Synthesis and Characterization of 2-amino 1,3,4-thiadiazole Based Azo Dyes

MONICALAKSHMI M

(20PCH011)

Thesis Submitted to

Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore- 641 043.

In Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE IN CHEMISTRY

May – 2022

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Signature of the

Supervisor

26/5/2022

Signature of the

Head of the Department


ACKNOWLEDGMENT

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It is with the choice of blessings and the divine grace of **LORD ALMIGHTY** that any human endeavor is achieved.

I record my sincere thanks to **Prof. S.P. Thyagarajan**, Chancellor, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for providing the support to do my research work.

I would like to thank **Dr. V. Bharathi Harishankar**, Ph.D., FRSA, Vice Chancellor, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for providing opportunity to develop and establish my skills.

I extend my thanks to **Dr. (Mrs.) S.Kowsalya**, M.Sc, Mphil, Ph.D., Registrar, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for providing the favourable infrastructure to do my research work.

I express my heartfelt thanks to **Dr. (Mrs.) G. Padmavathi**, M.Sc., M.Phil., Ph.D., Dean, School of Physical Sciences & Computational Sciences, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for her excellent support, and guidance during the course of the investigation.

I record my deep sense of gratitude to **Dr. (Mrs.) R. Saratha**, M.Sc., M.Ed, M.Phil., Ph.D., Professor and Head, Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for her encouragement and for providing all lab facilities at any time throughout my study.

I would like to extend my gratitude towards **Dr. (Mrs.) Subhashini.K.Sripathi**, M.Sc., Ph.D, Professor and Former HOD, Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for being as a motivation and guidance throughout my work.

I specially acknowledge my deep sense of gratitude and respect to my guide Dr. (Ms.) **V.Sharulatha**, M.Sc, M.Phil, Ph.D., NET, Assistant professor (SS), Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for her meticulous care, eminent guidance, and enormous help and continuous encouragement

throughout my project. I am grateful for her constant support for the successful completion of thesis work efficiently and effectively.

I would like to express my sincere thanks to all the Staff Members of the Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for their help and support in the successful completion of this dissertation.

My special thanks to Ph.D research scholars **Kiruthika.S**, **Abinaya.A and Keerthana.L**, Department of Chemistry and my friends who have been with me in all my stages of work and supported me to do my work successfully.

A personal note, my special tribute to my beloved parents and my brothers for their encouragement during my entire study.

MONICALAKSHMI M


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CONTENTS

S.NO	CHAPTER	PG.NO
	LIST OF ABBREVIATIONS	
	LIST OF FIGURES	
	LIST OF TABLE	
1.	INTRODUCTION	1
2.	REVIEW OF LITERATURE	14
3.	MATERIALS AND METHODS	37
4.	RESULTS AND DISCUSSION	41
5.	SUMMARY AND CONCLUSION	58
6.	REFERENCES	59

LIST OF ABBREVIATIONS

DMSO	Dimethyl Sulfoxide
DMF	Dimethyl Formamide
FT-IR	Fourier Transform Infrared
H^1 NMR	Proton Nuclear Magnetic Resonance
UV	Ultra Violet
PL	Photo Luminescence (Spectrofluorometer)
TLC	Thin Layer Chromatography

LIST OF FIGURES

FIGURE NUMBER	NAME OF FIGURE	PAGE NUMBER
1.	UV Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	43
2.	UV Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol	44
3.	UV Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	44
4.	FT-IR Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	47
5.	FT-IR Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol	48
6.	FT-IR Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	49

7.	H^1 NMR Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	52
8.	H^1 NMR Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol	53
9.	Expanded H^1 NMR Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol	54
10.	H^1 NMR Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	55
11.	Expanded H^1 NMR Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	56
12.	Fluorescence Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol	57

LIST OF TABLES

TABLE NUMBER	**NAME OF TABLE**	**PAGE NUMBER**
1.	The Yield and Melting point of the Synthesized Compounds	42

Introduction

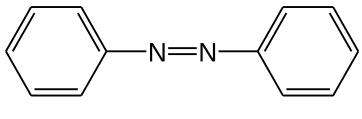
1. INTRODUCTION

1.1. DYES

In recent years, dyes are play an important role in everyday life. Generally, dyes are a soluble organic substance used to colour the materials. Dye was a coloured substance but all the coloured substance was not dye. The dyes are chemically bonds to the substrate to which it is being applied. They contained chromophore and auxochrome groups in their structure. The colour of the dye was depended on the chromophore and auxochrome groups present in the dye compound **(O.B. Agho *et al.*, 2016).**

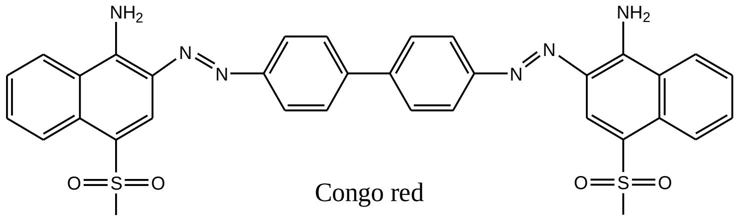
Dyes are characterised by their capacity to absorb light radiation in the visible spectrum from 380 to 750nm. The chromophoric groups are used to transformation of white light into coloured light by reflection on a body or by transmission or diffusion results from the selective absorption of energy. The dyes are capable of absorbing certain luminous radiations and then reflecting the complementary colours **(A. Benaissa 2012).**

The dye should fix itself on the substrate to produce a permanent coloured appearance but all the dyes are not necessarily exposed coloured substances. For example, azobenzene**(1)** produce red colour but it was not attached to substrate. Hence, it was not a dye compound when exhibit red coloured substance. While, Congo red**(2)** was applied on cotton fabric and retained by it. Therefore, it was a dye compound. Some colourless dye compounds are used as an optical brightners or white dyes. They have a special property of absorbing ultraviolet light and re-emitting the visible light so that the fabric appears bright. **(Gurdeep R.Chatwal ., 2004).**



Azobenzene (Red coloured but not a dye)

(1)

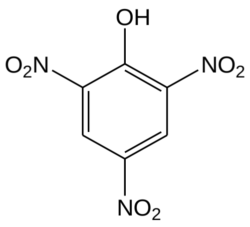


Congo red

(2)

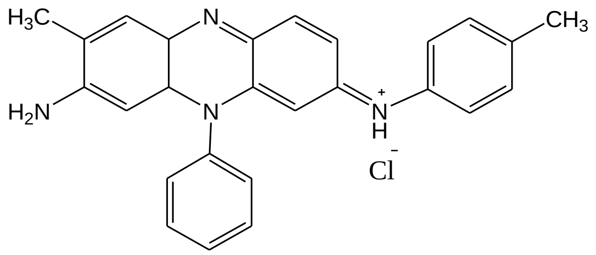
1.2. HISTORY OF DYES

The first synthetic Picric acid dye**(3)** was synthesised by Woulfe in 1771. It was not any significance rather than dyeing silk fabrics. For this reason, William H.Perkin was decided to make quinine from aniline but he was got a purple coloured dye instead of quinine. These dyes are called as Mauveine**(4)**. The brilliant work of Perkin immediately attracted much attention and stimulated other chemists to carry out similar experiments **(Gurdeep R.Chatwal ., 2004).**



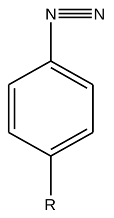
Picric acid

(3)



Mauveine

(4)

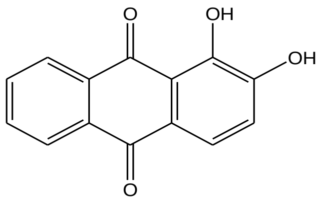


Aryl diazonium salt

(5)

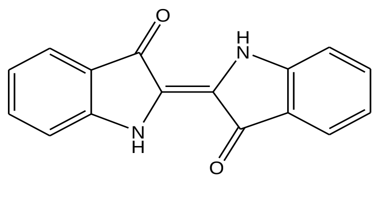
In 1858, aryl diazonium salts was discovered by Johann Peter Griess who working on azo dye compounds. After the discovery of aryl diazonium salts, many developments in dye and other organic industries are occurs. Aryl diazonium salt**(5)** was prepared by diazotisation of aromatic primary amines. Some of the aryl diazonium salt was unstable in organic reaction. They are the intermediates in the production of various azo dyes **(Griess JP *et al.*, 1858).**

After the brilliant work of Kekule on a quadrivalence of carbon in 1858 and on the constitution of benzene in 1865, the work was planned to started for the preparation of purely synthetic dyes and also for the artificial production of natural dyes. The first successful achievement for this direction was elucidation of constitution as well as the synthesis of alizarin**(6)** by Graebe and Liebermann in 1868. Then, Adolf von Baeyer was synthesised an indigo dye**(7)** in 1870 **(Gurdeep R.Chatwal ., 2004).**



Alizarin

(6)



Indigo dye

(7)

Most of the dyes are derived in nineteenth century were synthesised from the aromatic intermediate chemicals isolated from the coal tar distillation. Hence, the synthetic dyes are called as coal-tar dyes. At present, in our country several variety of dyes are manufactured in large scale and also they are exported to other countries. Therefore, dye-stuff firms are increased in the world wide competition for the dye stuffs and intermediates **(Gurdeep R.Chatwal ., 2004).**

1.3. AZO DYES

Azo dyes are play a major role in dye chemistry. The azo dyes are form the largest group of all the synthetic colorants. The chromophoric system of these dyes are the azo group -N=N- which was associated with one or more aromatic systems **(Gurdeep R.Chatwal ., 2004).**

The desired colour properties, yield and particle size of the dye for improved dispersibility was obtained by various routes and modifications.**(Ganapathi S.Shankarling *et al.,* 2017).**

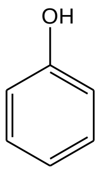
Approximately more than 60% of azo dyes was used in many fields of science then that of total dyes. In industry, around 70% of azo dye are used in all dyes **(O.I.Lipskikh *et al.,* 2017).**

Normally, Azo dyes are synthesised by simple method of diazotization of aromatic amines and coupling with various compounds.

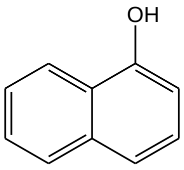
a) Diazotization: Diazotization are a process of conversion of a primary aromatic amino compound into a diazonium salt in presence of acid and at low temperature (0-5^{o}C). Most of the solid diazonium salts are explosives when are unless suitably stabilised. Therefore, diazonium salts are not isolated in industries.

b) Coupling reaction: Coupling reaction are also known as substituting reaction where the diazonium carbon act as an electrophilic reagent they are substituted on a carbon atom of the benzene ring activated by an amino hydroxyl group. Generally, aromatic amines and phenols are used as a coupling components. Coupling reactions are pH dependent to exist equilibrium but not only the pH. It also depended upon the reactivity of both the diazonium salt and coupling components. In some coupling reactions, the addition of an organic bases such as pyridine are used to increasing the rate of the coupling reaction **(M.G.Arora ., 1996).**

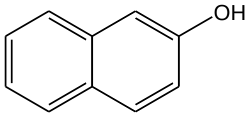
Phenols**(8)** and naphthols such as alpha naphthol**(9)**, beta naphthol**(10)** are the major role in production of commercial azo dyes. All naphthols moiety bearing hydroxy group as an auxochrome in a dye compound. Such a compound like 2,4-dihydroxybenzophenone**(11)** bearing two hydroxy group as an auxochrome and a keto group as a chromophore. Hence, these compounds have wide application as a polymer-additives, excellent UV absorber which prevented the photodegradation of most vinylpolymers **(Bharat C.Dixit *et al.*, 2007).**



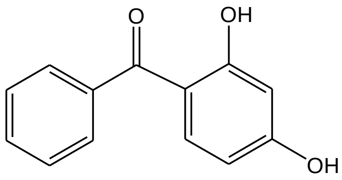
Phenol
(8)



alpha naphthol
(9)

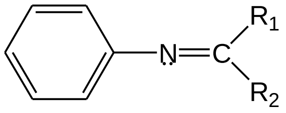


beta naphthol
(10)



2,4-dihydroxybenzophenone
(11)

Some of the azo dyes are synthesised from Schiff bases. Schiff bases**(12)** are produced by the reaction of primary amines with an aldehyde or a ketone derivative under specific conditions. Structurally, a Schiff bases are a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) have been replaced by an imine or azomethine group. Schiff bases are used as the applications in biology (including antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory, antimalarial and antiviral activities) and also a catalyst in several reactions such as polymerization reaction, reduction of thionyl chloride, oxidation of organic compounds, reduction of ketones, aldol reaction, Henry reaction, epoxidation of alkenes, hydrosilylation of ketones, synthesis of bis(indolyl) methanes and Diels-Alder reaction **(Ahmed M. Abu-Dief *et al.*, 2015).**



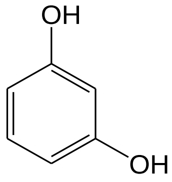
R_1=H ; R_2=CH_3
R_1=CH_3 ; R_2=CH_3

Schiff base
(12)

Initially, the azo based dyes are rarely pure due to the presence of impurities in the reactants and the occurrence of side reactions during manufacturing process. The synthetic precursor, intermediates and degradation products of these dyes are sometimes exhibit potential health hazards owing to both toxicity and their carcinogenicity. The presence of toxic amines in organism causes the biological reduction of an azo dyes. The reduction can also proceeds non-enzymatically. The identification of each elements especially for the detection of toxic degradation products such as aromatic amines from azo dyes are determined by selective chromatography separation techniques. The ability to quickly generate qualitative information are easily made by TLC method. TLC is one of the most popular technique of chromatography to differentiate many compounds and it is quite cost effective. **(Semiha Yenidogan *et al.*, 2009).**

The azo dyes are classified into various types depending on their number of azo group present in the dye molecules. For example, the azo dyes are called as monoazo, disazo (bisazo), trisazo, tetrakisazo and polyazo dyes according to whether there are one, two, three, four or more azo groups present in the dye molecule. The azo dyes are covered very wide hues **(Gurdeep R.Chatwal ., 2004).**

The synthesis of bifunctional colourants was the attention in recent years, because they are utilized as monomers for functional polymers via polyaddition and polycondensation reactions. For example, the resorcinol**(13)** undergoes coupling reactions at various pH conditions to yield monoazo and diazo dyes for textile fibres and leather **(Zhong Xin *et al.*, 2001).**



Resorcinol

(12)

Generally, the azo dyes are not fluorescent due to the azo linkage undergoes photoisomerization **(Cembran A *et al.*, 2004).** Other factors for non-fluorescence of the azo dye compound was the formation of excimer or exciplex forms **(Satam Manjaree *et al.*, 2013).** In solution, some azo dye compound showed weak fluorescence due to the existence of the hydrazone form in solution which decrease the population of azo form in the excited state and eventually photoisomerization. We need to get fluorescence compound should restrict its isomerization **(Yoshino J *et al.*, 2013).** The most essential feature of these dye was their existence in the azo-hydrazone equilibrium **(Umesh Warde *et al.*, 2016).**

1.4. HETEROCYCLIC AZO DYES

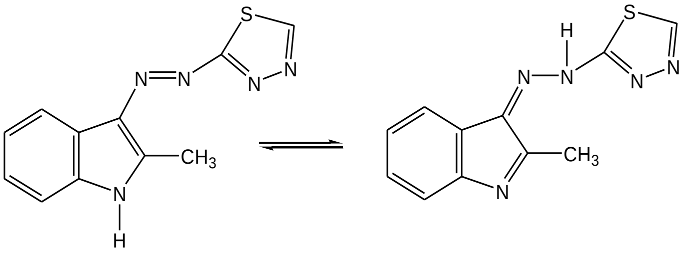
Heterocyclic compounds are a large number of naturally occurring substance which are essential for living cells in form of amino acids, proteins, pyrimidine and purine bases of DNA, enzyme co-factors, oxygen-carrying pigments haemoglobin, photosynthesizing pigment chlorophyll, etc. they are play a vital role in the metabolism of all living organisms and very important for almost all stage of biochemical processes necessary to support life **(Shukla *et al.*, 2017).**

Azo dyes based on heterocyclic amines have a lot of success since they have a more tinctorial strength and brighter dyeing than diazo dyes based on aniline. The majority of dispersed heteroarylazo and disazo dyes of technical significance for textile application are made up of five-membered rings with one sulphur atom and a diazotizable amino group. This heterocyclic ring may also be fused to an aromatic ring and include one or two nitrogen atoms. The best example of successful commercial exploitation of heterocyclic compounds is benzothiazole-based disperse dyes. In the synthesis of red dyes, the 2-aminobenzothiazole nucleus is used as a diazonium component. This type of dyes has been economically viable due to its low cost, brightness, and dyeing performance **(C. T. Keerthi Kumar *et al.*, 2016).**

