SYNTHESIS AND CHARACTERIZATION OF 4-AMINOANTIPYRINE WITH 4-[N,N-BIS(2-CHLOROETHYL)AMINO]BENZALDEHYDE

Submitted in partial fulfilment of the requirements for the award of

Bachelor of Science in Chemistry

by

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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-2023

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **PRAVEENA.A (40030026), SRI DHANYA.S (40030035)** who carried out the project entitled **SYNTHESIS AND CHARACTERIZATION OF 4-AMINOANTIPYRINE WITH 4-[N,N-BIS(2-CHLOROETHYL)AMINO]BENZALDEHYDE under our supervision from November 2022 to April 2023.**

08/05/2023

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DECLARATION

We, **PRAVEENA. A (40030026), SRI DHANYA.S (40030035)** declare that the Project Report entitled "**SYNTHESIS AND CHARACTERIZATION OF 4-AMINOANTIPYRINE WITH 4-[N,N-BIS(2-CHLOROETHYL)AMINO]BENZALDEHYDE**" done by us under the guidance of **Dr. J. KARTHIKEYAN** M.sc.,Ph.D., Head of the department, department of chemistry at **Satyabhama Institute Of Science And Technology**, Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai-600119 is submitted in partial fulfillment of the requirements for the award of Bachelor of Science degree in Chemistry.

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ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

I convey my thanks to **Dr. K. REKHA CHAKRAVARTHY, Dean, School of Science and Humanities and Dr. J. KARTHIKEYAN, Head of the Department, Dept. of Chemistry** for providing me necessary support and details at the right time during the progressive reviews.

I would like to express my sincere and deep sense of gratitude to my Project Guide **Dr. J. KARTHIKEYAN** for his valuable guidance, suggestions, and constant encouragement paved way for the successful completion of my project work.

I wish to express my thanks to all Teaching and Non-teaching staff members of the Department of Chemistry who were helpful in many ways for the completion of the project.

ABSTRACT

In this study, a hydrazone compound was synthesized through a condensation reaction between 4-aminoantipyrine and 4-[N,N-bis(2-chloroethyl)amino]benzaldehyde. The synthesized product was characterized using various spectroscopic techniques including FT-IR, TLC, UV-VISIBLE, LC-HRMS-ESI, and ^{1}H NMR. The spectroscopic data confirmed the successful synthesis of the desired hydrazone compound. This study provides important information for the development of potential new hydrazone-based compounds with potential applications in the fields of pharmaceuticals and materials science.

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LIST OF ABBREVATION

TLC	Thin layer chromatography
FTIR	Fourier transform infrared
NMR	Nuclear magnetic resonance
MS	Mass spectrometry

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CHAPTER 1
INTRODUCTION

Hydrazones are a class of organic compounds that have garnered significant attention due to their versatile applications in organic synthesis and medicinal chemistry. They are formed by the condensation of an aldehyde or ketone with a hydrazine or a derivative of hydrazine. These organic compounds contain a nitrogen-nitrogen double bond adjacent to a carbonyl group. They are generally stable compounds that can be isolated as solids and are soluble in organic solvents but insoluble in water.

Hydrazones can undergo various reactions, including oxidation, reduction, and hydrolysis, and can be used as starting materials in the synthesis of other compounds. They have various applications in organic synthesis, medicinal chemistry, and materials science. They are used as intermediates in the synthesis of pharmaceuticals, agrochemicals, and dyes, and as ligands in metal complex chemistry. Some hydrazones have been found to exhibit biological activity, such as antibacterial, antifungal, and antitumor properties.

Among the various hydrazones, those obtained from the reaction of 4-aminoantipyrine with aldehydes or ketones have attracted interest due to their potential as intermediates in the synthesis of bioactive compounds.

4-Aminoantipyrine, also known as aminopyrine, is a pyrazolone derivative that has been widely used as an analgesic and antipyretic agent. On the other hand, 4-[N,N-bis(2-chloroethyl)amino]benzaldehyde is an aldehyde derivative that has been used as a starting material in the synthesis of various bioactive compounds, including anticancer agents. The condensation of 4-aminoantipyrine with 4-[N,N-bis(2-chloroethyl)amino]benzaldehyde yields a hydrazone derivative that has potential applications in organic synthesis and medicinal chemistry. In this study, we aim to synthesize and characterize this hydrazone derivative and evaluate its potential as an intermediate in the synthesis of bioactive compounds.

Organic synthesis is the process of creating new organic molecules through chemical reactions. Synthesis involves planning a route to a target molecule, selecting appropriate reagents and reaction conditions, and carrying out the reactions in a stepwise manner to yield the desired product. One important aspect of organic synthesis is the characterization of the synthesized compounds. Characterization involves the use of various techniques to determine the identity and purity of the product, as well as its physical and chemical properties. These techniques may include spectroscopic methods, such as nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy, as well as chromatographic and elemental analysis techniques.The characterization of the synthesized hydrazone derivative will involve the use of various techniques, including nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, and elemental analysis. By characterizing the product, we can confirm its identity and purity, and assess the success of the synthetic route.

Overall, the synthesis and characterization of the hydrazone derivative obtained from the reaction of 4-aminoantipyrine with 4-[N,N-bis(2-chloroethyl)amino]benzaldehyde can provide valuable insights into the chemistry of hydrazones and their potential applications in organic synthesis and medicinal chemistry.

CHAPTER 2
LITERATURE SURVEY

1. ***Title: Synthesis of Some New Antipyrine Derivatives***

   Authors: Redha I. Al-Bayati College of Science, Al-Mustansiriyah Univ. Iyad S. Hameed and Mustafa K. Toema College of Education,Tikrit Univ.

   Year: 2011

The given work describes the synthesis and characterization of various derivatives of 4-aminoantipyrine, a heterocyclic compound containing both pyrazole and pyrrolidine moieties.The synthesis started with the preparation of 4-chloro acet amide derivative [2] from 4-amino antipyrine [1] and chloro acetyl chloride. This compound [2] was then converted into thiozolidine-4-one [3] by reaction with KSCN.

Compound [3] was further reacted with 3-nitrobenzaldehyde in the presence of NaOAC-acetic acid to give the derivative [4]. The hydrazide derivative [5] was prepared from compound [2] and hydrazine hydrate, which upon refluxing with acetyl aceton in absolute ethanol yielded antipyrine containing pyrazol moiety [6]. Refluxing of compound [2] with various amines in absolute ethanol yielded the corresponding acetamide derivatives [7-10]. Reaction of 4-aminoantipyrine [1] with CS2 and KOH afforded the salt [11], which upon reaction with hydrazine hydrate at 45-55oC for 1 hour, yielded the fused ring derivative [12].The Schiff base [13] was prepared from 3-nitrobenzaldehyde and compound [1], which was then oxidized by KMno4 into the acid derivative [14]. Diazotization of compound [1] with NaNo2/HCl led to azo derivative [15], which was further reacted with acetyl acetone to give compound [16]. Reaction of compound [16] with hydrazine led to ring closure, giving a derivative with a pyrazole moiety [17].

Finally, the reaction of [1] with tetrahydrofuran in acetic acid gave a derivative with a pyrrolidine moiety [18]. The synthesized derivatives were characterized using various spectroscopic techniques such as IR, 1H NMR, and elemental analysis.

2. ***Synthesis and Biological Activities of 4-Aminoantipyrine Derivatives Derived from Betti-Type Reaction***

   Authors: Ipsita Mohanram and Jyotsna Meshram

   Year: 2014

This study describes the synthesis of 4-aminoantipyrine derivatives through a three-component Betti reaction using a simple one-step protocol. The synthesized compounds were characterized using spectroscopic and elemental analysis. These derivatives were then evaluated for anti-inflammatory and anthelmintic activity in vivo and in vitro, respectively. The results showed that some of the compounds exhibited potential anti-inflammatory and anthelmintic activity, with some being more effective than the reference drugs. Additionally, the bioactivity of these derivatives was evaluated using Lipinski's rule of five through cheminformatics software. Overall, this study demonstrates the potential of 4-aminoantipyrine derivatives for therapeutic applications.

