somaye Kariminan et al (2021) the inhibitory action of a series of symmetrical azine derivatives containing various substituted benzyl moieties against tyrosinase was developed, produced and assessed. The results revealed that compounds 3e, 3f, 3h, 3i,3j, and 3k inhibit tyrosinase effectively, with IC50 values ranging from 7.30 to 62.60 M. Compounds 3f, in particular, showed a three-fold increase in potency (IC50=7.30 1.15 M) when compared to the positive control, kojic acid (IC50= 20.24 2.28 M). Compound 3f showed uncompetitive inhibitory activity against tyrosinase in a kinetic analysis, showing that it can bind to the enzyme-substrate complex. The contacts and binding mechanism of the most effective chemical 3f in the tyrosinase active site were next studied using molecular docking analysis. Furthermore, 3f's cytotoxicity, as well as

2.7 An azine-linked covalent organic framework

Sasanka Dalapti et al (2013) under solvothermal conditions, the condensation of hydrazine with 1,3,6,8- tetrakis (4-formylphenyl) pyrene creates extremely crystalline two-dimensional covalent organic framework. The pyrene units are found at the vertices, while the diazabutadiene (-CN-NC-) linkers are found at the edges of rohmbic- shaped polygon sheets, which stack in an AA-stacking mode to form regularly ordered pyrene columns and one-dimensional microporous channels. the azine- linked frameworks have a high surface are and persistant porosity, as well as excellent chemical stability. The azine-linked frameworks are extremely luminous due to the pyrene columnar ordering, and the azine units serve as open docking sites for hydrogen-bonding interactions. The azine- linked pyrene frameworks have extraordinarily high sensitivity and selectivity in chemo sensing such as the selective detection of 2,4,6-trinitrophenol explosive, due to the synergistic functions of the vertices and edge units. We anticipate that the extension will be granted.

2.8 Monoterpene indole alkaloid azine derivatives as MDR reversal agents

Angela paterna et al (2018) two epimeric indole alkaloids (1 and 2) were subjected to chemical transformations, yielding twenty-four derivatives (5-28) containing additional aromatic or aliphatic azine moieties, with the goal of developing a library of bioactive indole alkaloid derivatives as multidrug resistance (MDR) reversers. 1 D and 2 D NMR(COSY, HMBC, HMQC AND NOESY) investigations were used to determine the structure of the compounds. For evaluating their anti-MDR potential, two different approaches were used: evaluating their activity as inhibitors of typical MDR ABC transporters over expressed by cell transfection, such as ABCB1 (P-gp), ABCC1(MRP1), and ABCG2 (BCRP) or evaluating their ability as collateral sensitivity (CS) agents in MRP1 overexpressing cells. Compounds containing the aromatic azine moiety showed significant MDR reversal activity.

2.9 An azine based sensor for selective detection of Cu^{2+} ions and its copper complex for sensing of phosphate ions in physiological conditions and in living cells

Karishma Tiwari et al (2017) 5-diethylamino-2-[(2-hydroxy-benzylidene) hydrazonomethyl]- phenol (1) was produced as a simple and cost-effective unsymmetrical azine- based Schiff base that preferentially detects Cu^{2+} ions under physiological conditions (EtOH- buffer (1:1), HEPES 10Mm, pH=7.4). Cu^{2+} causes yellow green to yellow in Schiff base 1 UV-Vis spectra, as well as the formation of a new band at 450nm. In the presence of 2.7 equiv of Cu^{2+} ions, the fluroscence of Schiff base 1 (10M) was entirely muted. The fluorescence titration profile was used to calculate the sub-micromolar limit of detection (LOD=3.410-7M), the efficient stern- volmer quenching constant (KSV=1.8105L mol^{-1}), and the strong binding constant (log Kb=5.92). In addition, phosphate ions (PO43-HPO42) were detected using the 1- Cu^{2+} complex. Phosphate ions imaging is formulated by its poor aqueous soubility, extended excitation (406nm) and emission wavelength (537nm) and biocompatibility.

2.10 Electronic spectra of cycl[3.3.2] azine and related compounds: solvent effect on vibronic couplings

Yasuhiro Shigemitsu et al (2012) At the multistate CASPT2 (MS-CASPT2) level of theory, quantitative ab initio calculations for the ultraviolet-visible peaks of cycl [3.2.2] azine and its mono- and dibenzannulated polycyclic compounds are presented, with 11 nm deviation from the experimental S0 S1 absorption. The electrophilic substitution reactions of cycl [3.2.2] azine, benzo[a]/[g]annulated cycl [3.2.2] azines, and 6-dimethylamino [2.2.3] cyclazine-1-carboxylates with 3-cyano-4-methylthiomaleimide yielded functionalized cycl [3.2.2] azine derivatives with absorption maxima ranging from 510 to 630 nm. Time-dependent density functional theory was used to investigate the first intense peaks (TD-DFT). Within the acceptable accuracies of TD-DFT, these peaks were systematically underevaluated by 50 nm. We also calculated the vibronic. This is due to the solvent effect, which causes changes in the electron density difference on the phenyl ring, and the intensified overlap between the electron density difference and the potential derivative in the phenyl ring, which leads to increased vibronic couplings in ethanol**.**

2.11 Azine based smart probe for optical recognition and enrichment of Mo (vi)

Milan Ghosh et al (2018) Through green fluorescence emission, a single crystal X-ray structure-characterized azine derivative (L) was investigated for the selective detection of molybdenum (Mo(vi)) cations. Through chelation enhanced fluorescence (CHEF), the Mo(vi) cation assisted inhibition of photo-induced electron transfer (PET) resulted in a 37-fold fluorescence enhancement, allowing detection of Mo(vi) at concentrations as low as 2 10-9 M. The single crystal X-ray structure of the resulting complex confirmed the chelation of Mo(vi) cations by L. L has a fairly high binding constant for Mo(vi) (1.33 106 M-1). L is also very effective at enriching Mo(vi) from aqueous solution. DFT (density functional theory) studies back up the experimental findings.