In chemistry of disperse dyes, heterocycles are the first area to foster the industrial exploitation of heterocyclic amines. These diazo components having the ability to produce red to blue disperse dyes that meet the rigorous technical and economical requirements. Aminothiazole azo dye was the first heterocyclic diazo compounds of disperse dyes. They are used to produce brilliant red polyester dyes. 2-amino-5-ethylthio-1,3,4-thiadiazole was used in the replacement of red anthraquinone-based dyes which was commercially very successful. While, dyes synthesised from 2-amino-1,3,4-thiadiazole was the essential production of brilliant red shades. Generally, heterocyclic amines are produced brilliant scarlet to bluish-red shades on polyester fabrics depending on the various substituents in the diazo component and coupling agents used in the synthesis of dyes **(Hari R. Maradiya., 2002).**

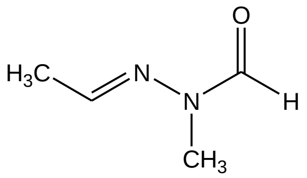
Disperse dyes are most essential class of dyes due to their brilliancy, broad range of colours and good fastness properties. These disperse dyes are used to dyeing the hydrophobic fibres such as nylon, polyester and acrylic fibres from an aqueous dispersion. In recent years, heterocyclic azo dyes have much attention for their greater molar extinction coefficients, brightness in colour and very high chromophoric strength and fastness properties. The heterocyclics contained with pyrazolone are essential dye and pigments which produce colorants of yellow to orange dye in industrial applications. Amino thiadiazole based azo dyes are incorporated with pyrazolone moiety, they exhibited the excellent tinctorial strength and brighter dyeing performance **(Mitchla S. M. *et al.*, 2018).**

In recent years, the dye synthesised from heterocyclic amines such as 2-aminothiazole and 2-aminothiophene derivatives as diazo components which tends to exhibit bathochromic shifts when compared to analogues dyes derived from benzenoid compounds. On the other hand, monoazo dyes are prepared from enol type coupling components shows two forms namely azo form**(13)** and hydrazone form**(14)** which is also called as azo-hydrazone tautomerism. From theoretical viewpoint and practical standpoint, the determination of azo-hydrazone tautomerism in solid state and in solution is very interesting since the tautomers have different technical properties and dyeing performance. From recent studies, the synthesis of bishetarylazo dyes such as hetarylazopyridones and hetarylazopyrazolones are exhibited the strong solvent dependence in their absorption spectra. These dyes are theoretically exhibited azo-hydrazone tautomerism in solution. **(Zeynel Seferoğlu *et al.*, 2008)**

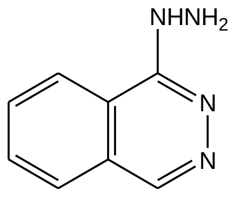


Azo form **(13)**   Hydrazone form **(14)**

In the field of synthetic chemistry, the hydrazone form of a dyes are the well known class of biologically and pharmacologically active compounds. Some hydrazones are very useful as potent drugs such as gyromitrin**(15)** and dihydralazine**(16)** are used as a toxin and hypertensive drug respectively. Besides the hydrazones are an essential class of chemical intermediates which act as electrophiles and as nucleophiles in chemical reactions. The tautomeric ratio was very important for the industrial application of azo dyes and the determination of azo-hydrazone tautomerism(AHT) in solid state and in solution. Therefore, it was very useful to determine the tautomeric structure of the products prior to exploring their applications. **(Mariam Al-Sheikh *et al.*, 2014)**



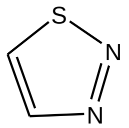
Gyromitrin
(15)



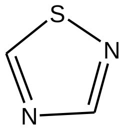
Hydralazine
(16)

1.5. THIADIAZOLE COMPOUNDS

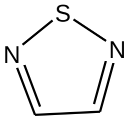
Thiadiazole was a heterocyclic aromatic compound with a five-membered ring system contained two nitrogen atoms and one sulphur atom with a molecular formula of $C_2H_2N_2S$. Thiadiazole compound was exhibited four various isomeric forms present in nature there are 1,2,3-thiadiazole**(17)**, 1,2,4-thiadiazole**(18)**, 1,2,5-thiadiazole**(19)**, and 1,3,4-thiadiazole**(20)**. In these isomers, 1,3,4-thiadiazole and its derivatives are possessed highly reactive to nucleophilic substitution reactions and provide a broad range of biological activities. Hence, these compounds are synthesised increasingly in the recent years and more research works are undertaken to these compounds **(Meltem Dagli *et al.*, 2020).**



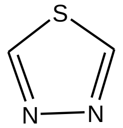
1,2,3-thiadiazole
(17)



1,2,4-thiadiazole
(18)



1,2,5-thiadiazole
(19)



1,3,4-thiadiazole
(20)

1,3,4-thiadiazole ring have a weak base because of the inductive effect of the sulphur atom and exhibited relatively high aromaticity although lower compared to 1,2,5-thiadiazole due to the relative position of a heteroatoms in the ring. They are thermally stable and relatively stable in acidic aqueous solutions but undergoes ring cleavage at basic conditions. The 1,3,4-thiadiazole ring was poor electron-deficient due to the electron-withdrawing effect of the nitrogen atoms and relatively inert to electrophilic substitution but easily exposed to nucleophilic attacks **(Y. Hu *et al.*, 2014).**

The sulphur atom possessed increasing lipophilicity and a great stability to the three-dimensional structure within a molecule **(M.Yoosefian *et al.*, 2015).**

The thiadiazole compounds contained one or more heteroatoms other than carbon and hydrogen such as nitrogen or sulphur and have maximum number of conjugated double bonds **(Meltem Dagli *et al.*, 2020).**

The pharmaceutically attractive 2-amino-1,3,4-thiadiazole derivatives was synthesised by the cyclization of thiosemicarbazides with nitroalkanes **(Nicolai A. Aksenov *et al.*, 2020).** Bioactive 1,3,4-thiadiazoles were synthesised from aromatic acids **(Zheng Li *et al.*, 2005).**

The thiadiazole and its derivatives are more focused in drugs, agricultural and material chemistry due to their high activity in 2’ and 5’ positions in substitution reactions. The two-electron donor nitrogen system (-N=C-S) and hydrogen-binding domain allow for great structural stability and it was responsible for biological activity **(Mustafa Er *et al.*, 2016).**

1.6. APPLICATIONS

1.6.1. DYES

Generally, the dyes are used in many fields like textile, foods, papers, colouring agents, cosmetics, liquid crystals, organic photoconductors, nonlinear optics and drug chemistry. In photography, the dyes are not only used for sensitizing photographic materials but also used for producing the image in colour photography. In colour photography, the pictures are obtained either by synthesis or bleaching of dyes in different light-sensitive layers, or by the transfer of dyes on to a receiving layer to form the picture **(M G Arora.,1996).**

1.6.2. AZO DYES

In addition to colouring properties, mono-azo dyes have broad interest in applications of optical materials such as optical storage capacity, optical switching, holography and non-linear optical properties, polymers with azo units represent promising photoactive materials **(He Jin-An *et al.*, 2000).** These properties depended on the environment of the molecules such as gas, solvent and liquid crystals **(Umesh Warde *et al.*, 2016).**

The pharmacological application of azo dye compounds originated from the discovery of antibacterial action of prontosil on streptococcal infections by dogmagk. Furthermore, azo dye compounds exhibited variety of biological activities including antibacterial, anifungal, pesticides, antiviral, antioxidant and anti-inflammatory activities **(Thawra Ahmad *et al.*, 2015).**

Azo dye chromophores are excellent photoisomerization properties and sensitivity towards the polarized light. **(Said Benkhaya *et al.*, 2019).**

Aromatic azo compounds are used as organic dyes, indicators, radical reaction initiators, therapeutic and drug delivery agents. They are essential in the area of nonlinear optics, optical storage media, chemo sensors, photochemical switches and electronic devices.

Azo compounds provide strong chromophoric label, so serve as an essential analytical tool. Their concentration was easily determined by colorimetric, spectrophotometric or spectrofluorimetric methods **(Thawra Ahmad *et al.*, 2015).**

In the field of science and technology, Azo dyes are most widely used class of colouring material due to their massive applications. These dyes are very essential in textile, printing, leather, paper making, drug and food industries **(V.G.Vidya *et al.*, 2018).**

Azo dyes are successfully employed as LCD colour fillers, chromophoric substrates for redox enzymes, optical switches, chemical sensors, textile dyes, lasers, optical data storage, non-linear optics and advanced applications in organic synthesis. Azo dyes exhibited bright and strong shades that range from red to green and blue **(C.T.Keerthi Kumar *et al.*, 2013).**

Among the azo dyes, heterocyclic azo dye compounds are very important because of their brilliant colour, excellent light, washing and sublimation fastness, and chromophoric strength **(Hessamoddin Yousefi *et al.*, 2012).**

1.6.3. HETEROCYCLIC AZO DYES

The majority of heterocyclic azo dyes was carried out by technical interest for application to textiles are derived from the diazo components containing a five-membered ring with one sulphur heteroatom and to which a directly attached a diazotisable amino group. The ring may also possess one or more nitrogen heteroatoms. These dye compound produced red to blue disperse dyes that are very important in technical and ecological requirements **(Hari R.Maradiya 2002).**

In the dyes, the activity of azo linkage increases with incorporation of suitable heterocyclic moiety. The uses of these dyes increased in electronic industry such as colorimetric sensors, Non-Linear Optical(NLO) devices, Liquid Crystalline Displays(LCDs) used as potential sensitizers for Photo Dynamic Therapy(PDT) has developed more interest in research **(Demirbas *et al.*, 2009).**

In addition to the ongoing studies on benzothiazole dispersion dyes have sparked attention in a variety of non-textile uses also. For example, Azobenzothiazole dyes have been used in liquid crystal technology, reprography and non-linear optics (NLO) and more recently used as potential sensitizers for photodynamic therapy(PDT). They are employed in a variety of applications in chemical and analytical methods such as spectrophotometry, solid phase extraction, liquid chromatography, and electrochemistry. They have the potential to be biologically active, which is significant for their use in the pharmaceutical industry **(C. T. Keerthi Kumar *et al.*, 2016).**

1.6.4. THIADIAZOLE AZO DYES

Thiadiazole was a versatile moiety that possessed a wide variety of biological activities. Thiadiazole moiety act as ‘hydrogen binding domain’ and ‘two-electron donor system’. They are also act as a constrained pharmacophore and the bio-isosteric replacement of the thiazole moiety. Therefore, they are act as third-generation and fourth-generation cephalosporins which can be used in antibiotic preparations. It also used in synthesis of cyanine dyes **(Wafaa S.Hamama *et al.*, 2013).**

1,3,4-thiadiazole analogues azo dyes are very interesting group for new pharmaceuticals with a number of desirable effects including neuroprotective, antifungal, antibacterial, anti-inflammatory, antioxidants, and anti-cancer activity **(Iwona Budziak *et al.*, 2019).**

1.6.5. FLUORESCENCE DYES

In 1960, the fluorene-based dye compounds are introduced to relief of the pain. Fluorene was homologous ring and they have medical and biological important in medicinal and pharmaceutical application. The heteropolymer fluorene derivative was considered as effectiveness against cancer and malaria. Fluorene based aromatic dye compounds are very interest as a building block for production of drugs, pharmaceuticals and fine chemicals of industrial relevance including application in the production of thermosetting plastics and lubricating materials. In addition, fluorene-based polymers and copolymers showed unusual optical and electrical properties, and used in organic light-emitting diodes, flat panel displays and solar cells **(Thawra Ahmad *et al.*, 2015).**

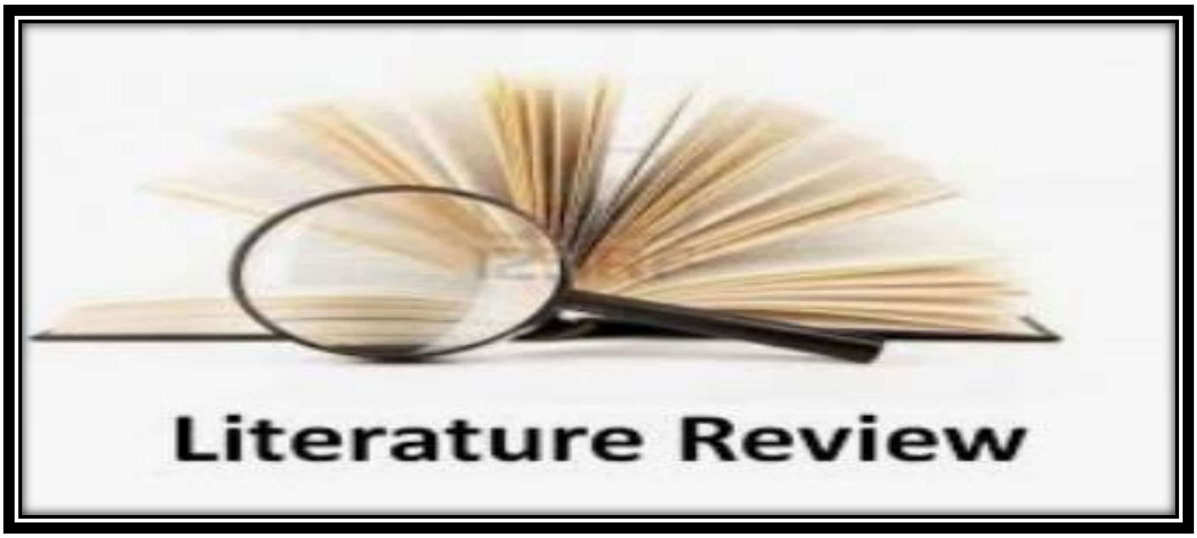
Adsorption indicators are generally fluorescent dyes which was used in very interesting application in precipitation titrations **(M G Arora.,1996).**

Fluorescent dyes are characterised by exceptionally bright colour due to their absorption and emission takes place in the visible region. Fluorescent dyes have extended pi-system and an extremely rigid. Fluorescence are suppressed by the substituents such as chlorine, bromine, nitro group and azo groups due to their intersystem crossing nature. The fluorescent dye compounds showed a thermogravimetric analysis value above 240^oC and they are potential for polymer applications. Fluorescent dyes are widely used in application of paints, inks, food, cosmetics, textile industry, for a solid-state dye laser system, polymer treatment, optical fibres and solid-state dye-labelled DNA to detect volatile compounds in the vapour phase **(Prakhar P Kasture *et al.*, 2010).**

OBJECTIVE

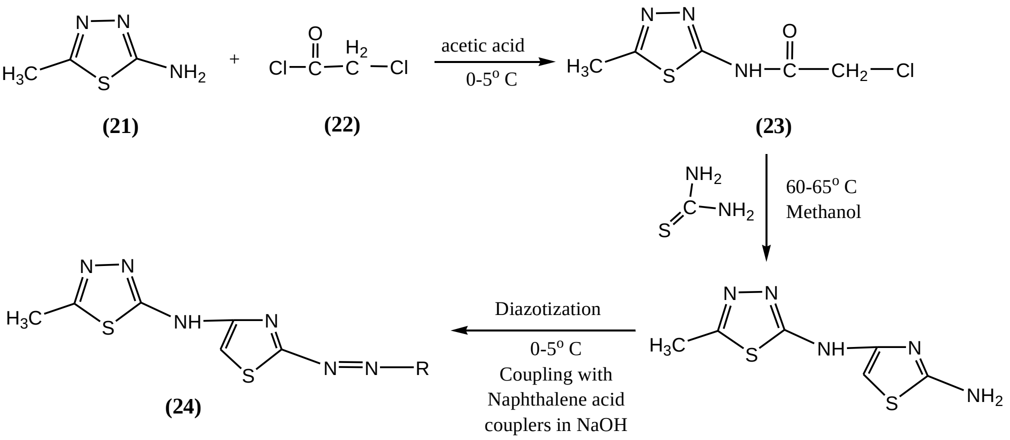
The reaction of diazotization of 5-phenyl-2-amino-1,3,4-thiadiazole with coupling components such as resorcinol and β-naphthol in presence of nitrosyl sulphuric acid yielded the corresponding 5-phenyl-2-amino-1,3,4-thiadiazole based azo dyes **Chinnagiri T. Keerthi Kumar in 2013**. But the structure was not confirmed by spectroscopic data. **Agnieszka Kudelko in 2020** established the structure as 2-amino 1,3,4-thiadiazole based azo dyes. The reaction of diazotization of 2-amino-1,3,4-thiadiazole with coupling components such as 2,4-quinolinediol in presence of nitrosyl sulphuric acid yielded the corresponding 2-amino-1,3,4-thiadiazole based azo dyes **(Izzet Sener *et al.*, 2006).** On the other hand, the reaction of diazotization of 5-methyl-2-amino-1,3,4-thiadiazole with coupling components such as β-naphthol in presence of nitrosyl sulphuric acid yielded the corresponding 5-methyl-2-amino-1,3,4-thiadiazole based azo dyes **(G. M. Malik *et al.*, 2018)** with the above-mentioned views, the present work aims.