3. ***Title: Synthesis, Characterization and Anti-Breast Cancer Activity of New 4-Aminoantipyrine-Based Heterocycles***

   Authors: Mostafa M. Ghorab, Marwa G. El-Gazzar and Mansour S. Alsaid

   Year: 2014

This work describes the synthesis and characterization of new pyrazolone derivatives containing biologically active groups. The compounds were evaluated for their anticancer activity against a human breast cancer cell line, MCF7, and compared to the positive control, Doxorubicin. The results showed that several of the synthesized compounds exhibited promising anticancer activity, with IC50 values ranging from 30.68 to 60.72 μM. The most active compounds were identified as (Z)-4-((3-amino-5-imino-1-phenyl-1H-pyrazol-4(5H)-ylidene)methylamino)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one 5, 3-(4-bromophenyl)-1-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-4-oxo-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carbonitrile 13, and (Z)-4-(3-amino-6-hydrazono-7-phenyl-6,7-dihydropyrazolo[3,4-d]pyrimidin-5-yl)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one 19

4. ***Physicochemical Analyses of a Bioactive 4-Aminoantipyrine Analogue - Synthesis, Crystal Structure, Solid State Interactions, Antibacterial, Conformotional and Docking Studies.***

   Authors: Mohammad Sayed Alam, Dong-Ung Lee

   Year: 2016

The passage describes the synthesis and characterization of a novel Schiff base derivative of 4-aminoantipyrine called MBA-dMPP. X-ray diffraction data showed that MBA-dMPP adopts a trans configuration and forms orthorhombic crystals with intermolecular van der Waals interactions. The solid-state behavior of MBA-dMPP was analyzed using 3D Hirshfeld surface analysis and 2D fingerprint plotting. MBA-dMPP was also tested for its in vitro antibacterial activity and compared to ciprofloxacin through in silico docking. Finally, the torsion energies of the crystal structure and optimized and bioactive conformers of MBA-dMPP were compared to predict its bioactive conformation.

5. ***Synthesis, Characterization and study biological activity of some Schiff bases derivatives from 4-amino antipyrine as a starting material.***

   Authors: Hutham Mahmood Yousif Al-Labban, Hawraa Mohammed Sadiq and Ahmed Abduljabbar Jaloob Aljanaby

   Year: 2019

The study involved synthesizing Schiff bases compounds [A1-A3] by reacting 4-aminoantipyrine with different aromatic aldehydes. The compounds were characterized using various techniques such as melting point, FT-IR spectroscopy, and thin layer chromatography (TLC). The antibacterial activity of the compounds was evaluated using the agar well diffusion method against multi-drug resistant bacteria causing urinary tract infections. Different concentrations of each compound were used, and A3 at a concentration of 150 mg/ml showed the best antibacterial activity against K.pneumoniae and C.freundii, with inhibition zone diameters of 21± 0.25mm and 22± 0.5mm, respectively, compared to other compounds.

6. ***Intermolecular interactions in antipyrine-like derivatives 2-halo-N-(1,5-dimethyl-3-oxo2-phenyl-2,3-dihydro-1-H-pyrazol-4-yl)benzamides: X-ray structure, Hirshfeld surface analysis and DFT calculations***

   Authors: Aamer Saeed, Asma Khurshid, Ulrich Flörke, Gustavo A. Echeverría, Oscar E. Piro, Diego M. Gil, Mariana Rocha, Antonio Frontera, Hesham R. El-Seedi, Amara Mumtaz, Mauricio F. Erbenj

   Year: 2020

This study reports the synthesis and characterization of two new antipyrine derivatives using various spectroscopic techniques. The crystal packing of both compounds was mainly stabilized by a combination of hydrogen bonding and π-interactions. Hirshfeld surface analysis and DFT calculations were used to analyze the solid-state structures and evaluate the different energy frameworks. The results showed that H-bonding interactions were energetically relevant, but the total binding energies of the different assemblies were dominated by a combination of π-interactions. The study provides insights into the molecular interactions that stabilize the crystal structures of the two antipyrine derivatives.

7. ***Synthesis, Characterization and Antibacterial Activity Evaluation of 4-amino Antipyrine Derivatives and Their Transition Metal Complexes***

   Authors: Salah Hamza Sherif, Dagne Addisu Kure, Endalkachew Asefa Moges, Bekele Argaw

   Year: 2021

The study describes the synthesis and characterization of Schiff base ligands derived from 4-aminoantipyrine and their Co(II), Ni(II), and Cu(II) metal complexes. The structures of the ligands and complexes were confirmed using various spectroscopic techniques. The complexes were found to have octahedral geometry and exhibited electrolytic behavior. The antibacterial activity of the ligands and complexes were evaluated against three bacterial strains, and compound Co(4) showed better activity than the standard antibiotic against Staphylococcus aureus. The study highlights the

potential of Schiff base ligands as drug agents and transition metal complexes as catalysts in various reactions.

8. ***Synthesis and spectroscopic characterization of fluorescent 4-aminoantipyrine analogues: Molecular docking and in vitro cytotoxicity studies***

   Authors: D. Premnath, P. Mosae Selvakumar, P. Ravichandiran, G. Tamil Selvan, M. Indiraleka, J. Jannet Vennila

   Year: 2015

Two new substituted aromatic carbonyl compounds of 4-aminoantipyrine were synthesized and characterized by various spectroscopic techniques. Both compounds showed significant fluorescence emission with two broad emission bands. The molecules were evaluated for their anticancer activity against cervical cancer cells by molecular docking and in vitro cytotoxicity assay. Compound 1 showed higher activity compared to compound 2 and was similar to that of the standard drug Pazopanib, indicating the importance of the substituent on the phenyl moiety for the activity of the compounds.

9. ***Synthesis, molecular docking and biological activity of 4-aminoantipyrine dithiocarbamate derivatives***

   Authors: S. Sharada, A.N.V. Sunitha, M. Rupa, O. Navneetha, S. Leemol, T. Saritha Jyostna
   Year: 2015

The investigation describes the synthesis and characterization of new compounds derived from 4-aminoantipyrine dithiocarbamates, followed by antimicrobial screening. In addition, the study utilized molecular docking analysis, a computational drug design technique, to understand the binding mode and affinity of the synthesized compounds with target receptors. The results of the docking analysis suggested that the

compounds exhibited strong hydrophobic interactions with the target receptors, indicating their potential as effective drug candidates.

10. ***Molecular modeling and docking studies of new antimicrobial antipyrine-thiazole hybrids***

    Author: Sraa Abu-Melha

    Year: 2022

The study reports the synthesis of novel antipyrine incorporated thiazole derivatives linked by a phenoxyacetamide moiety, and their evaluation as antibacterial and antifungal agents. The synthetic strategy involved the condensation of a precursor with thiosemicarbazide, followed by heterocyclization with various carbonyl compounds. The HOMO-LUMO energies and Fukui's indices were calculated using DFT/B3LYP level quantum chemical calculations. The synthesized compounds were evaluated for their antibacterial and antifungal activities, and the results showed that some compounds exhibited significant activity against both Gram-positive and Gram-negative strains. The theoretical molecular docking studies were also performed to simulate the reactivity of the synthesized compounds against the binding sites of the target proteins. The study suggests that the synthesized compounds have promising antibacterial and antifungal potential, which is supported by both theoretical and practical results.