2.12 The azine bridge as a conjugation stopper: an NMR spectroscopic study of electron delocalization in acetophenone azines

Michael Lewis et al (2002) A design based on the hypothesis that the azine bridge is a conjugation stopper was used to achieve dipole parallel-alignment of organic molecular crystals of azines. This hypothesis has now been thoroughly investigated, with (1)H and (13)C NMR spectroscopic data of symmetric and asymmetric acetophenone azines supporting this design concept. In molecules with the general structure DPhC(Me) [double bond] N [bond] N [double bond] C(Me)PhA, where D is a donor group and A is an acceptor group, previous structural, ab initio, and electrochemical studies have shown that the azine bridge largely inhibits through-conjugation. NMR spectroscopy is a powerful tool for determining the degree of azine bridge conjugation. The NMR results for nine symmetrical and asymmetrical structures are presented here. The chemical shifts of the aromatic hydrogen and carbon atoms on the acceptor-substituted phenyl ring are unaffected by changing the donor group. Similarly, changing the acceptor group has no effect on the atoms in the donor-substituted phenyl ring's chemical shifts.

2.13 Azines as histamine H4 receptor antagonists

Dorota Lazewska et al (2012) Since its cloning in 2000, the histamine H4 receptor (H4R) has been a promising target for drug development. Histamine H4R antagonists/inverse agonists may be useful in the treatment of inflammatory diseases such as allergic rhinitis, asthma, atopic dermatitis, colitis, or pruritus, according to pharmacological studies. H4R ligands were initially non-selective, but extensive chemical and pharmacological research led to the development of highly potent and selective H4R antagonists (e.g. JNJ7777120, CZC-13788, PF-2988403, A-940894, A-987306). The first compound (UR-63325) has now completed the phase I ascending dose trial and has been found to be safe and well tolerated in clinical trials for the treatment of allergic respiratory diseases. Every year, the number of scientific publications and patent applications in the H4 field grows. A 2-aminopyrimidine scaffold is repeatedly found among the various chemical structures of H4R antagonists described. Over the last two years, there have been significant advances in the search for H4R antagonists, as evidenced by patent applications/patents and peer-reviewed publications. The research focuses on azines (mono-, di-, and triazines), as well as their fused analogues. It has been described in terms of chemistry and pharmacology.

2.14 Azines: synthesis, structure, electronic structure and their applications

Sumit S Chourasiya et al (2019) Azines are traditionally made by condensation of hydrazine with ketones and aldehydes, but there are a variety of other options. Because of their importance in nonlinear optics, azines have been extensively studied using computational studies and crystal structure analysis to investigate the presence or absence of conjugation. The topic of tautomerism in azines is a hot topic right now. We present a review of recent advances in the structure and electronic structure properties of azines, as well as information on modern methods of synthesis and their use as precursors in the generation of heterocycles in organic synthesis and medicinal chemistry. There are also a few applications of azines in materials chemistry, such as the development of metal-organic frameworks (MOFs), covalent organic frameworks (COFs), energetic materials, and chemo sensors.

2.15 Diversity-oriented synthesis of bicyclic fragments containing privileged azines

Nicola Luise et al (2019) For fragment-based drug discovery (FBDD) programmes, an innovative and efficient reagent- and scaffold-based diversity oriented synthesis (DOS) of a fragment set was developed. In order to effectively modulate biomolecules, a convenient synthetic toolkit based on three privileged azine cores was used to quickly access twelve diverse, functionalized, and bicyclic scaffolds. Key motifs for interacting with a variety of biological targets via hydrogen bonds, as well as useful growth points for subsequent fragment optimization, characterise these structure.

CHAPTER 3

AIM AND SCOPE

AIM:

- On the basis of the literature overview for the synthesis of azine from carbonyl compound, it is necessary to synthesis of azine by simple method and which does not undergo number of by-product reaction.

- The aim is to synthesis an azine from 3,4 dimethoxy benzaldehyde and hydrazine hydrate under basic condition by the process of Iodine Catalyzed Synthesis.

- To study the characterization of the azine synthesized using different basic spectrochemical studies such as FT-IR, UV-VIS, Mass and Proton NMR>

- This will help the researchers to study more on azine through a simple method of synthesis.

SCOPE:

Scope of the present study is

- Synthesis of azine by simple method.

- Study about yield of synthesized azine.

- Utilization of minimum by product or no by- product during the synthesis of azine.

- The detailed spectrochemical studies were carried out for the synthesized

CHAPTER 4

EXPERIMENTAL METHOD

The chemicals All which are used for experiment are used without any further purification. The chemicals used are Hydrazine hydrate(0.15ml),3,4(dimethoxy benzaldehyde) (0.996g), ethanol(9ml)

4.1 Experimental procedure

Hydrazine hydrate (0.15ml) and 3,4-dimethoxybenzaldehyde (0.996g) in ethanol (5 to 9 ml) with constant stirring for 1 hour, at room temperature. A light yellow precipitate was obtained, which was separated by filtration, washed with ethanol and dried at room temperature. The compound was soluble in ethanol then we get a bright yellow precipitate. Then for further purification of the precipitate, the precipitate was again filter with ethanol and then kept for drying at room temperature.