- To prepare 2-amino 1,3,4-thiadiazole based azo dyes.
- To identify the chromophores and determine the absorbance of a sample with the help of UV double beam spectrometer.
- To characterize and predict the structure of compounds by FT-IR and H^1 NMR techniques.
- To analyse the fluorescence properties of the sample using PL (Spectrofluorometer).

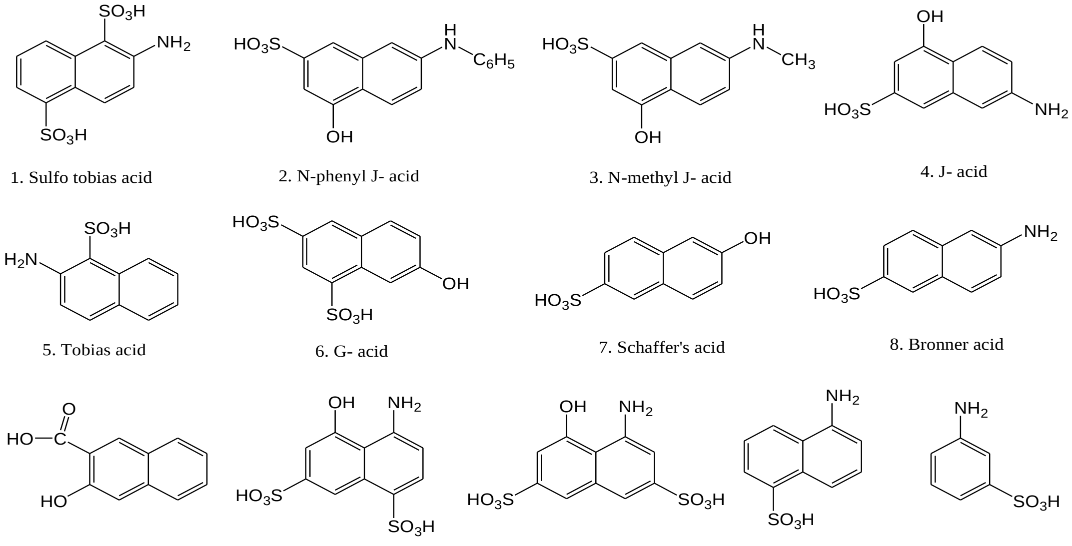

Literature Review

2. REVIEW OF LITERATURE

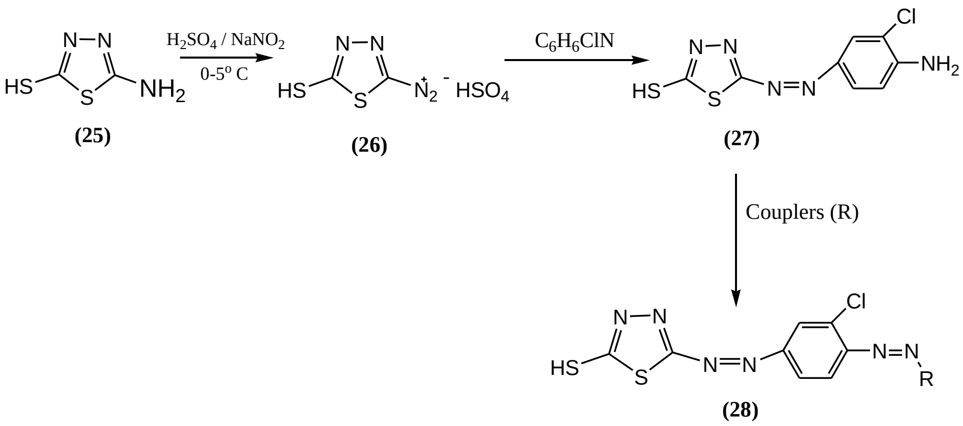
G.M.Malik *et al.*, (2018) developed the synthesis, characterization and dyeing performance of thiadiazole derivatives. In this study, 2-amino-5-methyl-1,3,4-thiadiazole**(21)** in acetic acid and chloroacetylchloride**(22)** reacts to form 2-chloro-N-(5-methyl-1,3,4-thiadiazol-2-yl)acetamide**(23)** which was diazotized with thiourea under cyclization at reflux temperature 60-65°C in methanol and coupled with series of naphthalene based acid couplers (like R= metanilic acid, sulfo tobias acid, bon acid, J-acid, G-acid, H-acid, K-acid, Bronner acid, Schaffer’s acid, Laurent acid, N-phenyl J-acid, N-methyl J-acid and tobias acid) in sodium hydroxide to yield series of azo dyes containing 1,3,4-thiadiazole moiety**(24).**



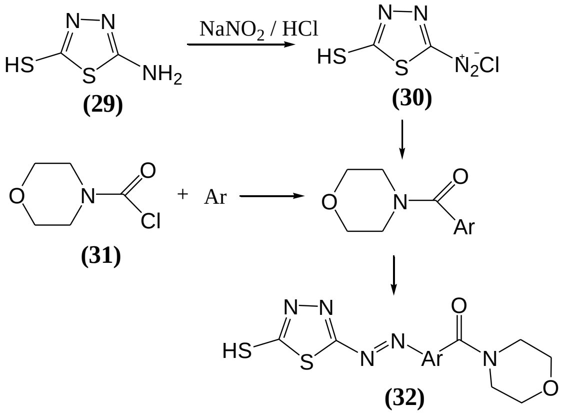
Chemical structure of coupling components (R)


1. Sulfo tobias acid
2. N-phenyl J- acid
3. N-methyl J- acid
4. J- acid
5. Tobias acid
6. G- acid
7. Schaffer's acid
8. Bronner acid
9. Bon acid
10. K- acid
11. H-acid
12. Laurent acid
13. Metanilic acid

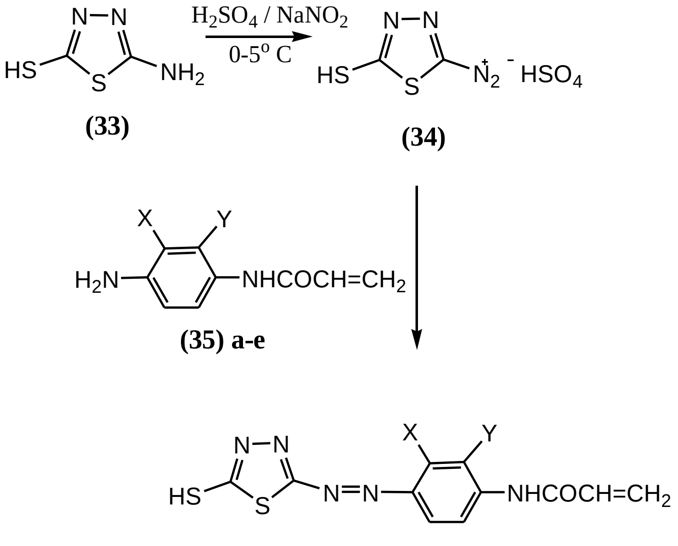
In recent years, the synthesis of disazo dyes from an environmental friendly heterocyclic compounds was predominantly investigated for dyestuff industry. In this investigation, 5-amino-2-mercapto-1,3,4-thiadiazole**(25)** in concentrated sulphuric acid treated with sodium nitrite in water to form an intermediate called diazonium salt**(26)** which was treated with 2-chloroaniline in acetic acid to give a azo dye compounds**(27)** further it was treated with couplers (like R= 2-chloroanilne, 2-amino-9-ethylcarbozole, 2-naphthol in NaOH, m-anisidine and 4-aminonaphthalene) in acetic acid to yield a disazo dyes **(28). (J.O. Otutu *et al.,* 2014).**



H. Hamidian *et al.,* (2013) studied the synthesis of new 1,3,4-thiadiazole derivatives containing of morpholine ring. In this study, 2-amino-5-mercapto-1,3,4-thiadiazole**(29)** was diazotized by concentrated hydrochloric acid and sodium nitrite to form diazonium salt**(30)** which was coupled with the reaction of morpholine carbonyl chloride**(31)** and aromatic compounds (Ar= aniline, 3-nitroaniline, 1-naphthole, Resorcinol, 1-amino-2-hydroxy-4-naphthalene sulphonic acid, 4-amino-5-hydroxy naphthalene-2,7-disulphuric acid) to give a azo dyes containing 1,3,4-thiadiazole derivatives with morpholine ring**(32).**

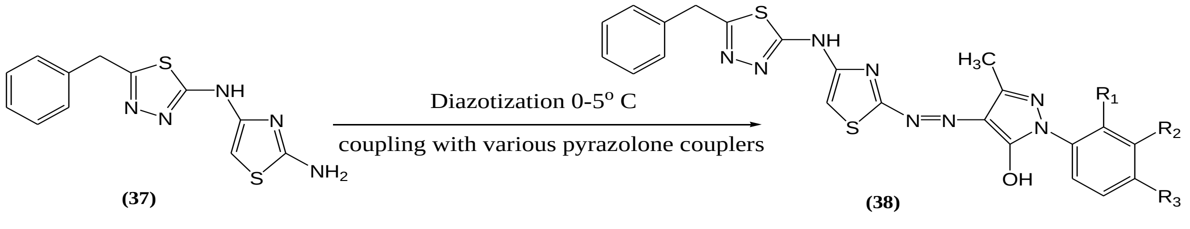


The diazotization of 2-amino-5-mercapto-1,3,4-thiadiazole**(33)** with concentrated sulphuric acid and sodium nitrite at 0-5°C to give diazonium salt**(34).** Then it treated with coupling components**(35)** such as N-(4-amino-3-nitrophenyl)acrylamide, N-(4-aminophenyl)acrylamide, N-(4-amino-3-chlorophenyl)acrylamide, N-(4-amino-3-methylphenyl)acrylamide and N-(4-amino-2-methylphenyl)acrylamide to form monoazo dyes based on 2-amino-5-mercapto-1,3,4-thiadiazole**(36). (Hari R. Maradiya *et al.*, 2009).**



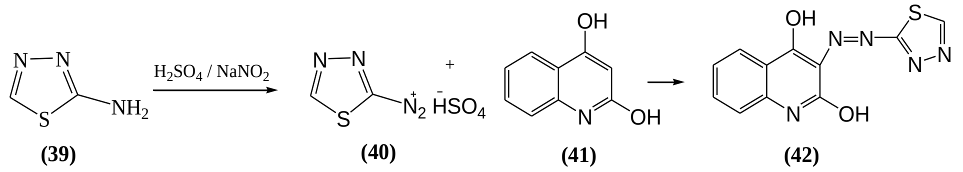
a- X=Y=H
b- $X=NO_2$, Y=H
c- X=Cl, Y=H
d- X=Me, Y=H
e- X=H, Y=Me

Mitchla S. M *et al.*, (2018) reported the synthesis and characterization of monoazo pyrazolone dyes based on 1,3,4-thiadiazole and their dyeing performance on polyester fabric. In this study, N^4-(5-benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine**(37)** was diazotised and coupled with various phenyl pyrazolone to produce a new series of 1,3,4-thiadiazole based heterocyclic monoazo dyes**(38).**

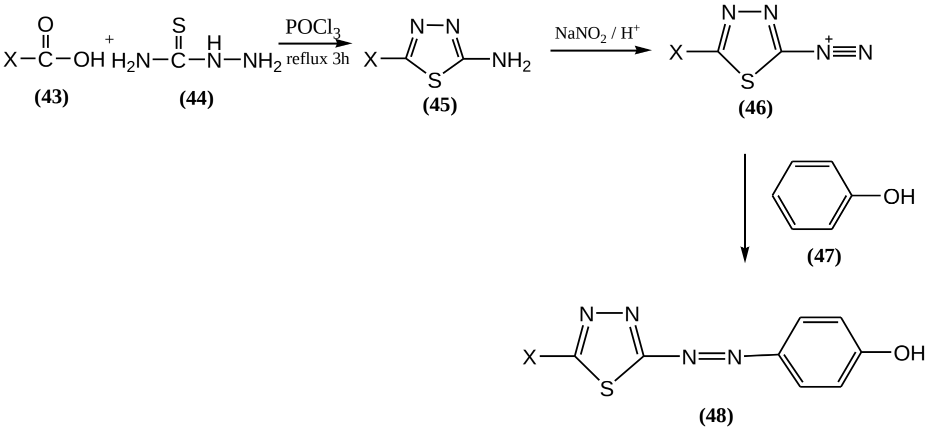


R_1=Cl, R_2=R_3=H ;
R_1=NO_2, R_2=H, R_3=NO_2;
R_1=H, R_2=NH_3, R_3=H ;
R_1=R_2=R_3=H ;
R_1=R_2=H, R_3=Cl ;
R_1=R_2=Cl, R_3=H.

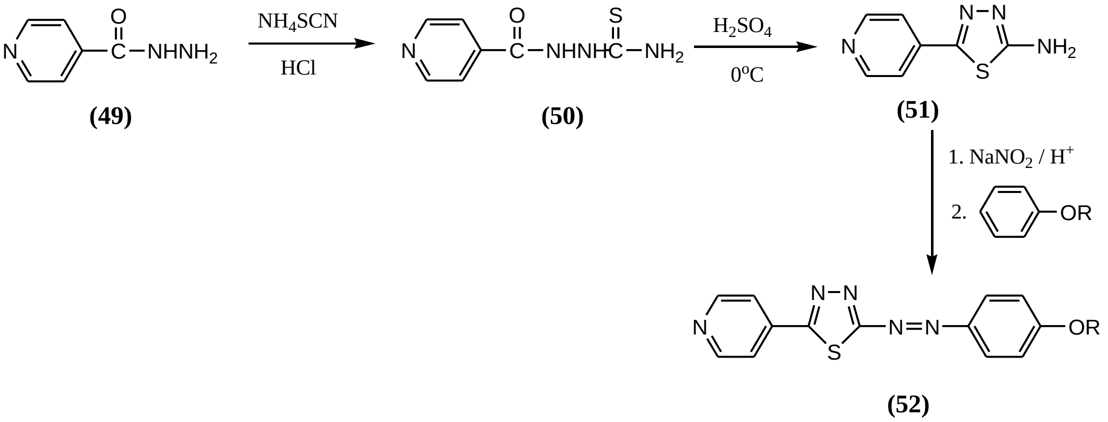
The reaction of 5-amino-1,3,4-thiadiazole**(39)** in glacial acetic acid with concentrated sulphuric acid and sodium nitrite under cold condition to form an intermediate which are diazonium salt**(40),** then it was treated with 2,4-quinolinediol**(41)** in sodium carbonate to give a product of azo dyes containing 1,3,4-thiadiazole**(42).** The crude product was recrystallised by DMF-H_2O mixture(1:1). **(Izzet Sener *et al.*, 2006).**



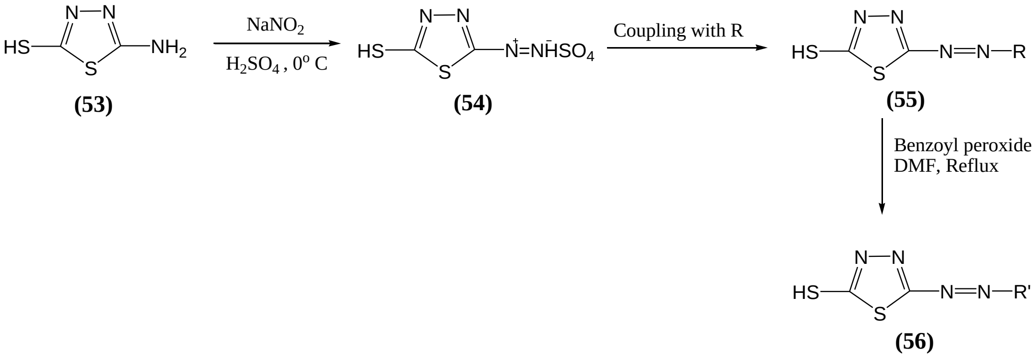
Ivan Hameed R. Tomi *et al.*, (2011) discovered the synthesis, characterization and biological activities study of some azo derivatives of aminothiadiazole derived from nicotinic and isonicotinic acids. In this study, the mixture of substituted carboxylic acid**(43)** and thiosemicarbazide**(44)** in presence of phosphorous oxychloride to produce 5-substituted-2-amino-1,3,4-thiadiazole**(45)** which dissolved in 85% phosphoric acid and then treated with concentrated nitric acid and sodium nitrite in water to give diazonium salt**(46).** Then it was reacted with phenol**(47)** in water to yield azo dyes with 1,3,4-thiadiazole**(48),** it was recrystallised from ethanol.