11. ***4-Aminoantipyrine Analogs as Anti-inflammatory and Antioxidant agents: Synthesis, Biological Evaluation and Molecular Docking Studies***

    Authors: Qazi Yasar, Zahid Zaheer

    Year: 2021

A novel series of 4-aminoantipyrine derivatives were synthesized and evaluated for their anti-inflammatory and antioxidant activities. The most active compounds 4a and 4b showed potent anti-inflammatory and antioxidant activities as compared to

standard drugs. They were also found to have good ADME properties and showed no significant cytotoxic activity against HeLa and MCF-7 cell lines. Molecular docking studies showed that these compounds had good binding interactions against oxidoreductase, cyclooxygenase-1 and cyclooxygenase-2 enzymes. Overall, the synthesized compounds had potential as lead compounds for further optimization and development.

12. ***Synthesis, Crystal Structure and Docking Studies as Potential Anti-Inflammatory Agents of Novel Antipyrine Sulfanyl Derivatives***

    Authors: Nail S. Akhmadieva, Ekaterina S. Mescheryakovaa, Vnira R. Akhmetovaa, Veronica R. Khairullina, Leonard M. Khalilova, Askhat G. Ibragimova

    Year: 2020

The InCl3-catalyzed green synthesis method allows for the production of sulfanyl- and oxasulfanyl-substituted antipyrine derivatives by thiomethylation of the substrate at the C(4)-H position with formaldehyde and thiols or α,ω-mercaptoalkanols in water. The X-ray diffraction study of the structures and molecular packing of the compounds showed that the substitution chain's extension results in the formation of either a 1D chain or a 2D network. Using the molecular docking method, it was possible to make assumptions about the selectivity of anti-inflammatory action for S- and O,S-derivatives of antipyrine. However, the specifics of these assumptions are not mentioned in the given context.

13. ***Synthesis, anti-inflammatory activity, and molecular docking study of novel azo bis antipyrine derivatives against cyclooxygenase-2 enzyme***

    Authors: Kaliyan Bhuvaneswari, Nagarajan Nagasundaram, Appaswami Lalitha

    Year: 2020

A new series of azo-bis antipyrine derivatives has been synthesized from a one-pot multicomponent Knoevenagel/Michael addition reaction of antipyrine with various azo aldehydes in ethanol, using L-Proline as a catalyst under reflux condition. The anti-inflammatory activity of the final products was evaluated using the inhibition of albumin denaturation technique. Compound 3f demonstrated significant inhibitory effect with IC50 values of 3.6 μM compared to the standard anti-inflammatory drug Aspirin, with IC50 values of 2 μM.

Molecular docking was performed to confirm the in vitro results against the enzymatic inhibition activity of COX-2 enzymes. Compound 3f showed good binding affinity with an inhibition constant (Ki) of 1.79 nM, indicating its potential as a COX-2 enzyme inhibitor with anti-inflammatory properties.

CHAPTER-3

AIM AND SCOPE OF HYDRAZONE

The objective of this work is to synthesize hydrazone from aldehyde and 4-aminoantipyrine using ethanol as a medium. The detailed spectroscopic studies of the synthesized compounds, using various analytical techniques such as FT-IR, UV-VISIBLE, H^1 NMR, LC-HRMS, and UV methods, involve the acquisition and analysis of spectral data of the synthesized compounds. These techniques provide information on the chemical structure, purity, and identity of the synthesized compounds.

For example, FT-IR spectroscopy can provide information on the functional groups present in the synthesized compounds based on their characteristic absorption frequencies. UV-Visible spectroscopy can provide information on the electronic transitions of the synthesized compounds, while ^1H NMR spectroscopy can provide information on the number and types of hydrogen atoms present in the synthesized compounds.

LC-HRMS can be used to determine the molecular weight of the synthesized compounds and to identify any impurities that may be present. UV methods can also be used to determine the purity of the synthesized compounds.

The detailed spectral assignments involve the interpretation and identification of the spectral peaks obtained from each analytical technique. The spectral peaks are compared to known standards or reference spectra to identify the functional groups, electronic transitions, and hydrogen atoms present in the synthesized compounds. This information can then be used to confirm the chemical structure and purity of the synthesized compounds.

CHAPTER-4

MATERIALS AND METHODOLOGIES

Experimental Procedure for the Synthesis of (E)-5-((4-bis(2-Chloroethyl)amino)benzylidene)amino)-1,4-dimethyl-2-phenyl-1H-pyrazol-3(2H)one:

4.1 MATERIALS:

4-[N,N-Bis(2-chloroethyl)amino]benzaldehyde(0.246g),4-aminoantipyrine (0.203g),Ethanol (30 mL),Magnetic stirrer, Dropping funnel, Round bottom flask,Beaker

4.2 PROCEDURE:

To a 100 mL round bottom flask equipped with a magnetic stirrer, add 4-[N,N-Bis(2-chloroethyl)amino]benzaldehyde (0.246 g) and 4-aminoantipyrine (0.203 g).Add ethanol (30 mL) to the flask and stir the mixture on a magnetic stirrer until all the solids dissolve. Continue stirring the mixture for 2-3 hours at room temperature until a yellow-coloured product is formed. After the completion of the reaction, filter the product using a Buchner funnel and wash the solid with cold ethanol to remove any impurities. Dry the solid product under vacuum to obtain (E)-5-((4-bis(2-Chloroethyl)amino)benzylidene)amino)-1,4-dimethyl-2-phenyl-1H-pyrazol-3(2H)one as a yellow powder. Purify the product using column chromatography with an appropriate solvent system. Characterize the product using spectroscopic techniques such as NMR, IR, and MS.

The synthesis of a yellow-coloured hydrazone through the reaction of 4-[N,N-Bis(2-chloroethyl)amino]benzaldehyde and 4-aminoantipyrine in an ethanol medium involves a condensation reaction. Specifically, a hydrazone formation reaction occurs, where the carbonyl group of 4-[N,N-Bis(2-chloroethyl)amino]benzaldehyde reacts with the hydrazine derivative (4-aminoantipyrine) to form a hydrazone. In this process, a water molecule is eliminated from the reactants, which is the characteristic feature of a condensation reaction. This chemical process involves the elimination of a water molecule and the formation of a carbon-nitrogen double bond, resulting in the stable conjugated pi-electron system in the product.

4.2 METHODOLOGIES:

TLC, FTIR, UV-VISIBLE SPECTROMETER, NMR, MASS SPECTROSCOPY AND GAUSSIAN STUDIES.

CHAPTER-5

RESULTS AND DISCUSSION

5.1 SYNTHESIS

A condensation reaction was employed to synthesize hydrazone from the reaction between 4-amino antipyrine and 4-[N,N-Bis(2-chloroethyl) amino] benzaldehyde in ethanol as a solvent. The resulting compounds exhibited solubility in CH_3OH, $CHCl_3$, DMF, and C_2H_5OH. Comprehensive analysis techniques, including FT-IR, TLC, UV-VISIBLE, ^1H NMR, and LCHR-MS-ESi, were utilized to confirm the molecular structures of the synthesized compounds, which were found to be in good agreement with the proposed structures. Overall, the synthesis of hydrazone from the condensation of aldehyde and amino antipyrine was successfully achieved, and the synthesized compounds were characterized by various analytical techniques to confirm their molecular structures.