4.2 Structural Analysis:

4.2.1 Fourier Transform Infrared Spectroscopy:

Infrared Radiation (IR) spectroscopy is also known as vibrational spectroscopy. The IR spectroscopy deals with infrared region of electromagnetic radiation. IR spectroscopy deals with analysis of interaction of a molecule with infrared light. The IR spectroscopy principle is that molecules tend to absorb specific frequencies of light that are characteristic of the corresponding structure of molecules. At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. The IR spectrum of sample is recorded by passing a beam of IR radiation through the sample. When the frequency of the IR radiation is equal to the frequency of a specific vibration, the molecule absorbs the radiation. The transmitted light reveals how much energy was absorbed at each wavelength. In IR spectrometer we can able to analyses the all types of samples such as gases, solid and liquids.

WORKING:

An IR spectrometer consists of three components- radiation source, monochromator and detector. The radiation sources of IR spectrometer are an inert solid, rare-earth oxide, silicon carbides or nichrome coil which is heated electrically to 1000ºC - 1800ºC. The monochromator is a device used to disperse a broad spectrum of radiation and provides a continuous calibrated series of electromagnetic energy bands of determinable wavelength. Detectors measure the heating effect produced by infrared radiation. The generally used detector are thermocouple and Golay detectors. The figure represents the working of IR spectroscopy

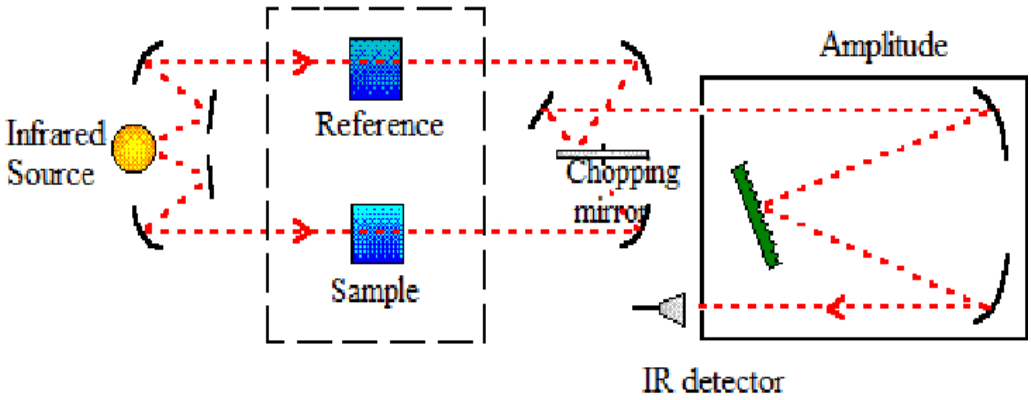


Fig 4.1: Schematic diagram of IR

4.2.2 Ultraviolet – Visible spectroscopy:

Ultraviolet -Visible spectroscopy is an analytical technique that measures the amount of discrete wavelength of UV or visible light which are absorbed by or transmitted through a sample with respect to reference or blank sample. This was influenced by sample composition and what is the concentration of sample. This spectroscopy technique mostly relies on the use of light.

UV-Vis spectroscopy is an analytical technique that measures the number 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. This property is influenced by the sample composition, potentially providing information on what is

in the sample and at what concentration. Since this spectroscopy technique relies on the use of light, let's first consider the properties of light. Light has a certain amount of energy which is inversely proportional to its wavelength. Hence, shorter wavelengths of light have higher energy when compared to longer energy. A specific amount of energy is needed to excite the electron to higher energy level which we can detect as absorption. Electrons in different bonding environments in a substance require a different specific amount of energy which is used to excite the electron to higher energy levels. Thus, absorption of light occurs at different wavelength for different samples.

WORKING:

Ultra violet light is focused into the entrance slit of the monochromator from the source. Monochromator uses dispersing elements, namely optical grating to separate the light by wavelength. The light is passed into a charged coupled device (CCD), which is made up of individual tiny detectors, hence the intensity of light at each wavelength will be measured. CCD is read-off to a computer and the results obtained is a spectrum, which shows the intensity of each wavelength of light. Spectrometers are able to measure the electromagnetic radiation from ultraviolet to infrared. Spectrum will show the intensity of light versus the wavelength.

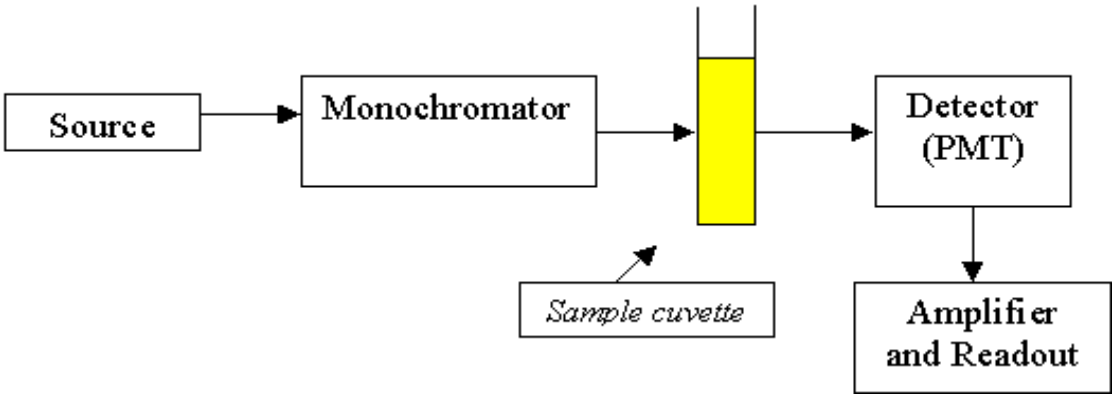


Fig 4.2 Schematic diagram of UV spectroscopy

4.2.3 Nuclear Magnetic Resonance Spectroscopy:

The nuclei in the atom of many have spin, and all nuclei are electrically charged, according to the NMR principle. An energy is transfer from ground state to

higher energy level is achievable when an external magnetic field is applied. The transfer of energy from ground state to higher energy level occurs at a wavelength that coincides with the ratio frequency. Also, energy is emitted at the same frequency when the spin comes back to its ground state.