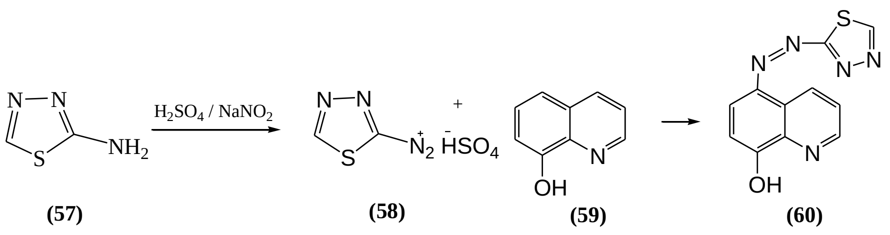
M. Parra *et al.*, (2001) reported the azo compounds exhibits the liquid crystalline properties and they showed monotropic nematic phase. The azo compound containing 1,3,4-thiadiazole was synthesised by the reaction of 4-pyridine-carbonylhydrazine**(49)** in alcoholic HCl solution and ammonium thiocyanate in ethanol to produce 4-pyridine-carbonylthiosemicarbazide**(50)** which was treated with concentrated sulphuric acid to form 5-(4-pyridyl)-2-amino-1,3,4-thiadiazole**(51),** it was dissolved in 85% phosphoric acid. Then diazotised by concentrated nitric acid with sodium nitrite in water and coupled with n-alkoxybenzene to yield a azo dyes containing 1,3,4-thiadiazole**(52).**



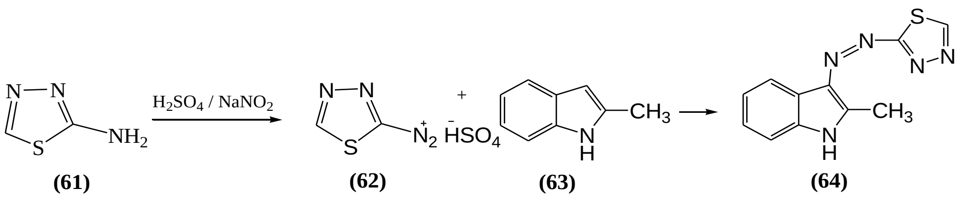
Hari Raghav Maradiya *et al.*, (2001) exhibited the polymeric dyes based on thiadiazole derivatives. In this paper, the 2-amino-5-mercapto-1,3,4-thiadiazole**(53)** was diazotized by concentrated sulphuric acid and sodium nitrite to form an intermediate called diazonium salt**(54).** The diazonium salt was coupled with various N-arylmaleimides (like R= N-phenylmaleimide) in acetic acid to give monomeric dyes**(55).** Then, it was reacted with benzoyl peroxide under free radical polymerization of monomeric dyes to produce the polymeric dyes with 1,3,4-thiadiazole**(56).**



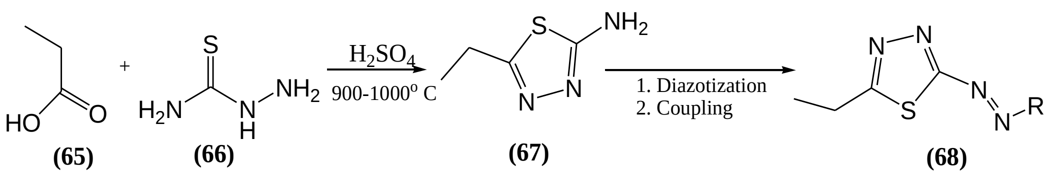
The reaction of 2-amino-1,3,4-thiadiazole**(57)** in hot glacial acetic acid-propionic acid mixture(2:1) with nitrosyl sulphuric acid prepared from concentrated sulphuric acid and sodium nitrite to produce diazonium salt**(58)** which was coupled with 8-hydroxyquinoline**(59)** in potassium hydroxide to yield the product of azo dyes**(60).** They are recrystallised by ethanol. **(Aytul Saylam *et al.*, 2006).**



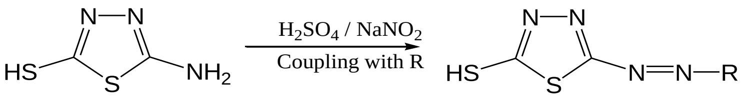
Zeynel Seferoğlu *et al.,* (2008) was described the synthesis, spectroscopic properties and crystal structure of novel bis-hetarylazo disperse dyes. In this study, 2-amino-1,3,4-thiadiazole**(61)** in hot glacial acetic acid-propionic mixture(2:1) was reacted with H_2SO_4 and $NaNO_4$ to give diazonium salt**(62),** then it was coupled with 2-methylindole**(63)** in glacial acetic acid-propionic mixture(3:1) to yield a series of hetarylazoindole dyes**(64).** They are recrystallazied by ethanol. They exist in two tautomeric forms, which was azo form and hydrozone form. Both these forms undergo deprotonation to give a common anionic form of hetarylazoindole dyes. The ʎ$_{max}$ shifted bathochromically in all solvents used due to the electron-donating substituents in the thiazole ring. The absorption maxima of the dyes shifted bathochromically in the order of sequence was acetic acid>DMSO>DMF>acetonitrile~methanol>chloroform. These were revealed by spectroscopic techniques.



C.T. Keerthi Kumar *et al.,* (2013) investigated the synthesis, characterisation and antimicrobial activity of heterocyclic azo dyes derived from thiadiazole. In this study, 5-ethyl-1,3,4-thiadiazole-2-amine**(67)** was synthesised by single step process from the reaction of propionic acid**(65)** and thiosemicarbazide**(66)** in sulphuric acid. A series of heterocyclic azo dyes**(68)** are synthesised from the diazotization by concentrated sulphuric acid and sodium nitrite and coupling components(R= 8-hydroxyquinoline, 2-naphthol, resorcinol, N,N-dimethyl aniline, 2,6-diaminopyridine).

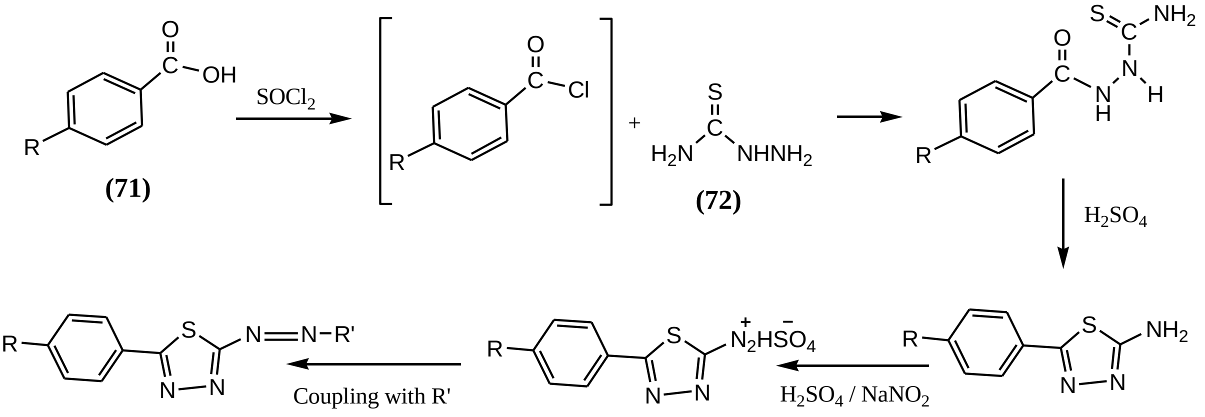


Z. Seferoglu *et al.,* (2006) exhibited the synthesis and spectral properties of new hetarylazo indole dyes. In this paper, a series of hetaryazo dyes**(70)** are manufactured from the reaction of a 5-amino-1,3,4-thiadiazole-2-thiol**(69)** with concentrated sulphuric acid in $NaNO_2$ and coupling with R (2-phenylindole, 2-methylindole, 1-methyl-1-phenylindole).



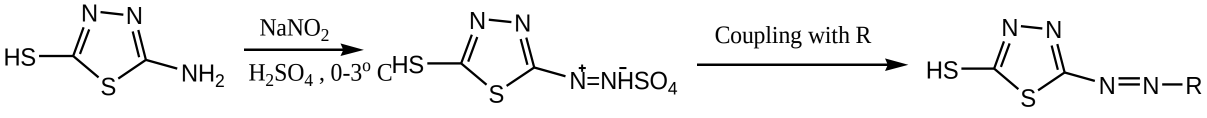
(69) (70)

Agnieszka Kudelko *et al.*, (2020) studied the 1,3,4-thiadiazole containing azo dyes: synthesis, spectroscopic properties and molecular structure. In this study, a substituted aromatic carboxylic acid**(71)** was treated with thionyl chloride($SOCl_2$) and thiosemicarbazide**(72)** in sulphuric acid to form a 2-amino 5-substituted 1,3,4-thiadiazole derivatives**(73),** which were diazotized by concentrated sulphuric acid and $NaNO_2$ to form diazonium salt**(74).** Finally, it was coupled with R' (R'= aniline, phenol, dimethylaniline) to yield a azo dyes containing 1,3,4-thiadiazole**(75).**



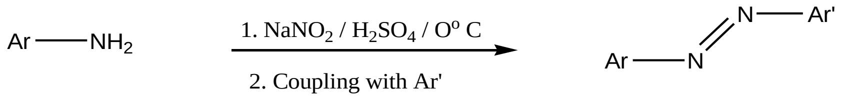
(71) (72) (75) (74) (73)

Hari Raghav Maradiya *et al.*, (2001) was described the synthesis and application of 2-aminothiadiazole disperse dyes for nylon fabrics. The 2-aminothiadiazole disperse azo dyes**(77)** were prepared by the coupling reaction of various N-arylacrylamides (R= N-phenylacrylamide, N-m-nitrophenyl-acrylamide, N-m-tolylacrylamide, N-o-tolylacrylamide) with the diazonium salt from 2-amino-5-mercapto-1,3,4-thiadiazole**(76)** in nitrosylsulphuric acid to yield of 65-85% at pH of 4-5. The colour changes from reddish brown to deep brown. These dyes have very good exhaustion and fixation in fabrics. This indicates, they have excellent affinity and solubility with nylon fabrics.



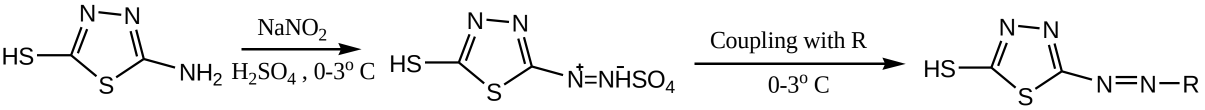
(76) (77)

Mingxing Wang *et al.*, (2003) studied the synthesis and properties of bis(hetaryl)azo dyes. In this study, a series of bis(hetaryl)azo dyes**(79)** are manufactured by diazotized arylamines**(78)** (Ar= 2-amino-1,3,4-thiadiazole) in presence of H_2SO_4 and $NaNO_2$ with coupling compounds(Ar'= N,N-diethylaniline) in methanol.



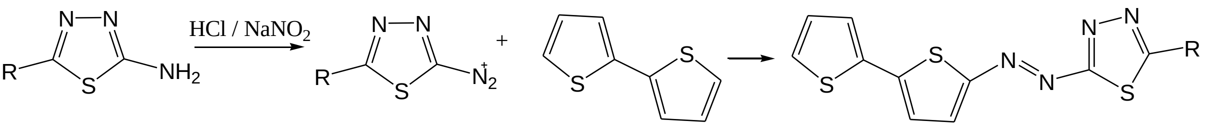
(78) **(79)**

Hari.R.Maradiya *et al.*, (2002) determined the monoazo disperse dyes based on 2-amino-1,3,4-thiadiazole derivatives. These dyes show excellent dyeing performance on nylon fabric. The reaction of 2-amino-5-mercapto-1,3,4-thiadiazole**(80)** in presence of nitrosylsulphuric acid to form diazonium salt**(81)** which was coupled with R (R= N-phenylmaleimide, N-o-chlorophenylmaleimide, N-nitrophenylmaleimide, N-m-chlorophenylmaleimide, N-m-tolylmaleimide, N-o-tolylmaleimide) to yield the Azo dyes**(82).** The purity of dye was estimated by TLC using ethyl acetate - benzene (1:4) as the solvent system. In this study, the presence of heterocyclic ring on azo compounds gives excellent performance on dyeing nylon fabric.



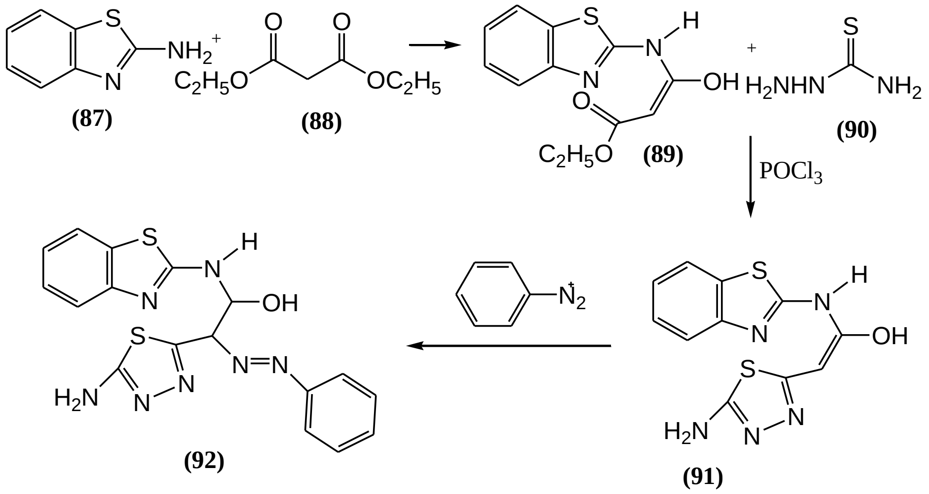
(80) **(81)** **(82)**

Two series of novel thermally stable second-order nonlinear optical (NLO) heterocyclic azo dyes are synthesised by two series of compounds which was based on various combination of acceptor groups (like thiadiazole) attached to bithiophene acts as donor group and as a pi conjugated bridge. From the investigation, 2-amino-1,3,4-thiadiazole**(83)** dissolved in HCl and mixed with $NaNO_2$ in water to form diazonium salt**(84)** which was coupled with bithiophene**(85)** in acetonitrile and acetic acid to yield azo dyes**(86).** They are diluted by chloroform, washed with water and finally dried with anhydrous $MgSO_4$. **(M. Cidália R.Castro *et al.*, 2012).**

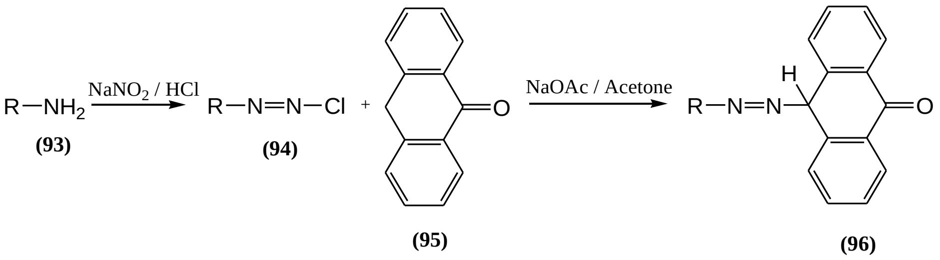


(83) **(84)** **(85)** **(86)**

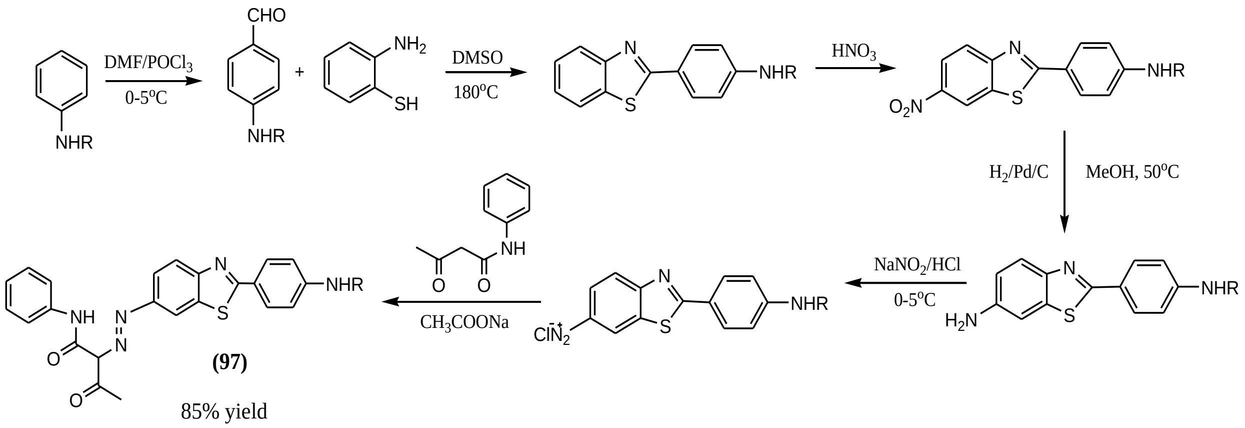
2-amino-1,3-benzothiazole**(87)** was reacted with malonic ester**(88)** to form benzothiazole ester derivatives**(89)** which was treated with thiosemicarbazide**(90)** in presence of $POCl_3$ to produce 2-[5-amino-1,3,4-thiadiazol-2-yl]-1-(benzothiazole-2yl-amino)-ethanol**(91).** They are dissolve in DMF and coupled with diazonium salt of aniline to yield the product of azo dyes**(92).** They are recrystallised from DMSO and H_2O (3:1). **(Mahmut Gür., 2019).**



Hemat M. Dardeer *et al.*, (2020) studied the synthesis, spectroscopic and molecular docking studies of novel 10-hetarylazo-9-anthrone derivatives as potential antimicrobial and anticancer agents. In this study, hetaryl amines**(93)** (like 2-amino-1,3,4-thiadiazole, 2-amino-benzo-1,3-thiazole, 3-amino-pyridine, 2-amino-1,3-thiazole) was diazotised by HCl and $NaNO_2$ to produce diazonium salt**(94)** which was coupled with anthrone**(95)** in presence of sodium acetate and acetone to yield the product of azo dyes**(96).**



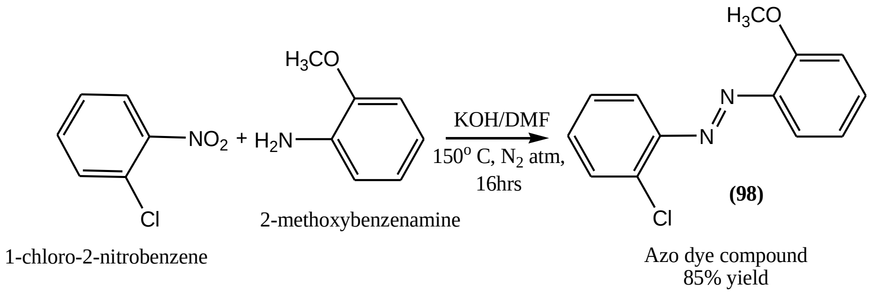
Prakhar P Kasture *et al.*, (2010) investigated the synthesis and characterization of benzothiazole-based solid-state fluorescent azo dyes. The strong solid-state fluorescence under long UV light of 365nm was used to characterised these azo dye compounds**(97).** TGA analysis of these dyes showed thermal stability up to 270°C. Therefore, the fluorescent azo dye was used as polymer application. These dyes were applied to polyester fabric through the disperse dyeing method.