REACTION SCHEME

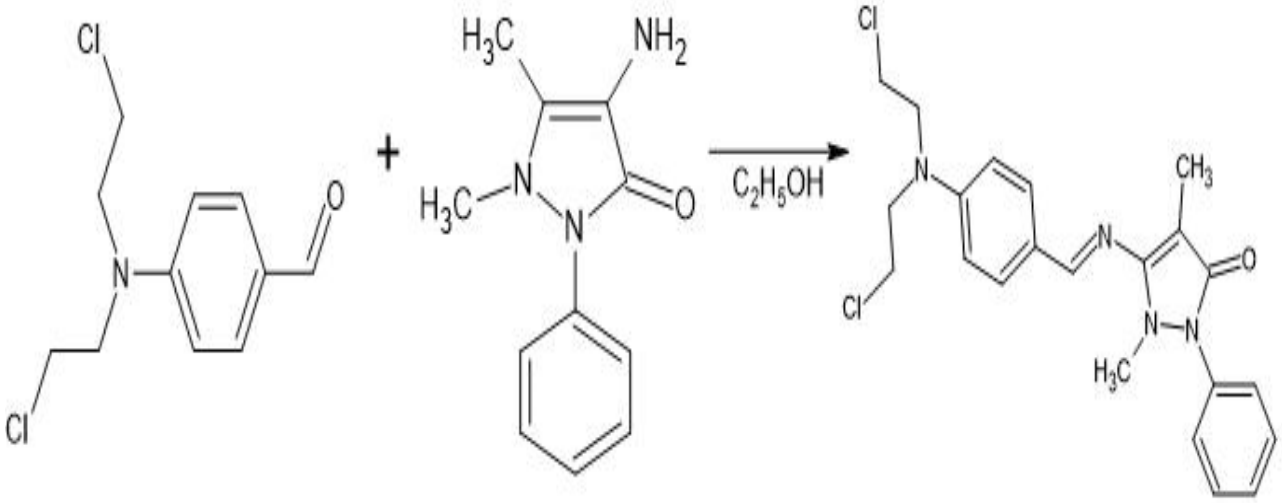

Fig: 5.1: Reaction scheme

5.2 STRUCTURE PREDICTED BY GAUSSIAN SOFTWARE

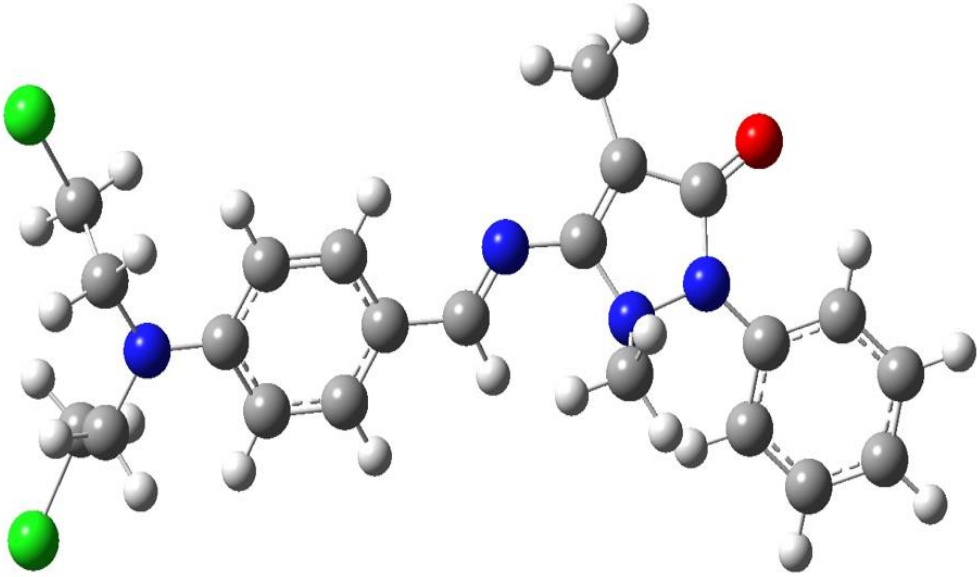

Fig: 5.2: Hydrazone structure

- indicates the presence of carbon atoms

- indicates the presence of hydrogen atoms.

- indicates the presence of nitrogen atoms.

- indicates the presence of chlorine atoms.

- indicates the presence of oxygen atom.

From the above representation, we can write down the molecular formula of the newly synthesized product which is $C_{22}H_{24}Cl_2N_4O$ and molecular weight of this product is 431.358g.

5.3 THIN LAYER CHROMATOGRAPHY [TLC]

TLC stands for Thin Layer Chromatography, which is a common analytical technique used to separate and identify different components in a mixture. In this case, the TLC was performed using 30% ethyl acetate as the mobile phase, which is a polar solvent.

During TLC, the mixture is spotted onto a thin layer of a stationary phase (such as silica gel or alumina) on a glass plate. The mobile phase (in this case, 30% ethyl acetate) moves up the stationary phase by capillary action, carrying the components of the mixture with it. The different components of the mixture have different affinities for the stationary and mobile phases, and thus move at different rates. This results in the separation of the components on the stationary phase, which can be visualized by staining or exposure to UV light.

In this case, the product and impurities in the mixture are separated on the stationary phase using 30% ethyl acetate as the mobile phase. The polar nature of ethyl acetate allows for good separation of polar compounds in the mixture, making it easier to identify the product and assess its purity level by visualizing the spots on the TLC plate.

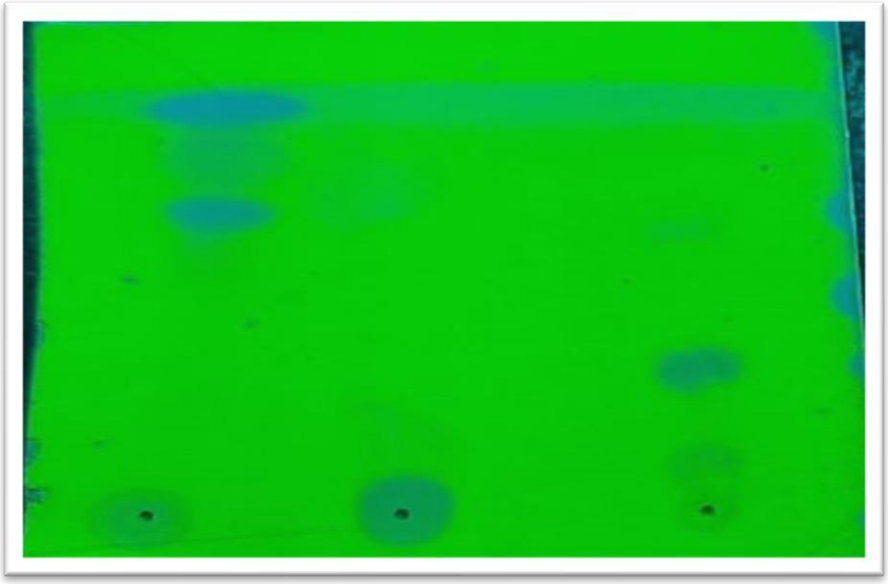

Fig:5.3: TLC

5.4 FOURIER TRANSFORM INFRARED ANALYSIS [FTIR]

IR gives us an idea about the presence of functional groups in the formed product. The functional group region starts from 4000 cm^{-1} – 1500 cm^{-1} and fingerprint region fall from 1500 cm^{-1} to 400 cm^{-1}.

1. CH=N stretching is at 2955 cm^{-1} with medium absorption strength.
2. C-N stretching is at 1233 cm^{-1} with medium absorption strength.
3. C=C stretching is at 1593 cm^{-1} with the absorption strength in between weak and medium.
4. C= O stretching is at 1647 cm^{-1} with the strong absorption strength.

The given information pertains to the infrared (IR) spectra of a compound, which provides valuable information about the functional groups and chemical bonds present in the molecule. The IR spectra is obtained by passing infrared radiation through the sample and measuring the frequencies at which the radiation is absorbed by the sample.