WORKING:

The sample is placed in a magnetic field. The nuclei sample is excited from ground state to higher level. These excited nuclei is transferred into nuclear magnetic resonance with the help of radio waves to produce NMR signals. These NMR signals are detected with sensitive radio receivers. The resonance frequency of an atom in a molecule is charged by the intramolecular magnetic field surrounding it. The NMR gives the information of a molecule's individual functional groups and its electronic structure. Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds. The method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.

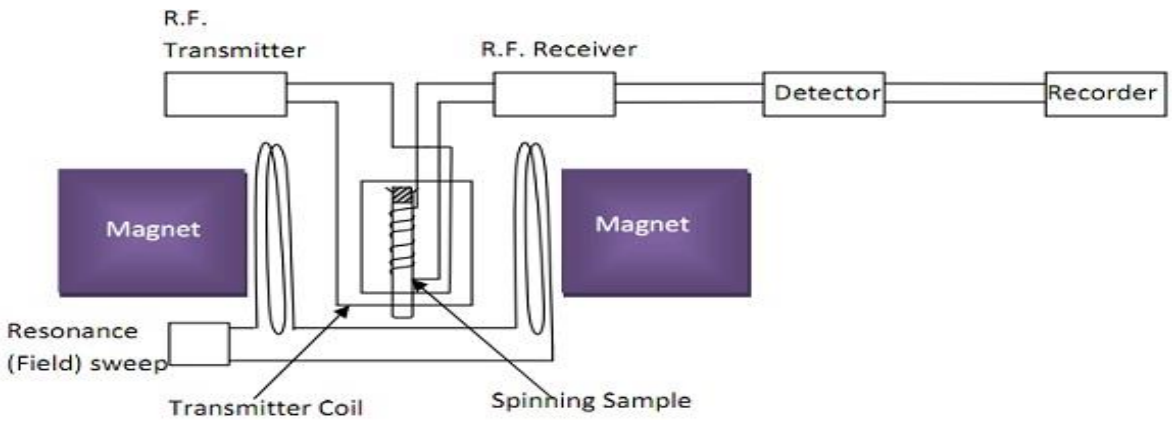


Fig 4.3: Schematic diagram of NMR spectroscopy

4.2.4 Mass Spectroscopy:

Mass spectroscopy allows us to determine the molecular mass and the molecular formula of a compound, as well as certain structural features of the

compound. In mass spectroscopy, a small sample of a compound is introduced into an instrument called a mass spectrometer, where it is vaporized and then ionized as a result of an electron's being removed from each molecule. Ionization can be done in several ways. The most common method bombards the vaporized molecules with a beam of high-energy electrons. The energy of the electron beam can be varied, but a beam of about 70 electron volts (eV) is commonly used. When the electron beam hits a molecule, it knocks out an electron, producing a molecular ion, which is a radical cation a species with an unpaired electron and positive charge.

WORKING:

The first part of the process within a mass spectrometer is ionization, and occurs when an atom within the sample gains a negative or positive charge. Most standard mass spectrometers work with positive ions. Once the ions are generated, they are all accelerated to ensure they all have the same kinetic energy, and they are then deflected by a field according to their mass-to-charge ratio to filter the ions into a detector.