(97)

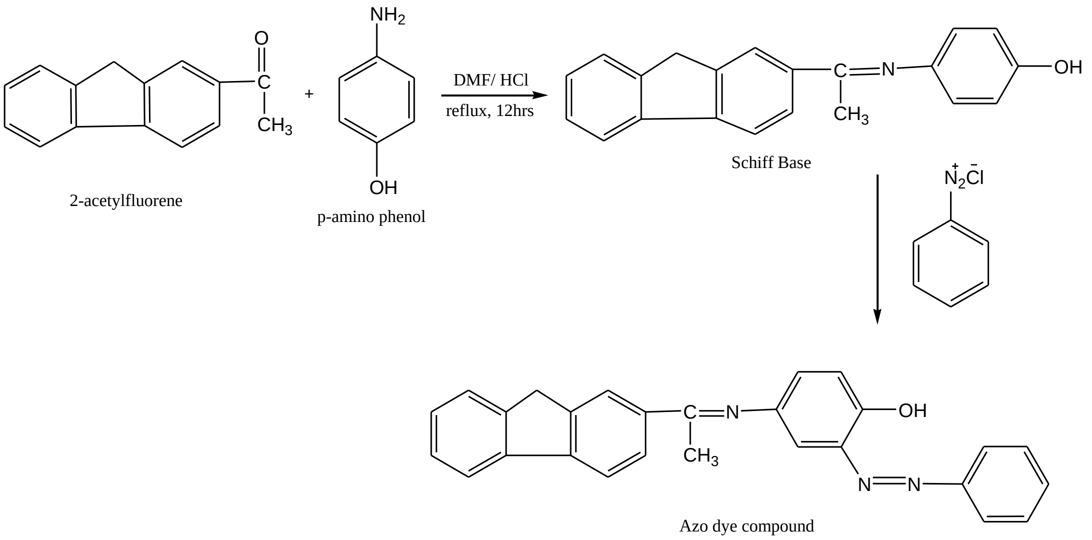
85% yield

Rui Zhao *et al.*, (2011) developed one step synthesis of azo compounds from nitroaromatics and anilines. In this study, azo dyes**(98)** were produced from the aromatic nitro compounds and substituted anilines in a single step of reaction. Here, aromatic nitro compounds were reduced and substituted aniline were oxidised, then react to each other to form azo dyes without any metal base condition. Hence, this method was very convenient and eco-friendly in nature for synthesis of azo dyes with good yield.



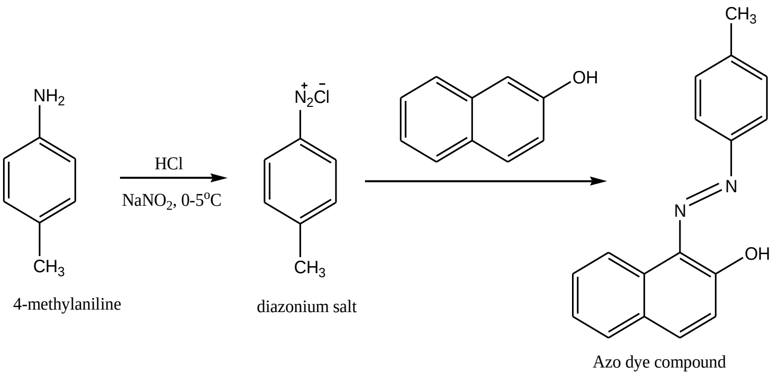
(98)

Thawra Ahmad *et al.*, (2015) investigated the preparation and characterization of some new azo dyes, azomethine dyes and heterocyclic – Schiff bases derivatives. In this study, they synthesized a series of Schiff bases and their fluorene derivatives from the reaction of primary amines (like p-amino phenol, p-phenylenediamine) with 2-acetylfluorene in presence of DMF and concentrated Hydrochloric acid as a catalyst under refluxed condition. The Schiff bases was treated with variety of diazotised compounds to yield the corresponding dye derivatives**(99).**



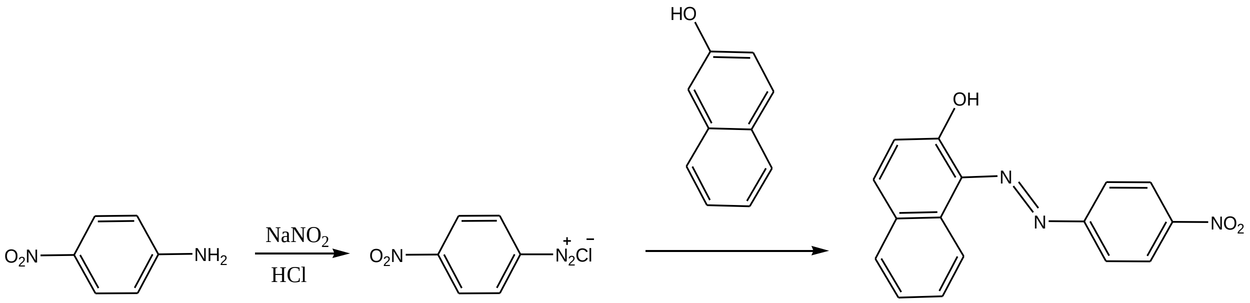
(99)

Chandrashekhar J. Patil *et al.*, (2019) highlighted the coupling reactions involving aryldiazonium salt: part-IX. Review on synthesis of azo-phenolic derivatives, their applications and biological activities. In this study, a series of azo dyes**(100)** was prepared from the diazotisation of various aromatic primary amines followed by coupling with different aromatic phenols. These azo dyes also serve as a building block for many organic intermediates.



(100)

L Abd-Alredha R. Al-Rubaie *et al.*, (2012) developed the synthesis and characterization of azo dye para red and new derivatives. In this study, the para red azo dye**(101)** was prepared from the reaction of diazonium salt of p-nitroaniline with β-naphthol. The dye was characterized by FTIR and UV-Visible spectrophotometer. The dye exhibited no biological activity from in vitro study.



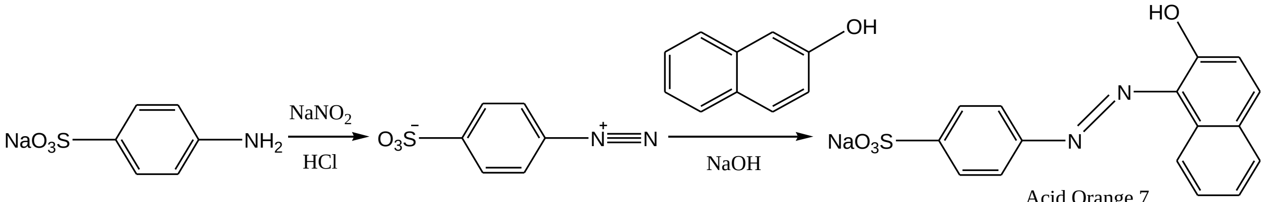
4-nitro aniline

diazonium salt

Azo dye compound

(101)

Harold S. Freeman ., (2013) studied the aromatic amines: use in azo dye chemistry. The aromatic primary amines were the essential precursors for formation of azo dye compounds. The azo dye**(102)** formation take place when aromatic primary amines was diazotised in presence of mineral acid (such as HCl, H_2SO_4) and sodium nitrite ($NaNO_2$), then treated with electron-rich aromatic compound to yield of high quantity. The nature of the aromatic amine was very important for colouration of the materials and dyeing performance.

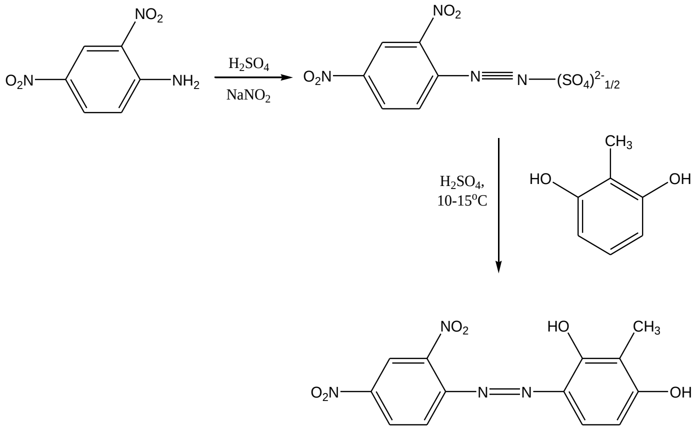


Sulphanilic acid

Acid Orange 7

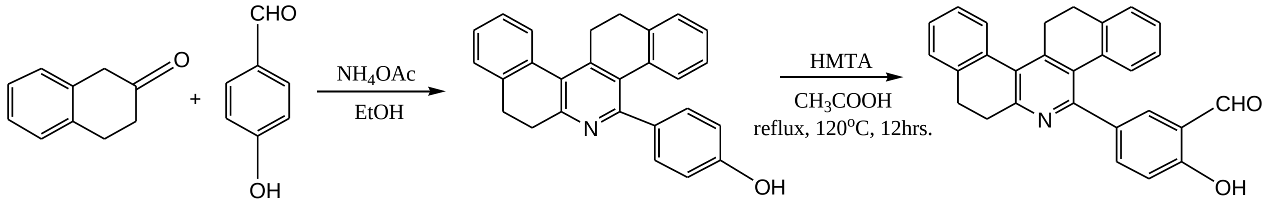
(102)

Zhong Xin *et al.*, (2001) determined the synthesis and characterisation of coloured monomers based on 2-methylresorcinol. The coloured monomers based on 2-methylresorcinol**(103)** was synthesized from the diazotisation of substituted aniline and coupling with 2-methylresorcinol to yield of 87-91%. Their structure was determined by IR, NMR and elemental analysis.



(103)

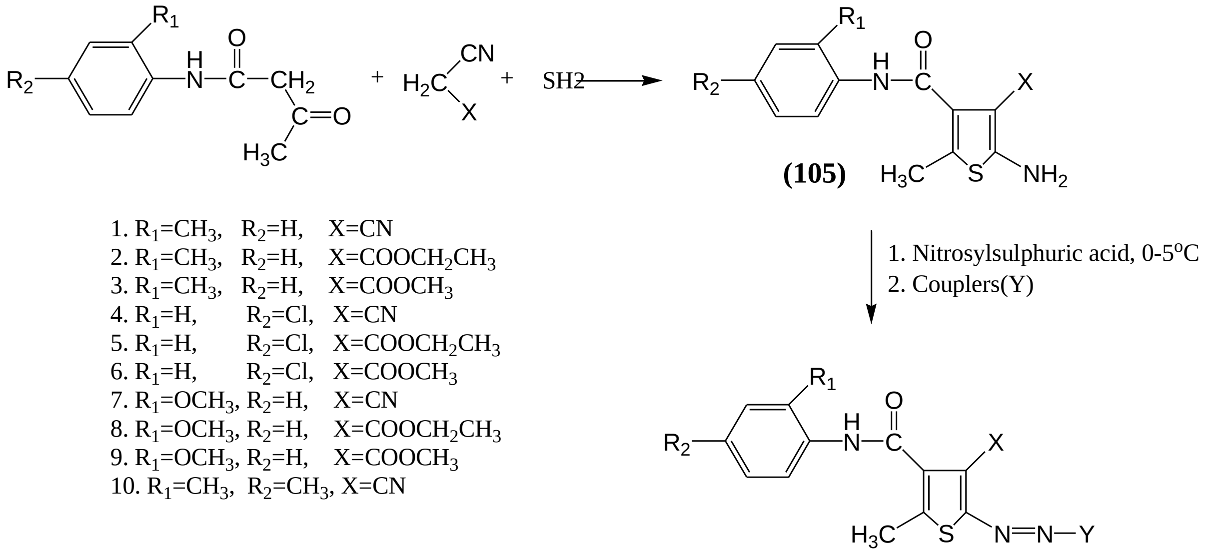
Sathish Sawminathan *et al.,* (2021) derived the phenanthridine-based donor/acceptor fluorescent dyes: synthesis, photophysical properties and fluorometric sensing of biogenic primary amines. In this study, the phenanthridine-based fluorescent dye**(104)** was prepared by Duff method. They produce colour from yellow to greenish-blue. The fluorescent ratiometric detection towards primary amine was very high selectivity and sensitivity.



Phenanthridine-based fluorescent dyes

(104)

Alaa S. Abd-El-Aziz *et al.,* (2006) evaluated the novel azo disperse dyes derived from aminothiophenes: Synthesis and UV-visible studies. In this study, a series of thienyl-2-azo and thienyl-5-azo disperse dyes were synthesised through Gewald's method. By Gewald's method, aminothiophene derivative intermediates**(105)** was prepared and then they are treated with Nitrosylsulphuric acid and couplers(Y= Resorcinol, 1-substituted-2,3-dihydroxynaphthalene and substituted aniline derivatives) to yield a azo dyes**(106).** The azo disperse dye exhibited the absorption in the visible region ranging from 461nm to 555nm, when various substituents present in azo dyes as well as polarity of solvent. It was characterised by IR, NMR, MS and UV-visible techniques.