The CH=N stretching vibration at 2955 cm^{-1} with medium absorption strength is indicative of the presence of a hydrazone functional group (C=N-NH-R), which is formed by the condensation of a ketone or aldehyde with a hydrazine or hydrazide. This peak is caused by the stretching of the carbon-nitrogen double bond in the hydrazone group.

The C-N stretching vibration at 1233 cm^{-1} with medium absorption strength is also indicative of the presence of the hydrazone functional group. This peak is caused by the stretching of the single bond between the carbon and nitrogen atoms in the hydrazone group.

The C=C stretching vibration at 1593 cm^{-1} with the absorption strength in between weak and medium is indicative of the presence of a carbon-carbon double bond in the molecule. This peak is caused by the stretching of the carbon-carbon double bond.

The C=O stretching vibration at 1647 cm^{-1} with strong absorption strength is indicative of the presence of a carbonyl functional group (C=O). This peak is caused by the stretching of the carbon-oxygen double bond in the carbonyl group.

Overall, the information provided by the IR spectra gives us valuable insight into the functional groups and chemical bonds present in the molecule, allowing us to identify and characterize the compound.

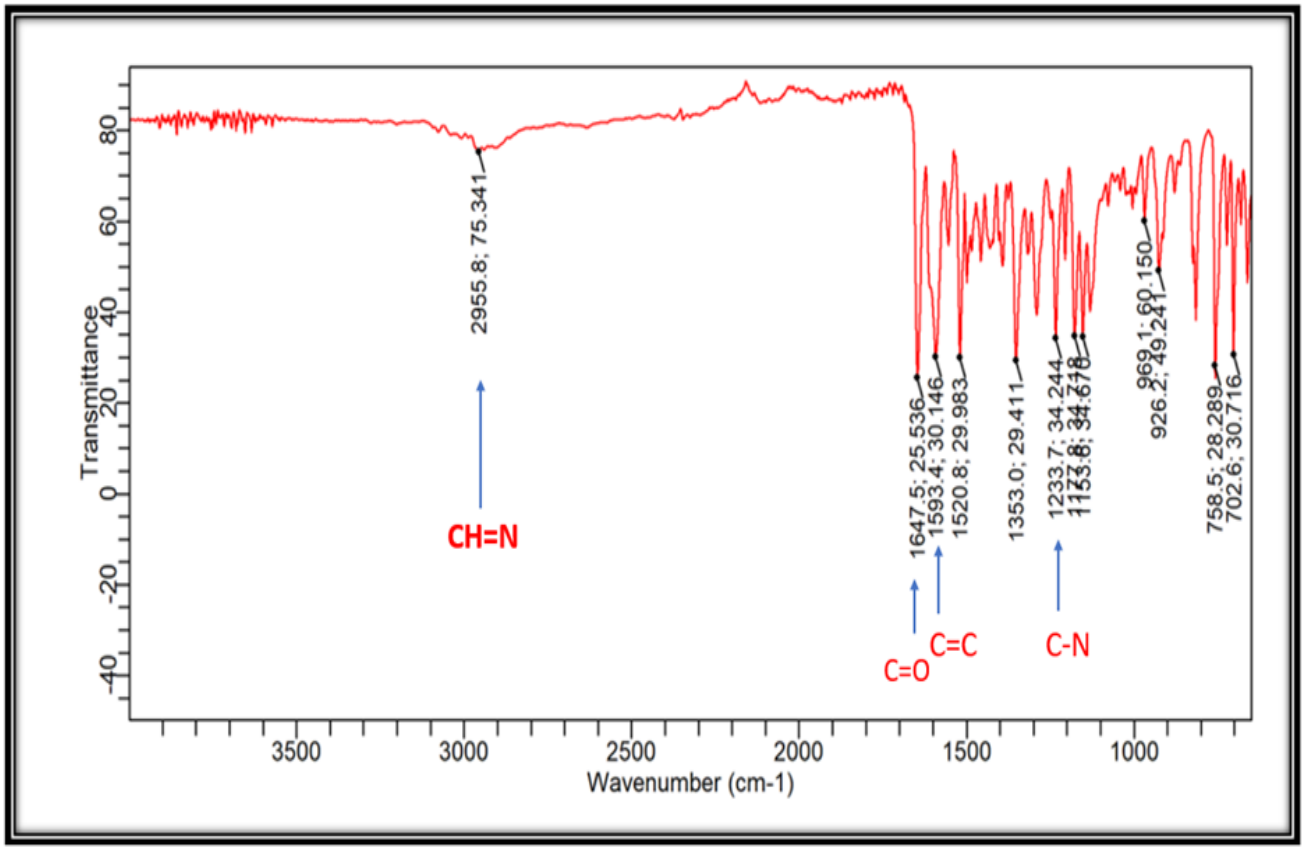

Fig: 5.4: Spectral data of FTIR

5.5 UV-VISIBLE SPECTROSCOPY

A UV-visible spectrophotometer is a scientific instrument used to measure the absorption and transmission of light in the ultraviolet (UV) and visible (Vis) regions of the electromagnetic spectrum. It works by shining a beam of light through a sample and measuring the amount of light that is absorbed or transmitted. This information can then be used to determine the concentration or purity of the sample, as well as to identify and quantify certain compounds. UV-visible spectrophotometers are widely used in analytical chemistry, biochemistry, and materials science, among other fields.

The UV-VISIBLE spectra of the compound show maximum absorption peak at 356.5nm. this maximum absorption of hydrazone was assigned to (n-π*) transition.
The maximum absorption peak at 356.5 nm in the UV-visible spectrum of the compound is indicative of a (n-π*) transition. This type of transition involves the excitation of an electron from a non-bonding nitrogen orbital (n) to an antibonding π*

orbital, which is typically localized on a carbon-nitrogen double bond in the case of a hydrazone. The (n-π*) transition is often observed in hydrazones and other compounds containing N=C or N=N double bonds.

The (n-π*) transition is a type of electronic transition that occurs in molecules with conjugated double bonds or with a lone pair of electrons on a heteroatom such as nitrogen or oxygen. In the case of a hydrazone, the presence of the nitrogen atom with a lone pair of electrons makes it susceptible to this type of transition. The energy required to promote an electron from the non-bonding nitrogen orbital to the antibonding π* orbital corresponds to a wavelength of light in the UV-visible region, which in this case is 356.5 nm. In the main, the presence of a maximum absorption peak at 356.5 nm in the UV-visible spectrum of the compound and its assignment to a (n-π*) transition provides valuable information about the electronic structure and bonding in the molecule.