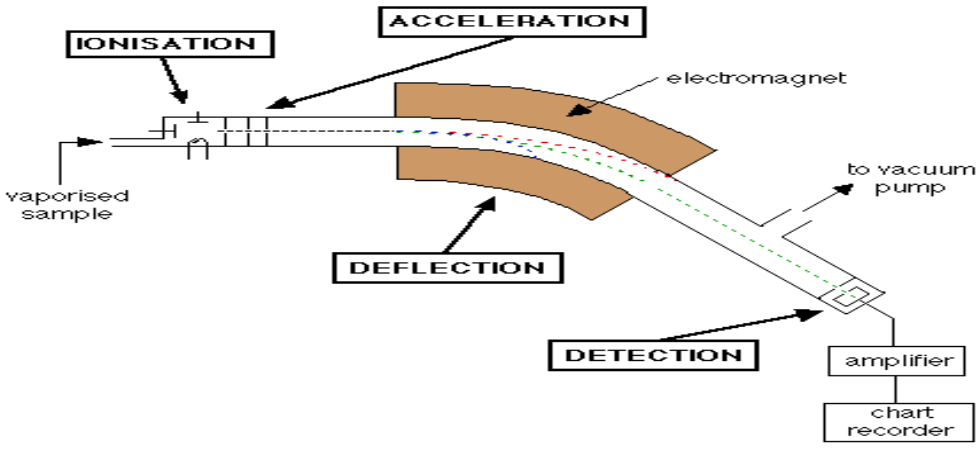


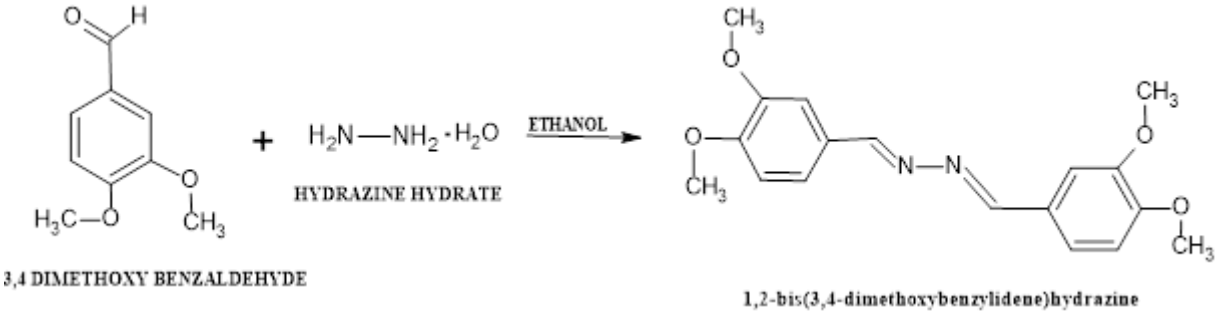
Fig 4.4: Schematic diagram of Mass spectroscopy

CHAPTER-5

RESULTS AND DISCUSSION

5.1 Synthesis of 1,2 bis (3, 4- dimethoxy benzylidene) hydrazine:

The synthesis of 1,2 bis (3,4- dimethoxy benzylidene) hydrazine is done by the process called Iodine Catalyzed Synthesis. The Iodine Catalyzed synthesis of symmetrical azine by the treatment of hydrazine hydrate () with carbonyl compound here the carbonyl compound is 3,4 dimethoxy benzaldehyde. The synthesis by this method gives rapid yield. If the carbonyl compound that is 3,4 dimethoxy benzaldehyde is liquid there is no need for any solvent but in the case of solid carbonyl compounds there is need for solvent which may be either THF or ethanol. This solvent help to dissolve the substrate. IN this study the carbonyl compound used is a solid 3,4 dimethoxy benzaldehyde so it has to be dissolved in an ethanol which gives a yellow color precipitate. This yellow color precipitate indicates the 1,2 bis (3,4- dimethoxy benzylidene) hydrazine.



3,4 DIMETHOXY BENZALDEHYDE

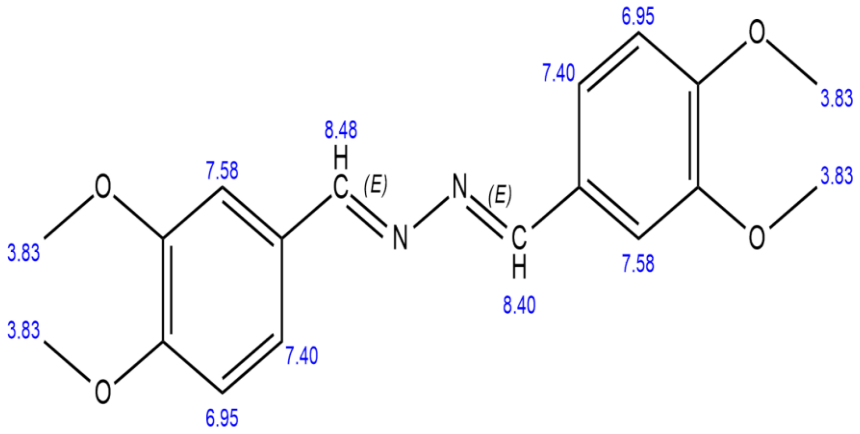
1,2-bis(3,4-dimethoxybenzylidene)hydrazine

5.2 CHARACTERISATION:

5.2.1 NUCLEAR MAGNETIC RESONANCE:

The ^{1}H spectra are recorded for the synthesized 1,2- bis (3, 4- dimethoxybenzaldehyde) hydrazine with DMSO as the solvent. In ^{1}H NMR spectrum of all the compounds, two singlets observed in the region of 3. 89- 3.90 ppm with integral value of three were assigned to methoxy methyl (OCH_3). The olefinic protons appeared as expected as two individual's doublets at 7.21 -7.38 and 7.54 –

7.74 ppm with the splitting constant of 15 Hz. This confirm that the olefinic protons are trans to each other. The singlet peak at 8.63 ppm represents the CH═N-