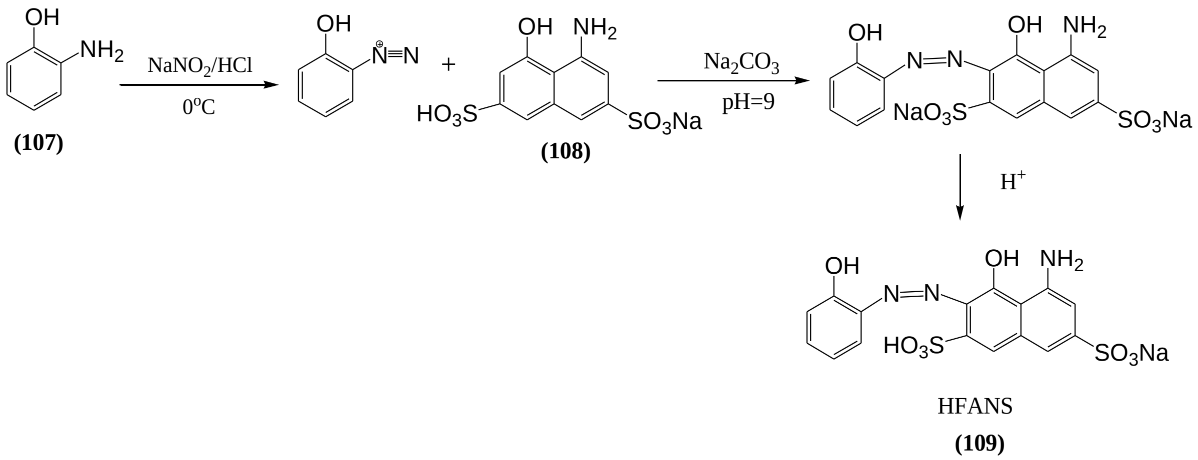
(105)

1. R_1=CH_3, R_2=H, X=CN
2. R_1=CH_3, R_2=H, X=$COOCH_2CH_3$
3. R_1=CH_3, R_2=H, X=$COOCH_3$
4. R_1=H, R_2=Cl, X=CN
5. R_1=H, R_2=Cl, X=$COOCH_2CH_3$
6. R_1=H, R_2=Cl, X=$COOCH_3$
7. R_1=OCH_3, R_2=H, X=CN
8. R_1=OCH_3, R_2=H, X=$COOCH_2CH_3$
9. R_1=OCH_3, R_2=H, X=$COOCH_3$
10. R_1=CH_3, R_2=CH_3, X=CN

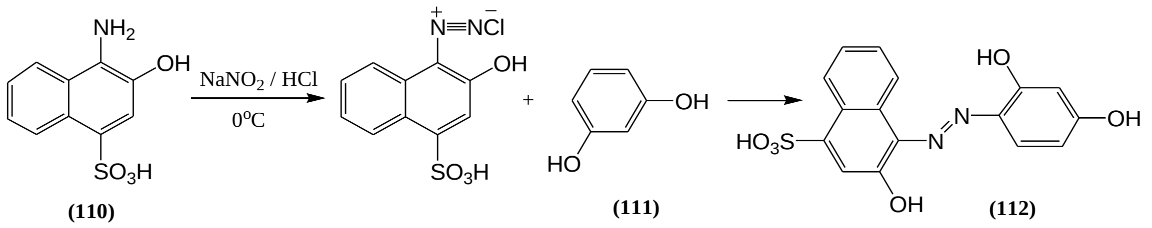
Azo dyes

(106)

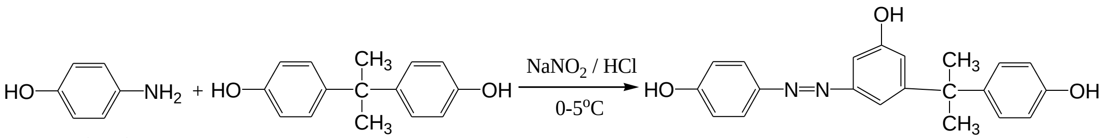
Emel YILDIZ *et al.*, (2002) investigated the synthesis of novel acidic mono azo dyes and an investigation of their use in the textile industry. The dye was prepared from the diazotisation of o-amino phenol**(107)** in presence of HCl and $NaNO_2$ at 0°C to give an intermediate of diazonium salt, then it reacted with 1- hydroxy 8-amino naphthalene 3,6-disulfonic acid of mono sodium salt**(108)** of pH ranges (9-10) to yield acidic mono azo dyes**(109)** of 96.7% which was reddish violet colour. It was used in dyeing of polyamide fiber in textile industry.



V.G.Vidya *et al.*, (2018) was described Synthesis, characterization and application of some azo dyes derived from various aromatic amines. The coupling reaction of diazotised aromatic primary amines with various compounds to yield the corresponding monoazo dyes, which used to dye the cotton fabric. The substitution and position of electron withdrawing and electron donating groups on reactants affects the fastness properties of dyeing into cotton fabric. The azo dye**(112)** prepared from resorcinol**(111)** in NaOH and 1-amino-2-naphthol 4-sulphonic acid**(110)** in HCl and $NaNO_2$ under ice cooled condition to yield 83% which used as good dyeing property into cotton fabric.

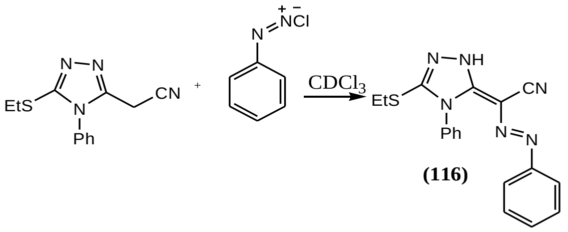


O.B.Agho *et al.*, (2016) investigated the application of bisphenol as a coupler in the synthesis of azo dyes and its assessments on vegetable tanned leather. The coupling reaction of Bisphenol-A**(114)** with diazotised 4-aminophenol**(113)** gives corresponding azo dyes**(115)** respectively. The RF(Retention Factor) values for diazonium salt of p-phenylenediamine shows 0.72 and 0.76 because they exhibited two possible formation of monoazo and diazo derivatives while RF value for 4-aminophenol shows 0.78 because it exhibited formation of monoazo derivatives only. These dyes have been very good potential for coloration of vegetable tanned leather.



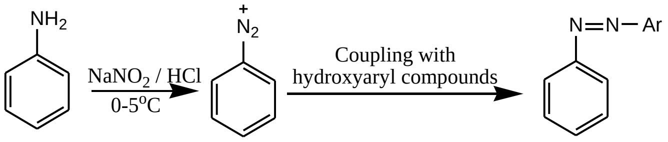
(113) **(114)** **(115)**

Mariam Al-Sheikh *et al.*, (2014) evaluated the synthesis and spectroscopic properties of new azo dyes derived from 3-ethylthio-5-cyanomethyl-4-phenyl-1,2,4-triazole. The 1,2,4-triazole derivative azo dyes**(116)** were prepared from the coupling reaction of 3-ethylthio-5-cyanomethyl-4-phenyl-1,2,4-triazole with diazotised aniline derivatives to yield of 82%. The tautomerism was exhibited by nature of substituent at the para position of aniline coupling component and it was characterised by NMR studies.



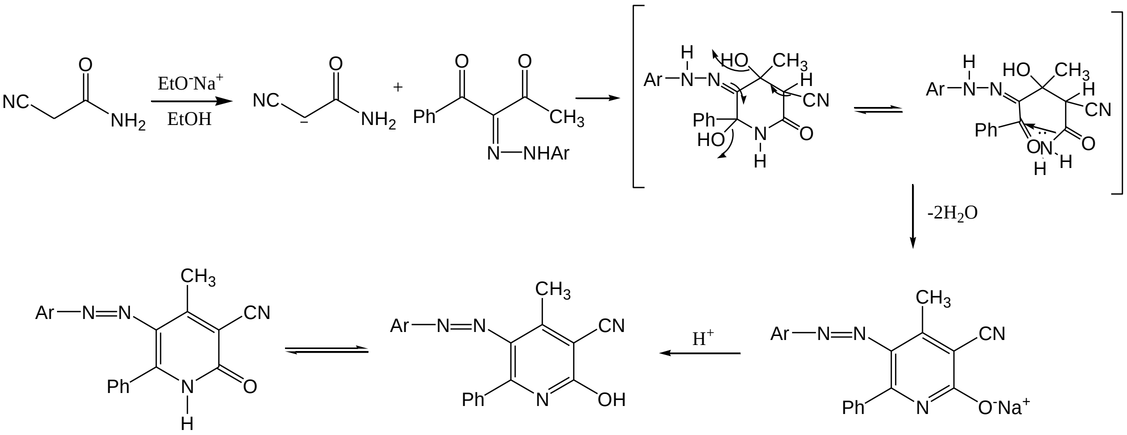
(116)

Pavel Makedonski *et al.*, (2004) analysed the synthesis of new kinds of reactive azo dyes and their application for fibre-optical pH-measurements. In this study, the azo dye containing formyl group was prepared from two different methods. One was the introducing functional group to a suitable substituent within pre-formed azo dyes while other to the dye precursors. The azo dyes**(117)** are prepared from the diazotised amine and coupling with hydroxyaryl compounds(Ar= naphthol, resorcinol). A new pH-indicating sensor based on thin film was derived from these azo dyes covalently bonded to an acetal linkage of a vinylalcohol-ethylene copolymer. The dye exhibited long term stability even under strong basic condition and does not affect the optical properties of the dyes. The reactive azo dye served as optical fibres and reversible pH-sensors.



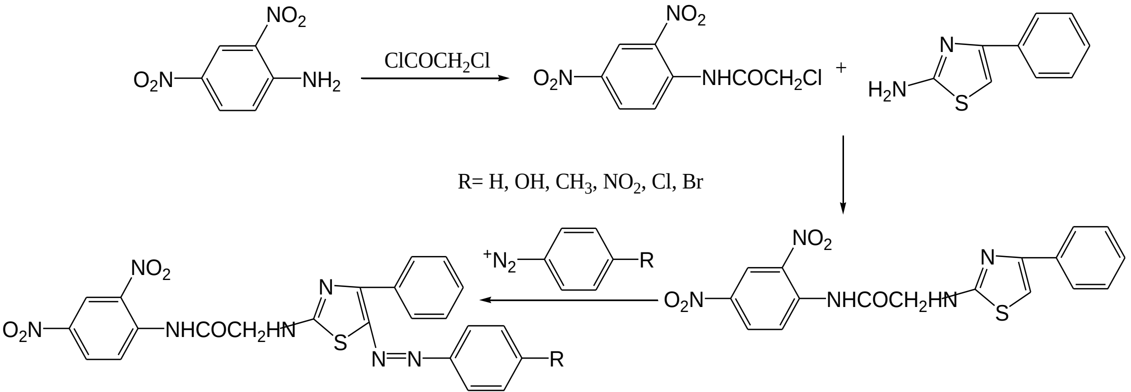
(117)

M.H.Helal., (2004) studied the synthesis and characterisation of a new series of pyridinone azo dyes for dyeing of synthetic fibers. 5-arylazosubstituted-pyridinone**(118)** was synthesised from the reaction of cyanoacetamide in presence of boiling ethanolic sodium ethoxide and acetylacetone (or benzoylacetone) to yield good product. The azo dye was good colour strength, good wash-fastness, good light-fastness and good rub-fastness on polyester and polyamide fabrics.



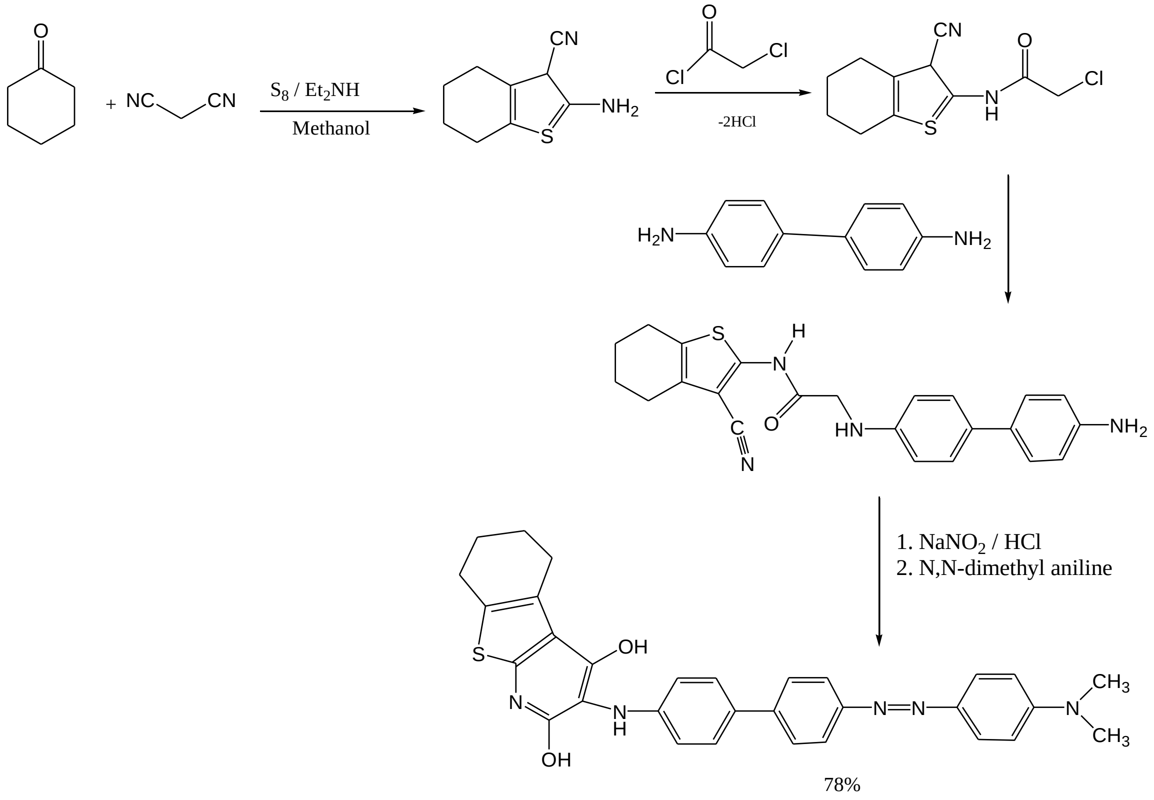
(118)

Malik G. M *et al.,* (2010) evaluated the thiazole based disperse dyes and their dyeing application on polyester fiber and their antimicrobialactivity. In this study, a series of thiazole disperse dye**(119)** were prepared from the different diazotised aryl amines and coupling with N-(2,4-dinitrophenyl)-2-[(4-phenyl-1,3-thiazol-2-yl)amino]acetamide. The spectroscopic study of these dye gives a good fastness property and excellent dyeing performance on polyester fabrics. They also provided excellent anti-fungal and anti-bacterial activity.



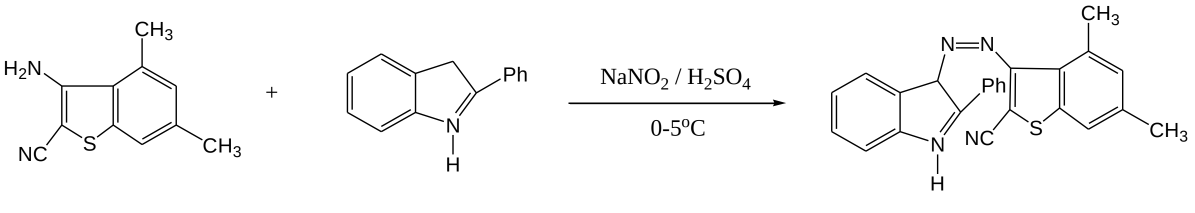
(119)

Mohsen K. A. Regal *et al.,* (2019) analysed the synthesis, characterization and dyeing performance of some azo thienopyridine and thienopyrimidine dyes based on wool and nylon. In this study, the thienopyridine azo dye**(120)** was synthesised from chloroacetamide derivatives and diamino compounds followed by diazotised compound to yield 74-78%. While thienopyrimidine azo dye was synthesised from chloroacetamide derivatives treated with ammonium thiocyanate followed by various diazotised compounds to yield 56-81%. From spectroscopic study, the dye exhibited excellent dyeing performance on wool rather than nylon fabrics.



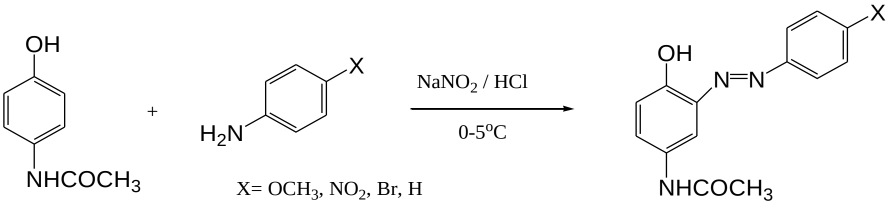
(120)

Zeynel Seferoğlu *et al.*, (2007) determined the synthesis of some novel bis(hetaryl)azo disperse dyes and investigation of their absorption spectra. The coupling reaction of 2-phenylindole with 3-amino-2-cyano-4,6-dimethyl-thieno[2,3-b]pyridine or 3-aminopyridine in nitrosyl sulphuric acid to yield 55-80% of hetarylazoindole dyes**(121).** The absorption maxima were strongly depended on solvent used in these dyes and vary with solvent polarity. The colour of the dye was depended on the nature of heterocyclic ring and substituents present in it.



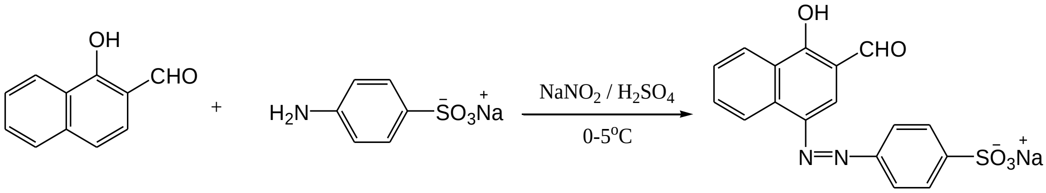
(121)

S.M. Abdallah., (2012) estimated the metal complexes of azo compounds derived from 4-acetamidophenol and substituted aniline. In this study, the azo dyes**(122)** are manufactured from the reaction of 4-acetamidophenol and substituted aniline in presence of $NaNO_2$ and HCl under 0-5°C. From this method, the four azo compounds containing Ni(II) and Cu(II) complexes were synthesized. The ligands binded with transition metals in octahedral structure. It was analysed by IR, TG and DTG techniques.