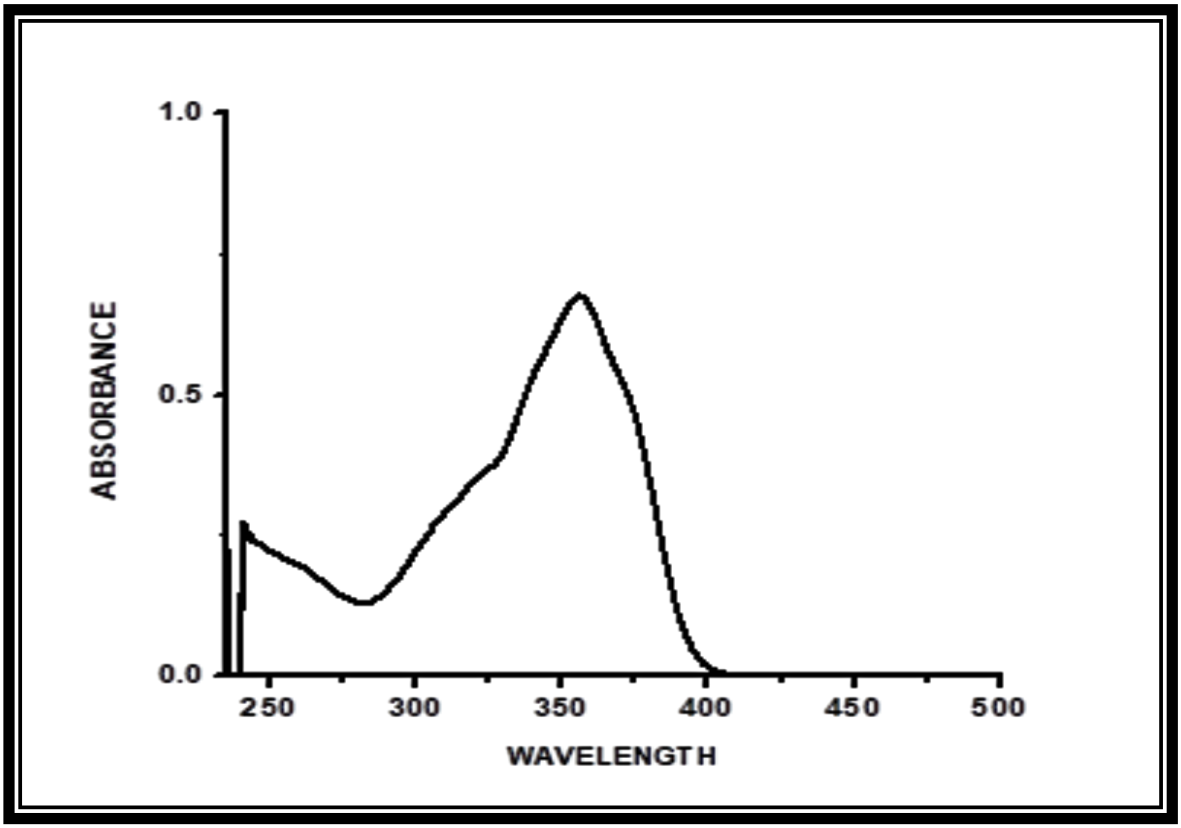

Fig: 5.5: Spectral data of UV-VISIBLE

5.6 NUCLEAR MAGNETIC RESONANCE ANALYSIS [NMR]

[THEIORTICAL PERDICTION OF NMR INTERPRETATION PEAKS]