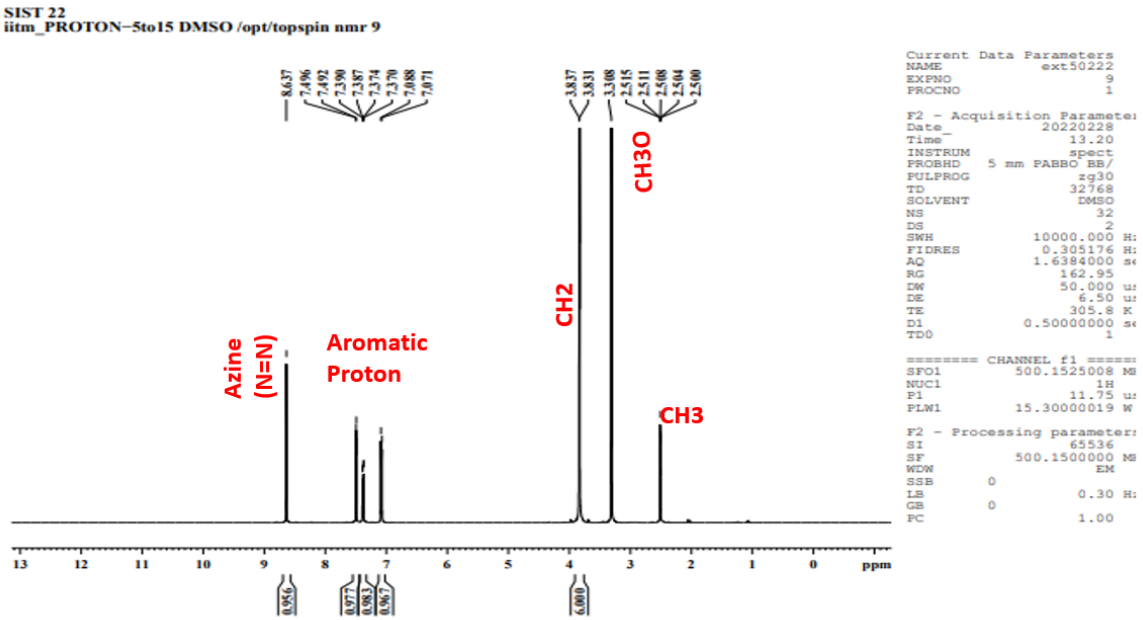


Fig 5.1 : NMR spectrum of 1,2 bis-(3,4-dimethoxy benzylidene)hydrazine

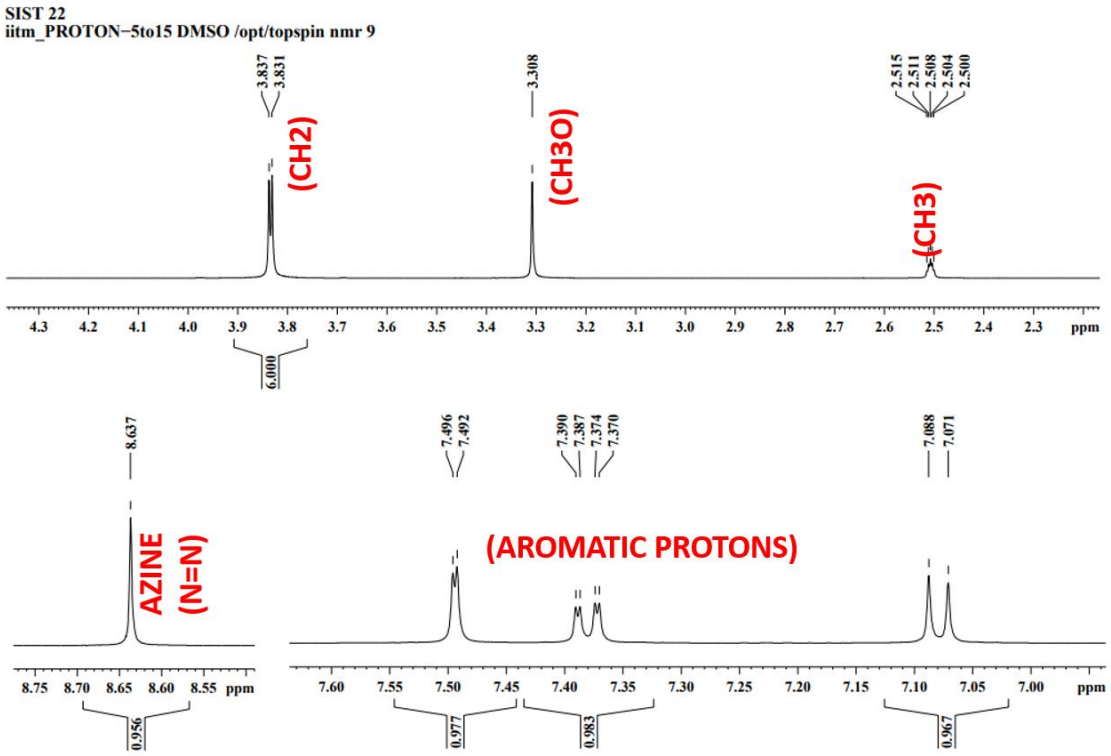


Table 5.1: ^{1}H NMR spectral assignment of 1,2 bis-(3,4- dimethoxy benzylidene) hydrazine.

S.NO	TYPE OF PROTONS	CHEMICAL SHIFT
1	CH3	2.515
		2.511
		2.508
		2.504
		2.500
2	CH3O	3.308
3	CH2	3.837
		3.831
4	AROMATIC PROTONS	7.701
		7.088
		7.370
		7.374
		7.387
		7.390
		7.492
		7.496

5	AZINE	8.637

5.2.2 UV spectrum:

The UV -visible adsorption spectrum of the compounds was taken in the region around 200-800 nm using ethanol as solvent. The compound 1,2 bis –(3, 4-dimethoxy benzylidene) hydrazine contains α β unsaturated carbonyl group, it is expected to show two absorption bands pertaining to the n-π^* and π-π^* transitions. The compound shows strong absorption band at 350 nm which was due to n- π^* and weak absorption band around 213- 278 nm which is due to π-π^* transitions.