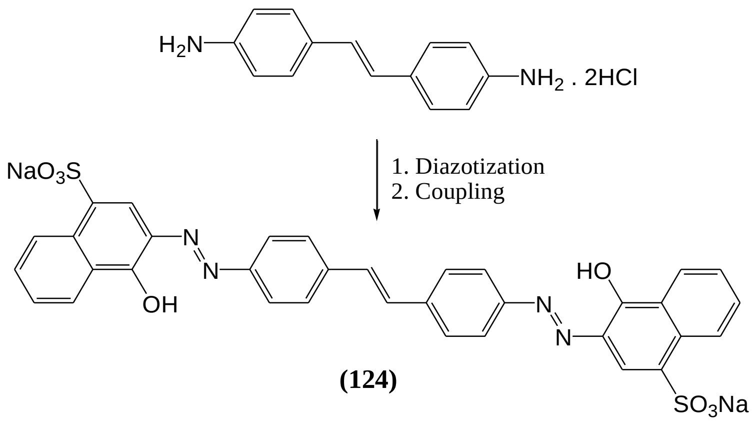
(122)

Rim Driouich *et al.*, (2006) identified the synthesis of water-soluble phenylazosalicylaldehyde analogues and their application to capillary electrophoretic determination of primary amines. In this study, the water-soluble phenylazosalicylaldehyde dye derivatives**(123)** was synthesised from 4-sulfo-arenediazonium chloride and coupling with 1-hydroxy-2-naphthaldehyde to yield ~76%. Some aromatic primary amines were detected by Capillary Zone Electrophoresis(CZE) method. This method was applied to detection of trace amounts of amines in routine analysis of organic compounds.



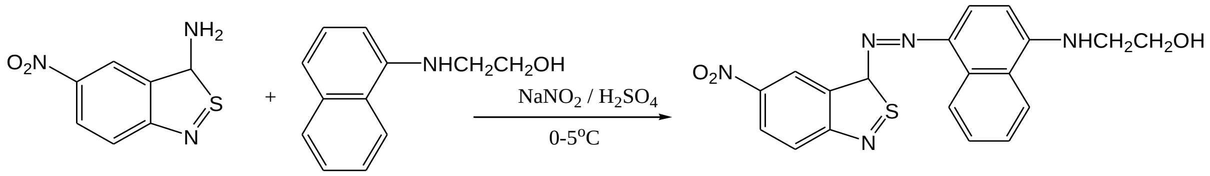
(123)

Dong Hyun Song *et al.*, (2007) developed the synthesis of stilbene-based azo dyes and application for dichroic materials in poly(vinyl alcohol) polarizing films. Stilbene-based azo dyes**(124)** were synthesised from diazotisation of 4,4'-diaminostilbene dihydrochloride and coupling with 1-naphthol-4-sulphonic acid of monosodium salt at 0-5°C. The reaction should maintain at pH of 7-9. These dye was used to preparing polarizing films due to intramolecular hydrogen bonding and high degree of polarization.



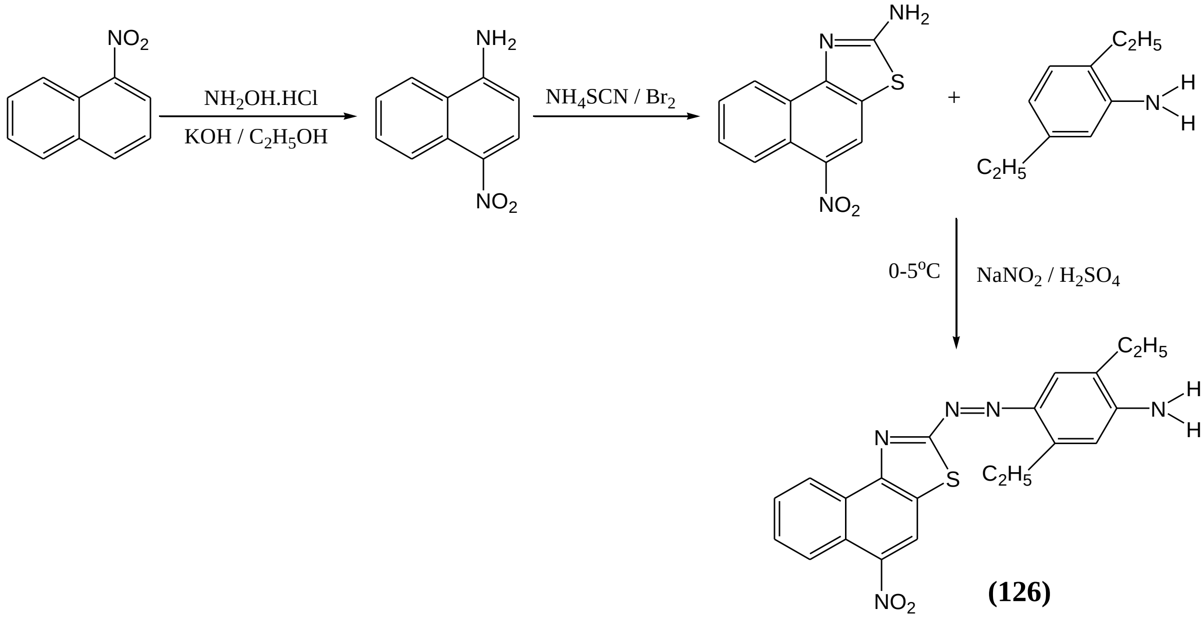
(124)

K.L.Georgiadou *et al.,* (2001) evaluated the synthesis, characterisation and application of disperse dyes derived from N-2-hydroxyethyl-1-naphthylamine. A series of azo disperse dyes**(125)** were prepared from the diazotisation of heterocyclic arylamines(like 3-amino-5-nitro[2,1]benzoisothiazole) and coupling with N-2-hydroxyethyl-1-naphthylamine. These dyes were colour changes from violet to greenish blue depending on heterocyclic amines. Then dye was applied on cellulose acetate fabric to give a low to moderate colour with good dyeing performance.



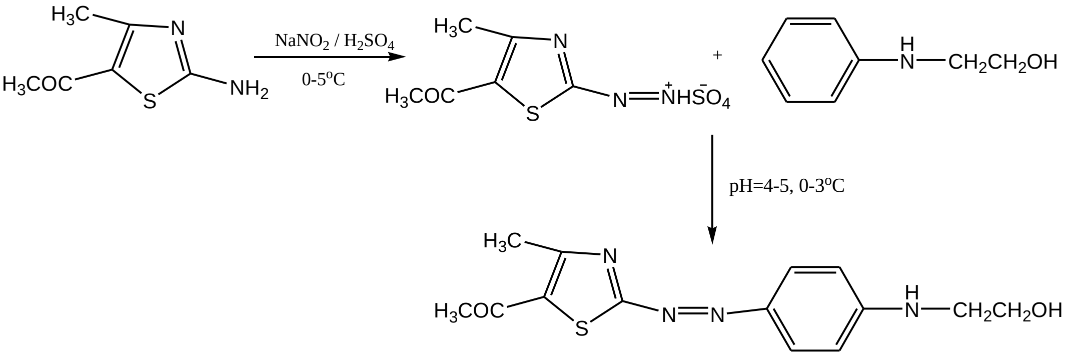
(125)

Dinesh W. Rangnekar *et al.,* (2000) analysed the synthesis and application of 2-(arylazo)-8-nitronaphtho[1,2-d] thiazole disperse dyes. 2-amino-8-nitronaphtho[1,2-d]thiazole derivative azo dye**(126)** was synthesised by 1-nitronaphthalene reacted with hydroxylamine hydrochloride and KOH to form 4-nitro-1-naphthylamine which was treated with ammonium thiocyanate and bromine to give a 2-amino-8-nitronaphtho[1,2-d]thiazole. Then coupled with diazotised substituted N.N-dialkylated anilines(like 2,5-diethylbenzenamine) to yield a disperse azo dye compounds. They give a good fastness property on polyester fabrics.



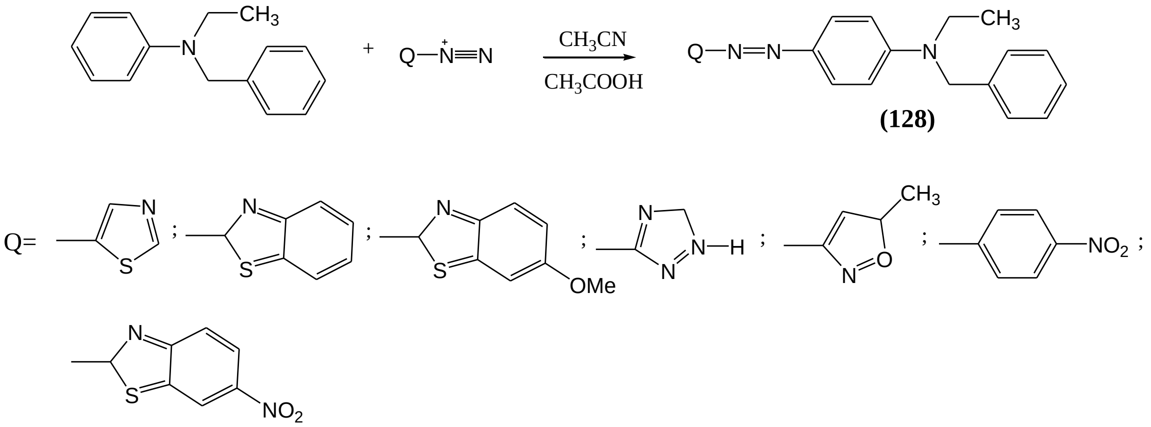
(126)

Vithal S. Patel *et al.*, (2001) determined the synthesis and dyeing performance of some novel heterocyclic azo disperse dyes. The heterocyclic azo disperse dye**(127)** was synthesised from the 5-acetyl-2-amino-4-methylthiazole and coupling with various N-alkyl derivatives of aniline(like 2-(phenylamino)ethanol) to yield 80-85%. Their dyeing performance was determined through polyester and nylon fabrics. The bright colour was obtained due to the greater planarity of the thiazole dye and lower steric hindrance of a five membered ring.



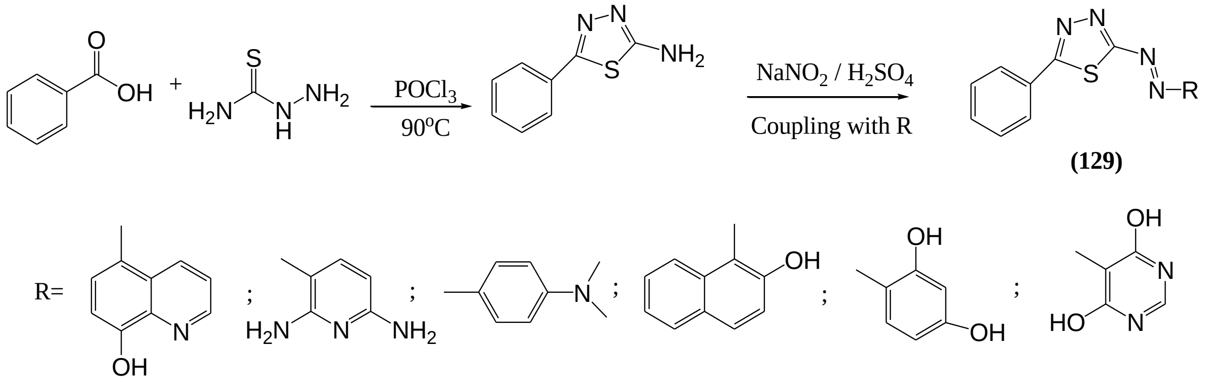
(127)

M.R. Yazdanbakhsh *et al.*, (2010) explained the novel azo disperse dyes derived from N-benzyl-N-ethyl-aniline: synthesis, solvatochromic and optical properties. In this study, there are seven azo disperse dyes**(128)** were synthesised from N-benzyl-N-ethyl-aniline. These exhibit different polarity on different solvents which was estimated by solvatochromic properties. Heterocyclic azo dyes give a good optical property while homocyclic azo dyes.



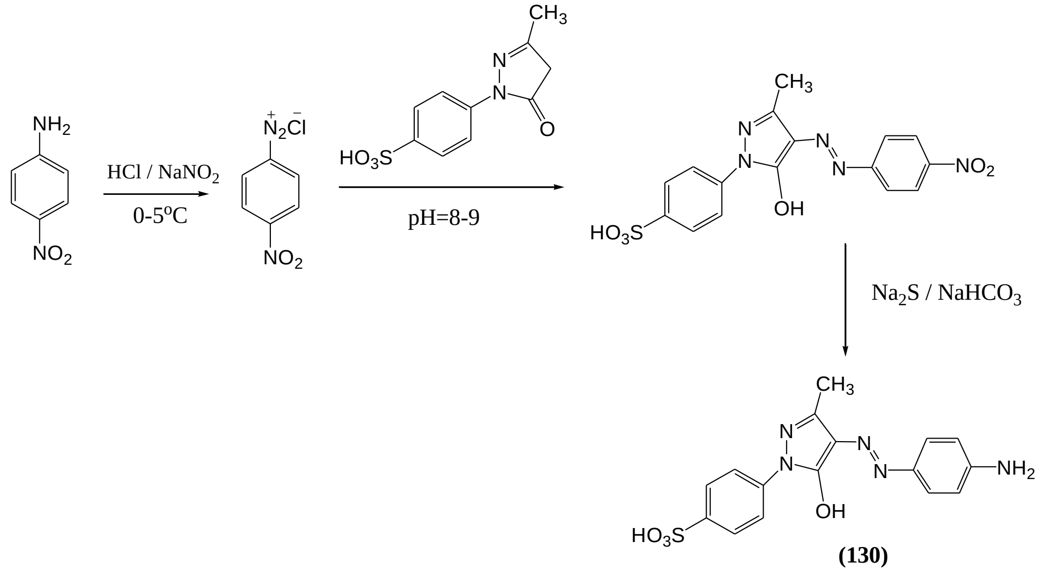
(128)

Chinnagiri T. Keerthi Kumar ***et al.*****, (2013)** have analysed the synthesis, characterization and biological activity of 5-phenyl-1,3,4-thiadiazole-2-amine incorporated azo dye derivatives. 5-phenyl-1,3,4-thiadiazole-2-amine was prepared from benzoic acid and thiosemicarbazide in presence of phosphorous oxychloride under refluxed condition. Then it was treated with nitrosylsulphuric acid followed by coupling with various heterocyclic compounds to yield corresponding azo dyes**(129)** compounds. These azo dyes are excellent antimicrobial and antioxidant agents.



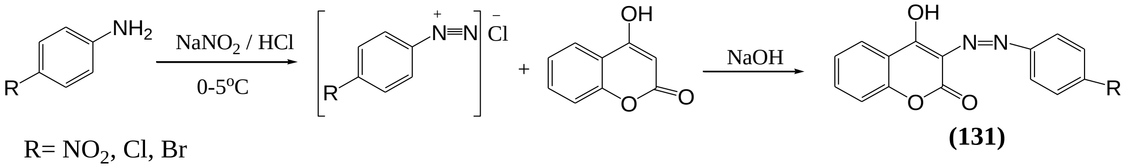
(129)

Xiao-Jun Zhao ***et al.*****, (2014)** estimated the synthesis of an electron-rich aniline-containing dye and its dyeing behaviors on silk through a three-component Mannich-type reaction. A three-component Mannich-type reaction was predominantly used to dyeing silk fabric. In this study, silk containing phenolic side chain in the tyrosine residues was treated with formaldehyde and aromatic primary amine-containing functional compound to form stable azo dye due to strong -CH_2-NH- covalent bond formation between tyrosine residue of silk and electron-rich aniline-containing dye**(130).** Hence, its known as a three-component Mannich-type reaction. The method was suitable for dyeing silk fabrics and Eco friendly in nature.



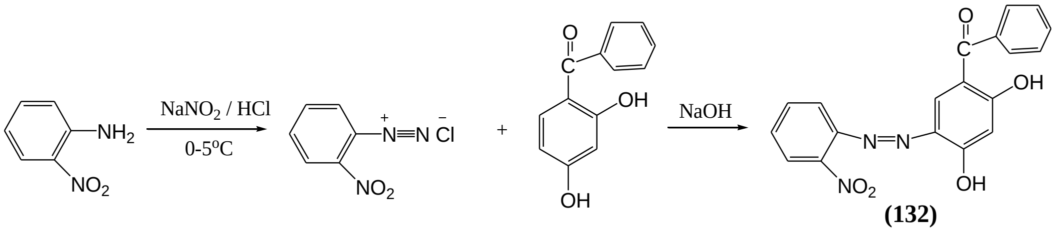
(130)

Malaz Albasha *et al.*, (2018) evaluated the synthesis, characterization of new azo compounds and their biological evaluation. The azo dye**(131)** was synthesized from coupling of coumarin with diazotised aromatic primary amines at 5-9°C to yield 64-79%. They were characterised by IR, HPLC and MS techniques. Then the purity of azo dye was estimated by TLC using dioxane-methanol (1:1) as a solvent system.