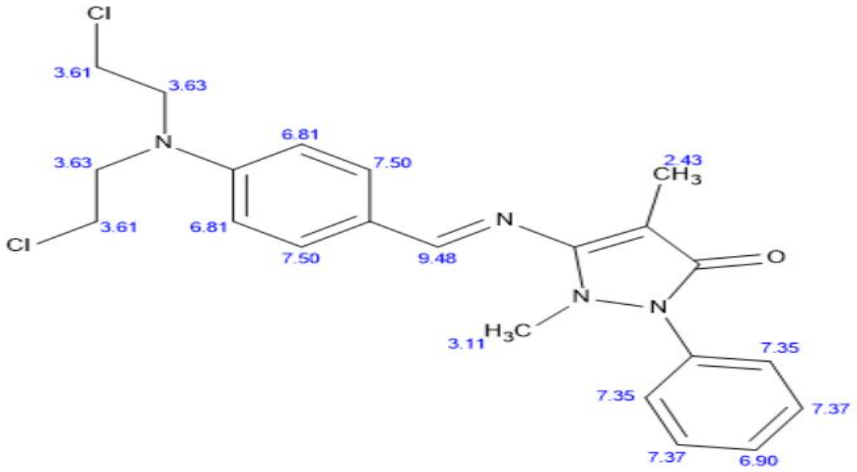

Fig:5.6: Theoretical view of NMR peaks

EXPERIMENTAL GRAPH

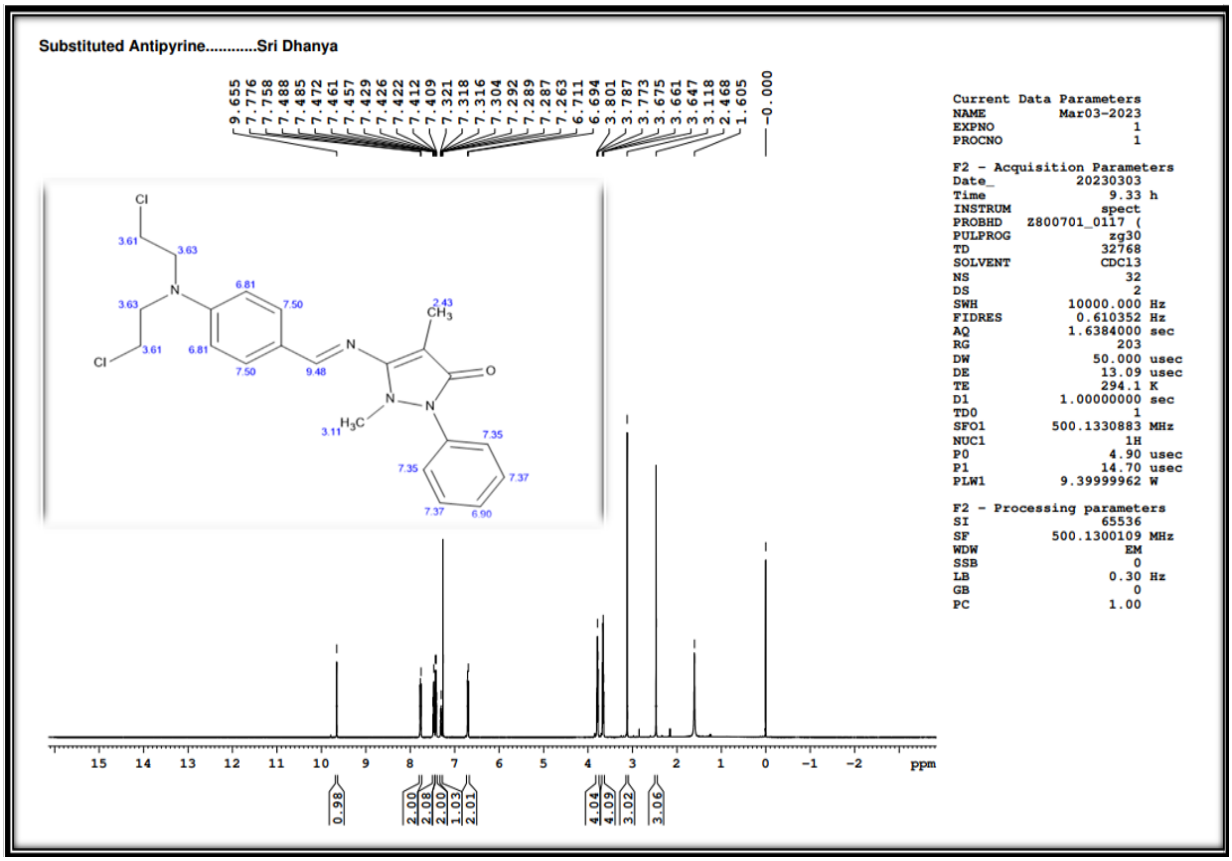

Fig:5.7: Spectral data of NMR

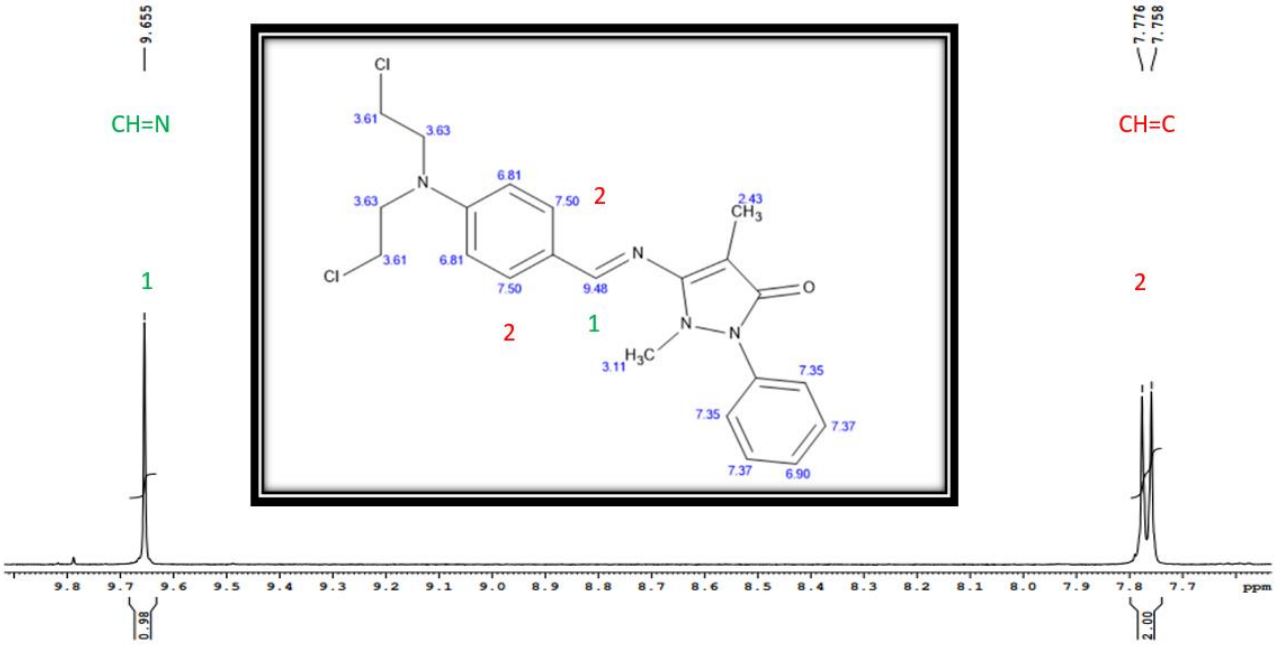

Fig:5.7.1: Spectral data of NMR

Single peak at 9.655ppm may be due to CH=N. This has singlet with 1 H atom. Two peaks at 7.776-7.758 may be due to CH=C of benzene ring, which is doublet with 2 H atoms.

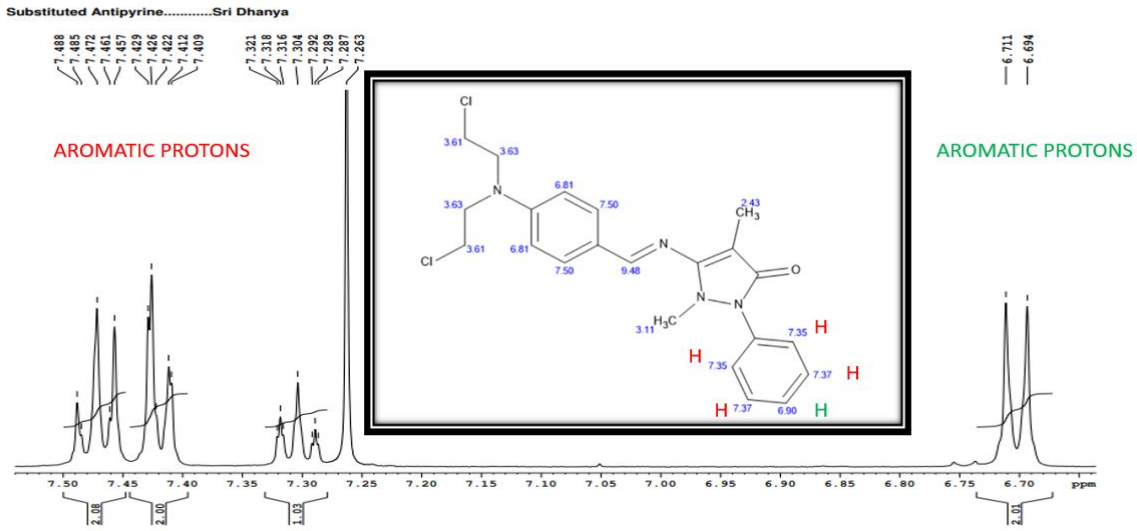

Fig:5.7.2: spectral data of NMR

AT 2ppm to 7.4ppm range have aromatic protons which is of benzene. Here, 7.45-7.48 shows triplet with 2 H atoms, 7.40-7.42ppm range shows doublet with 2 H atoms and 7.32-7.26ppm shows triplet with 1 H atom. At 6.7-6.9ppm shows doublet with 2 H atoms.

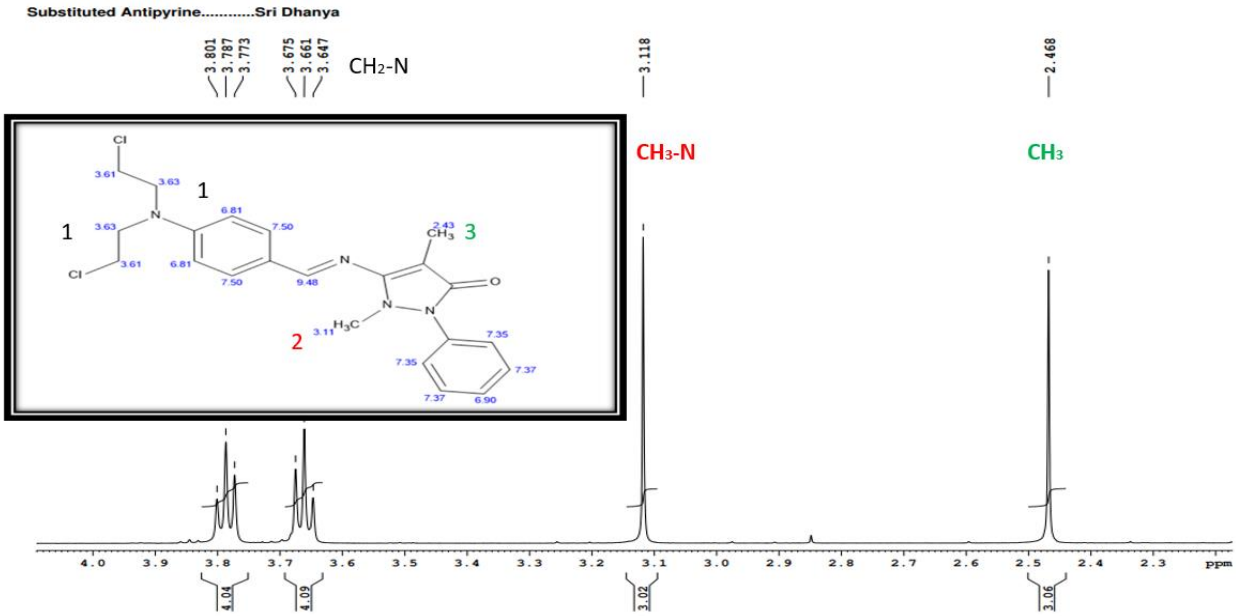

Fig:5.7.3: spectral data of NMR

Single peak at 2.468ppm may be due to methyl group, which forms singlet with 3 H atoms. Single peak at 3.118ppm may be due to CH3-N group, which forms singlet with 3 H atoms. The range of 3.64-3.67ppm may be due to CH2-N group, which forms triplet with 4 H atoms.

Basically, these NMR signals provide information about the different types of protons present in the molecule, including those in functional groups such as CH=N, CH=C, aromatic rings, methyl groups, and nitrogen-containing groups such as CH3-N and CH2-N. The chemical shifts and peak patterns can be used to identify these functional groups and aid in determining the molecular structure of the compound.