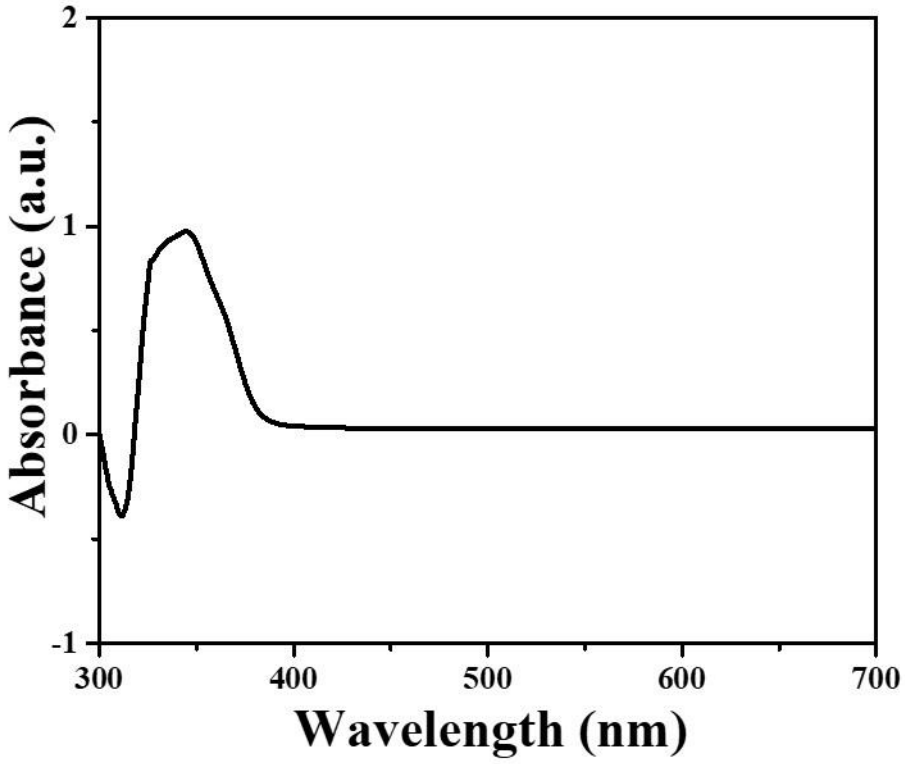


Fig 5.2: UV Spectrum of 1,2 bis-(3,4- dimethoxy benzylidene) hydrazine.

Table 5.2: UV Spectral assignment of 1,2 bis-(3,4- dimethoxy benzylidene) hydrazine.

S.NO	WAVELENGTH	ABSORBANCE
1	350	0.919
2	349.5	0.929
3	349	0.938
4	348.5	0.946
5	348	0.954
6	347.5	0.959
7	347	0.963
8	346.5	0.963
9	346	0.971
10	345.5	0.973
11	344.5	0.974
12	343.5	0.972
13	341	0.961

5.2.3 FT- IR SPECTROSCPY:

The FT-IR spectrum of the compound 1,2 bis- (3,4-dimethoxy benzylidene) hydrazine exhibits a strong C=N stretching vibration at. Absorption band at 1435-1595 cm^{-1} is due to C=C stretching vibration which is present in aromatic ring of 1,2 bis (3,4-dimethoxybenzylidene) hydrazine. The C- O stretching occurs at 1024-1347 cm^{-1}. The peak at 2905cm^{-1} correspond to the strong sp^3 C-H stretching of methoxy group (OCH_3). The presence of peak at 900-700 cm^{-1} corresponds to C-H bending of aromatic group.

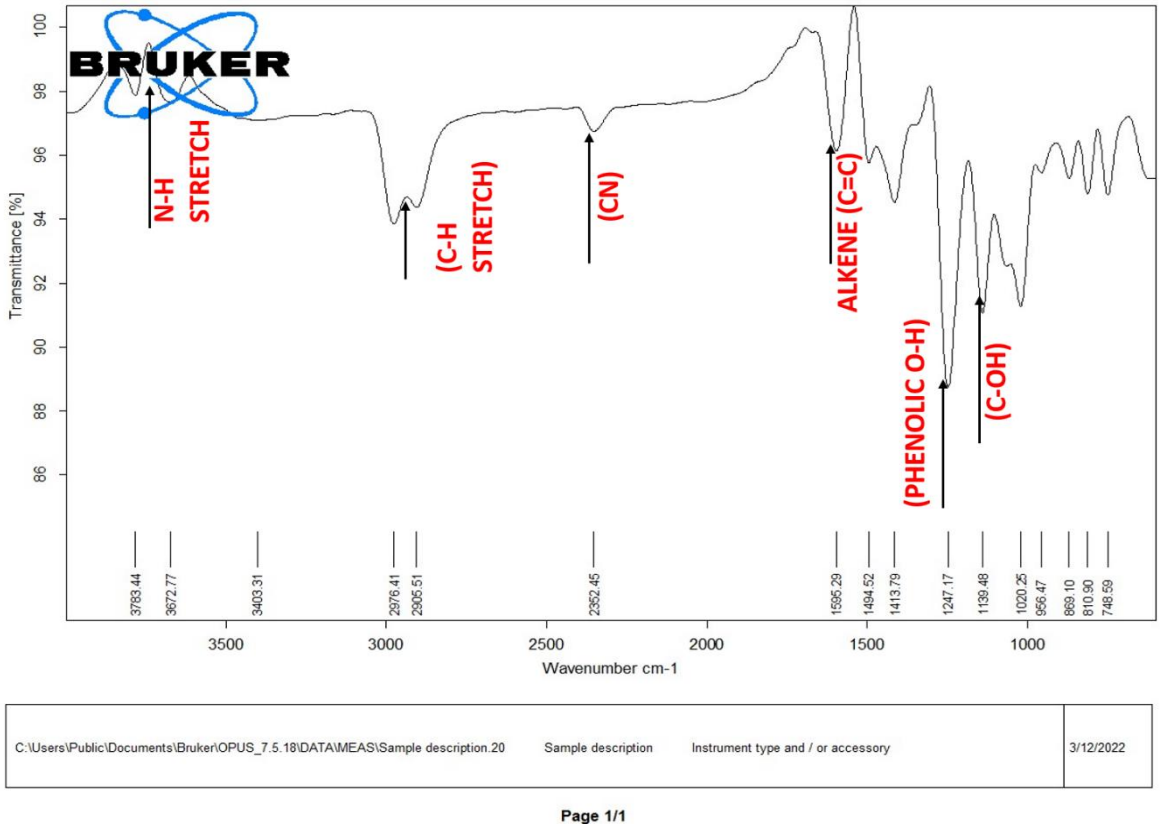


Fig 5.3: FT-IR spectrum of 1,2 bis-(3,4- dimethoxy benzylidene) hydrazine.

Table 5.3: FT-IR spectral assignment of 1,2 bis-(3,4- dimethoxy benzylidene) hydrazine.

S.NO	FUNCTIONAL GROUP	WAVENUMBER(CM^{-1})
1	N-H	3783.44
		3672.77
2	C-H	2976.41
		2905.51
3	CN	2532.45
4	ALKENE (C=C)	1595.29
5	PHENOLIC (O-H)	1247.17
6	C-OH	1139.48

5.2.4 MASS SPECTROSCOPY:

The DMSO solution of 1,2 -bis-(3,4 -dimethoxy benzylidene) hydrazine were used to record High resolution ESI mass spectrum in positive mode. The strong peak is observed $(M+ H)^+$ at m/z 329.1497 A good argument was observed for calculated

m/z values and experimental m/z values for $(M+H)^+$ ions which indicates the purity of the synthesized compound.

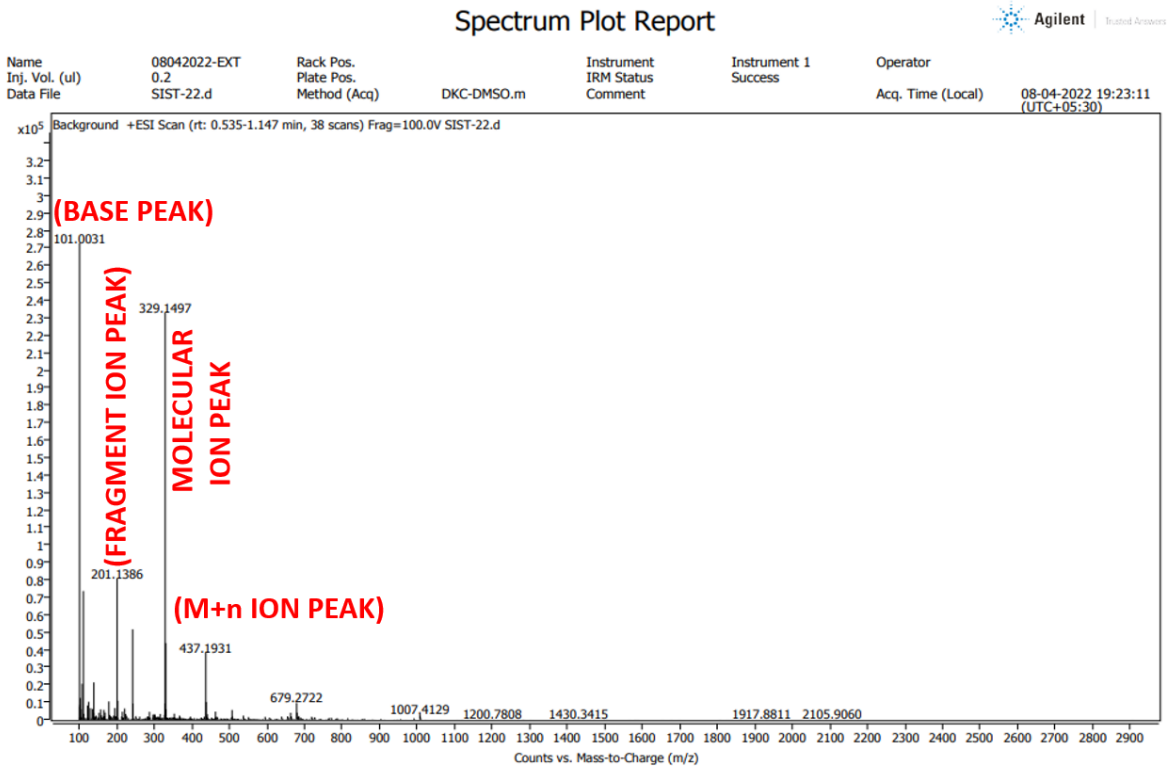


Fig 5.4: Mass spectrum of 1,2 bis-(3,4- dimethoxy benzylidene) hydrazine.

Table 5.4: Mass spectral assignment of 1,2 bis-(3,4- dimethoxy benzylidene) hydrazine.

S.NO	TYPE OF PEAK	MASS TO CHARGE (M/Z)
1	BASE PEAK	101.0031
2	FRAGMENT ION PEAK	201.1386
3	MOLECULAR ION PEAK	329.1497
4	M+n ION PEAK	437.1931

CHAPTER 6

CONCLUSION

Thus, conclusion from the present study is that synthesis of azine was carried out by condensation of hydrazine with the substituted aldehyde. The synthesis was carried out in shorter period of time and yield of the synthesized azine is good during the period of synthesis.

The synthesis compound was characterized by different spectrochemical studies which confirmed the product formed by the synthesis. Thus, from characterization the properties of compounds were more, especially in the biological activities. This may be studies in future.

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