5.7 MASS SPECTROMETRY [MS]

The hydrozone compound synthesized through the condensation reaction of aldehyde and amino antipyrine was analyzed using high-resolution ESI mass spectrometry in positive mode. The spectrum revealed a highly intense peak at m/z 475, which corresponds to the [M+H]+ ion and represents the molecular weight of the compound. The calculated m/z values agreed well with the experimental values, indicating the reliability and accuracy of the mass spectrometry data. This information is critical for identifying and characterizing the hydrozone compound accurately, which can further

be utilized for developing new applications or optimizing existing ones. The mass spectrometry analysis results provide valuable insight into the chemical properties of the synthesized compound, which can be utilized to further investigate its potential applications in various fields, including pharmaceuticals and materials science.

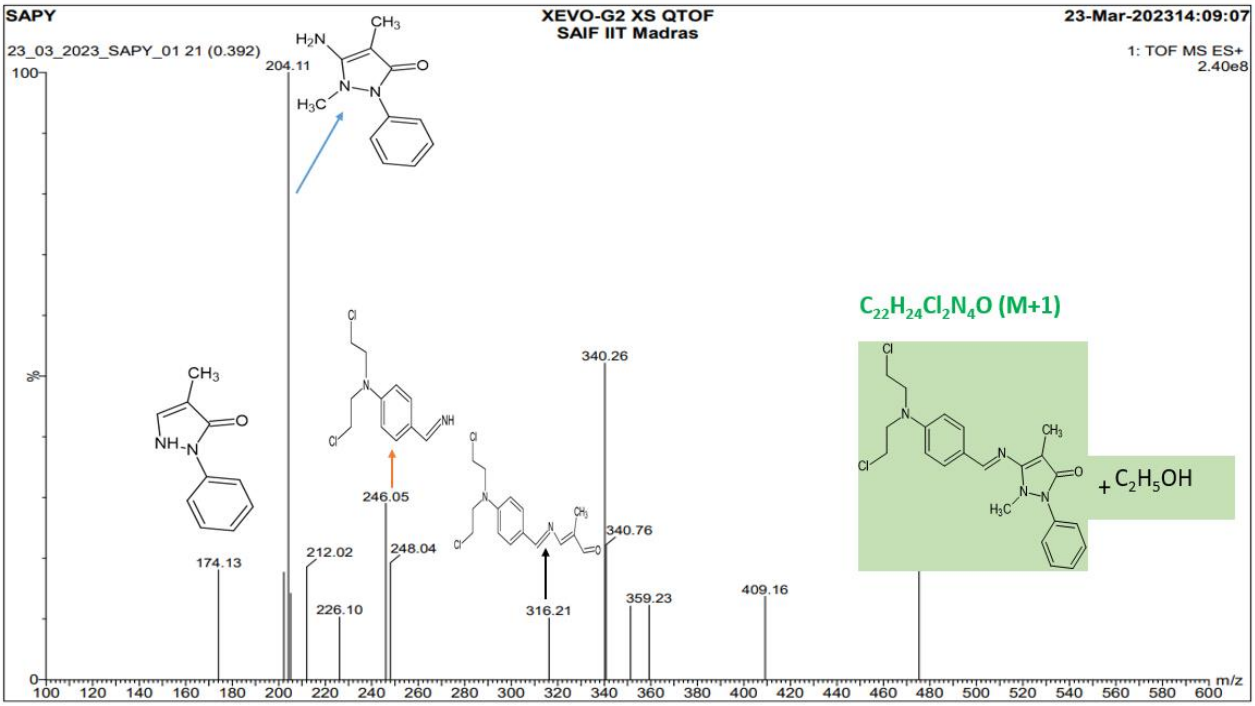

Fig:5.8: spectral data of MS

5.8 FRONTIER MOLECULAR ORBITALS ANALYSED BY USING GAUSSIAN SOFTWARE

In quantum chemistry, the frontier molecular orbitals (FMOs) are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a molecule. These orbitals play a critical role in determining the electronic and optical properties of a molecule, including its reactivity, stability, and band gap. The band gap is the energy difference between the HOMO and LUMO orbitals and represents the minimum amount of energy required to excite an electron from the valence band (HOMO) to the conduction band (LUMO).

In the given paragraph, it is stated that the HOMO and LUMO values of the newly synthesized hydrazone were determined to be -0.21509eV and -0.08710eV, respectively. These values indicate the relative energies of the orbitals and can be used to calculate the overall energy band gap of the molecule. The energy band gap is obtained by subtracting the HOMO energy from the LUMO energy, and in this case, it lies between -0.21509eV and -0.08710eV.

A narrow band gap, as indicated by a small energy difference between the HOMO and LUMO orbitals, generally indicates a high electrical conductivity and a higher likelihood of the molecule being a good electron donor or acceptor. On the other hand, a wide band gap, as indicated by a large energy difference between the HOMO and LUMO orbitals, indicates a low electrical conductivity and a lower likelihood of the molecule being a good electron donor or acceptor.

In summary, the determination of the HOMO and LUMO values of the newly synthesized hydrazone provides valuable insight into its electronic and optical properties. The calculated band gap can be used to predict the molecule's potential applications in various fields, including materials science, electronics, and energy conversion.

HOMO

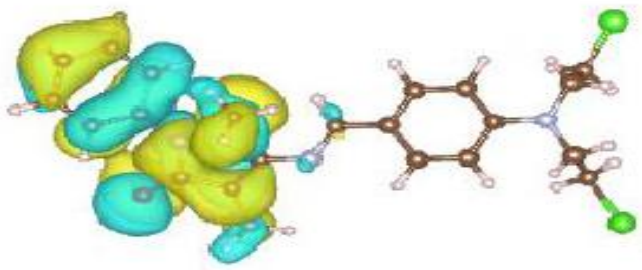

Fig:5.9: HOMO molecular orbital

LUMO

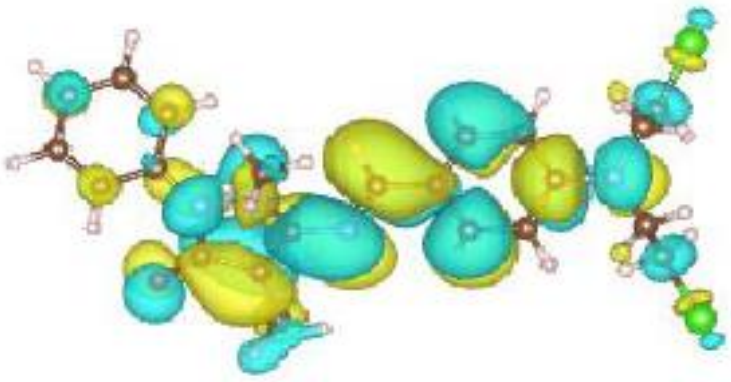

Fig:5.10: LUMO molecular orbital

CHAPTER 6

CONCLUSION

Based on the synthesis and characterization of 4-aminoantipyrine with 4[N,N-bis(2-chloroethyl)amino]benzaldehyde, it can be concluded that the desired product was successfully synthesized using the appropriate reaction conditions and purification techniques.

The characterization data, including FTIR, NMR, and mass spectrometry, confirmed the identity and purity of the synthesized product. The TLC analysis also provides the evidence of the product's purity.

In total, this study provides valuable information on the synthesis and characterization of 4-aminoantipyrine with 4[N,N-bis(2-chloroethyl)amino]benzaldehyde, which can be useful in the development of new applications and the optimization of existing ones. The results of this study can also contribute to the knowledge base of the scientific community in the field of organic chemistry.

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