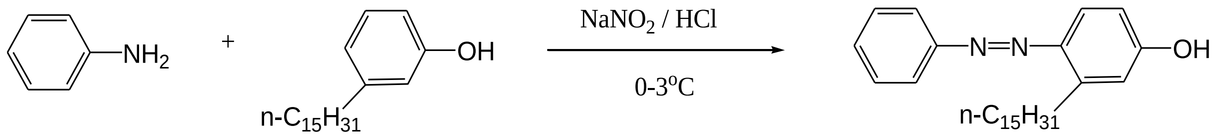
(131)

Bharat C. Dixit *et al.*, (2007) evaluated the synthesis and application of new mordent and disperse azo dyes based on 2,4,-dihydroxybenzophenone. The mordent and disperse azo dyes**(132)** were prepared from the diazotization of various aromatic amines (like nitro aniline, chloro aniline, hydroxy aniline, methyl aniline) and coupling with 2,4-dihydroxybenzophenone in NaOH. The disperse azo dyes was used to dyeing polyester fiber while mordent dyes were used to dyeing wool fabrics. The dye produced good fastness properties but less rubbing fastness. In this study, we known that mordent dyes give better shades of colour than the disperse dyes.



(132)

Somsaluay Suwanprasop *et al.*, (2004) derived the petroleum marker dyes synthesized from cardanol and aniline derivatives. In this study, the marker dyes**(133)** for petroleum product was synthesised from diazotization of aniline derivatives (like aniline, chloro aniline, chloronitro aniline, methylaniline) and coupling with n-alkyl phenol (which was naturally occurring as byproduct in cashew nuts industry in form of cardanol) to yield 80-85%. These dyes were stable for three months in fuel oils. The marker dye was invisible in gasoline and high-speed in diesel fuel.



Where, n = 0, 2, 4, 6

(133)

Materials AND Methods

3. MATERIALS AND METHODS

3.1. GENERAL

- Melting points of the samples were determined by using SAFIRE melting point apparatus and were uncorrected.
- The UV spectra were recorded by UV double beam spectrometer. Ethanol were used as solvent. The wavelength are measured in nanometer (nm). The UV spectrum graph were plotted using OriginPro 8.5 software.
- The Fluorescence (PL-Photo Luminescence) Spectra were detected by JASCO Spectrofluorometer Model FP8200. The fluorescence were measured over a wide time range from picoseconds to milliseconds. DMSO, ethanol and acetone are used as solvents. The Fluorescence spectrum graph were plotted using OriginPro 8.5 software.
- The Fourier transform infrared (FTIR) spectra were recorded by ATR technique in a SHIMADZU PRESTIGE 20 FT-IR Spectrometer. Absorption frequencies were quoted in reciprocal centimeter.
- Nuclear Magnetic Resonance (^{1}H -NMR) Spectra were determined by Bruker Avance III 300 MHz NMR instrument in DMSO-d_6 as solvent with tetramethyl silane as the internal reference. Chemical shift were quoted in parts per million (ppm).
- Thin Layer Chromatography (TLC) was performed using glass plates coated with silica gel G to monitor and check the completion of each reaction.
- Ethanol and hexane are used as the developing solvents. Spots are identified with iodine.
- The solvents and reagents used for the synthesis are reagent grade and they are purified by standard methods such as distillation and extraction.

3.2. PREPARATION OF AZO DYES FROM 2-AMINO-1,3,4-THIADIAZOLE DERIVATIVES

3.2.1. PREPARATION OF (Z)-4-((5-(HYDROXY(PHENYL)METHYL)-1,3,4-THIADIAZOL-2-YL)DIAZENYL)BENZENE-1,3-DIOL

0.02g of (5-amino-1,3,4-thiadiazol-2yl)(phenyl)methanol**(134)** was dissolved in 2ml of Dimethylformamide(DMF) and 0.6 ml of concentrated sulphuric acid (Solution A). Solution A was stirred constantly for 20 minutes under ice cold condition.

0.68g of dry sodium nitrite was slowly added to 1.2ml of concentrated sulphuric acid over a period of 5 minutes with constant stirring under ice cold condition. After completion of the addition, the stirring was continued further for 10 minutes with heating at 65^{o}C (Solution B).

Diazotization was carried out by dropwise addition of Solution B to a well stirred Solution A under ice cold condition (Solution C). Then add a pinch of urea to the Solution C. Further the Solution C was stirred for 1 hour 30 minutes under ice cold temperature below 10^{o}C.

0.076g of Resorcinol**(135)** (Coupling component) was dissolved in the mixture of NaOH (0.1g) and water (2ml), then cooled to -10^{o}C (Solution D). To this well stirred Solution D, the above resulting diazonium Solution C was added dropwise maintaining temperature below 10^{o}C. The pH of the reaction mixture was maintained by adding a pinch of sodium carbonate. Then the mixture was stirred for 1 hour 30 minutes under ice cold condition below 10^{o}C. The progress of the reaction was followed by TLC using an Ethanol-Hexane mixture(1:2).

The resulting solid precipitate was filtered, washed with cold water and dried. The crude product was purified from acetone. 0.1g yield of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol**(136)** was obtained. **(Izzet Sener *et al.*, 2006)**

3.2.2. PREPARATION OF (Z)-6-((5-(HYDROXY(PHENYL)METHYL)-1,3,4-THIADIAZOL-2-YL)DIAZENYL)NAPHTHALEN-2-OL

0.02g of (5-amino-1,3,4-thiadiazol-2yl)(phenyl)methanol**(134)** was dissolved in 2ml of Dimethylformamide(DMF) and 0.6 ml of concentrated sulphuric acid (Solution A). Solution A was stirred constantly for 20 minutes under ice cold condition.

0.68g of dry sodium nitrite was slowly added to 1.2ml of concentrated sulphuric acid over a period of 5 minutes with constant stirring under ice cold condition. After completion of the addition, the stirring was continued further for 10 minutes with heating at 65^{o}C (Solution B).

Diazotization was carried out by dropwise addition of Solution B to a well stirred Solution A under ice cold condition (Solution C). Then add a pinch of urea to the Solution C. Further the Solution C was stirred for 1 hour 30 minutes under ice cold temperature below 10^{o}C.

0.068 g of β-naphthol**(139)** (Coupling component) was dissolved in the mixture of NaOH (0.08g) and water (1ml), then cooled to -10^{o}C (Solution D). To this well stirred Solution D, the above resulting diazonium Solution C was added dropwise maintaining temperature below 10^{o}C. The pH of the reaction mixture was maintained by adding a pinch of sodium carbonate. Then the mixture was stirred for 1 hour 30 minutes under ice cold condition below 10^{o}C. The reaction mixture was heated at 90^{o}C in waterbath for 5 minutes with addition of solid NaCl(pinch) and cooled the mixture at room temperature.

The progress of the reaction was followed by TLC using an Ethanol-Hexane mixture(1:2).

The resulting solid precipitate was filtered, washed with 5% NaCl solution (preparation - 0.5g of NaCl in 10ml water) and dried. The crude product was purified from chloroform. 0.035g yield of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol**(140)** was obtained. **(G. M. Malik *et al.*, 2018)**

3.2.3. PREPARATION OF 4-((E)-(5-((E)-4-HYDROXYSTYRYL)-1,3,4-THIADIAZOL-2-YL)DIAZENYL)BENZENE-1,3-DIOL

0.01g of (E)-4-(2-(5-amino-1,3,4-thiadiazol-2-yl)vinyl)phenol**(137)** was dissolved in 1ml of Dimethylformamide(DMF) and 0.3 ml of concentrated sulphuric acid (Solution A). Solution A was stirred constantly for 20 minutes under ice cold condition.

0.34g of dry sodium nitrite was slowly added to 0.6ml of concentrated sulphuric acid over a period of 5 minutes with constant stirring under ice cold condition. After completion of the addition, the stirring was continued further for 10 minutes with heating at 65^{o}C (Solution B).

Diazotization was carried out by dropwise addition of Solution B to a well stirred Solution A under ice cold condition (Solution C). Then add a pinch of urea to the Solution C. Further the Solution C was stirred for 1 hour 30 minutes under ice cold temperature below 10^{o}C.

0.038g of Resorcinol**(135)** (Coupling component) was dissolved in the mixture of NaOH (0.05g) and water (1ml), then cooled to -10^{o}C (Solution D). To this well stirred Solution D, the above resulting diazonium Solution C was added dropwise maintaining temperature below 10^{o}C. The pH of the reaction mixture was maintained by adding a pinch of sodium carbonate. Then the mixture was stirred for 1 hour 30 minutes under ice cold condition below 10^{o}C.

The progress of the reaction was followed by TLC using an Ethanol-Hexane mixture(1:2).

The resulting solid precipitate was filtered, washed with cold water and dried. The crude product was purified from acetone. 0.05g yield of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol**(138)** was obtained. **(Izzet Sener *et al.,* 2006)**

Result and Discussion

4. RESULTS AND DISCUSSION

In recent years, 2-amino-1,3,4-thiadiazole based azo dyes play an important role in medicine, agriculture and dyeing industries. They are used as drugs due to their high activity in 2' and 5' positions in substitution reactions. The two-electron donor nitrogen system (-N=C-S) and hydrogen-binding domain allow for great structural stability and it was responsible for biological activity. **(Mustafa Er *et al.*, 2016)**

In the present work, the reaction of 2-amino 1,3,4-thiadiazole derivatives with coupling components such as resorcinol (**Izzet Sener *et al.*, 2006**) and β-naphthol (**G. M. Malik *et al.*, 2018**) in presence of nitrosyl sulphuric acid under ice cold condition (below 5°C) to give corresponding 2-amino-1,3,4-thiadiazole based azo dyes.

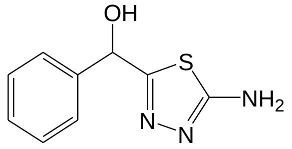
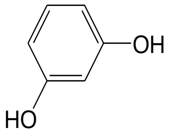
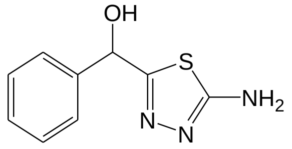
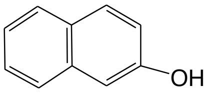
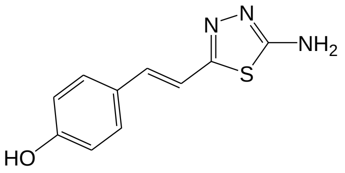
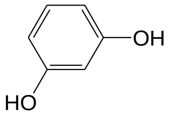
The reaction is carried out by stirring the mixture of 2-amino 1,3,4-thiadiazole derivatives in DMF and concentrated H_2SO_4 with Nitrosyl sulphuric acid at ice cold condition(-5°C), then add a pinch of urea to remove excess nitrosyl sulphuric acid. Initially, stirred for 1 hour and 30 minutes and then the stirring is continued at -5°C (ice cold condition) for another 1 hour 30 minutes after adding the coupling components such as resorcinol or β-naphthol in NaOH and H_2O at -5°C. The reaction is maintained at same pH using a small pinch of sodium carbonate. After completion of the reaction is checked by TLC using hexane and ethanol solvent (2:1).

The precipitate obtained from resorcinol **(135)** as a coupling component is filtered and washed with cold water. Then the crude product is purified from acetone. **(Scheme I)**

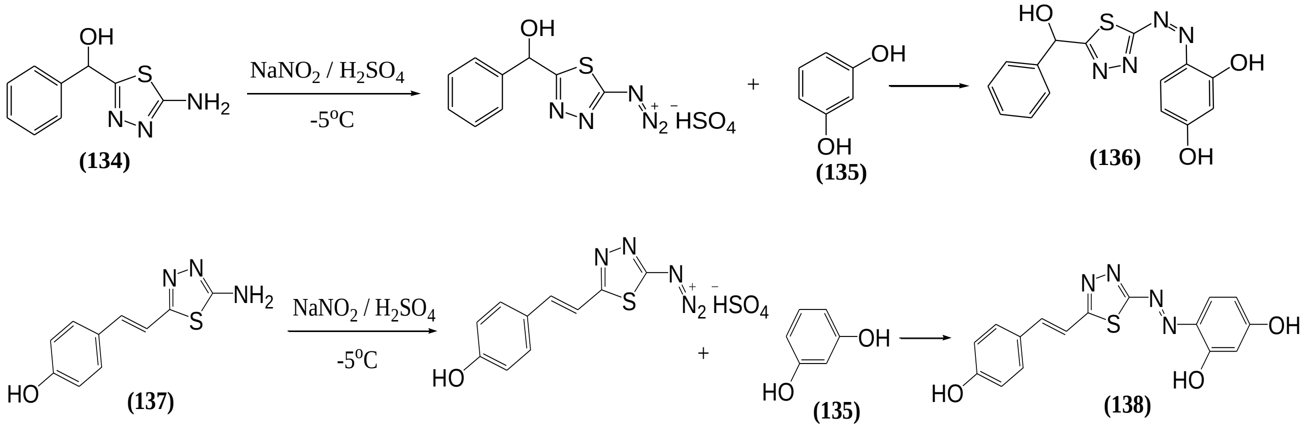
If β-naphthol **(139)** used as a coupling component, then the mixture is heated at 90°C for 5 minutes with a small pinch of sodium chloride. The precipitate obtained is filtered and washed with cold water and 5% NaCl solution. The crude product is purified from chloroform. **(Scheme II)**

The yield and melting point of the products are given in the **Table-I**.

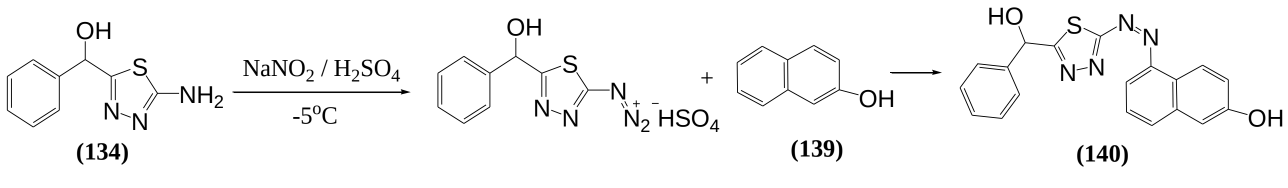
Table I: The Yield and Melting point of the Synthesized Compounds.

REACTANT	COUPLING COMPONENT	COLOUR	MELTING POINT (^{o} C)	YIELD
 **(134)**	 **(135)**	Yellow	160^{o} C	98 %
 **(134)**	 **(139)**	Brown	108^{o} C	75 %
 **(137)**	 **(135)**	Greenish Yellow	166^{o} C	99 %

Scheme I



Scheme II



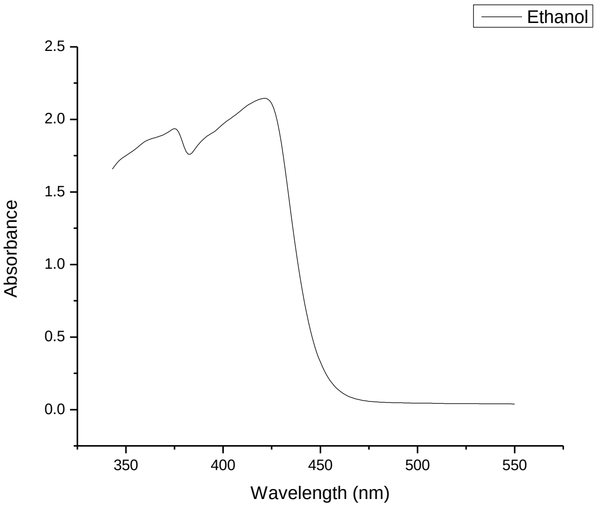
4.1. CHARACTERIZATION OF THE SYNTHESIZED COMPOUND

The synthesized compounds are characterized using **UV, FT-IR, H^1 NMR** and **PL (Spectrofluorometer)** spectral studies.

4.1.1. UV ANALYSIS

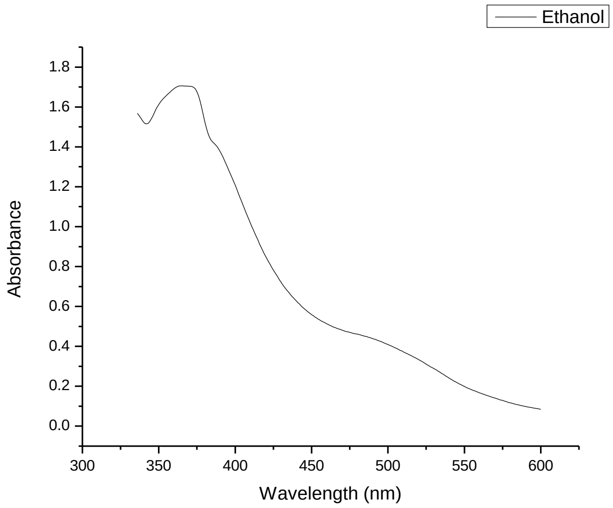
UV spectrum are used to detect the chromophores in the molecule. The UV absorption spectra of 2-amino-1,3,4-thiadiazole based azo dyes are recorded in ethanol solvent at a concentration of $3x10^{-7}$ M.

FIGURE 1: UV Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol



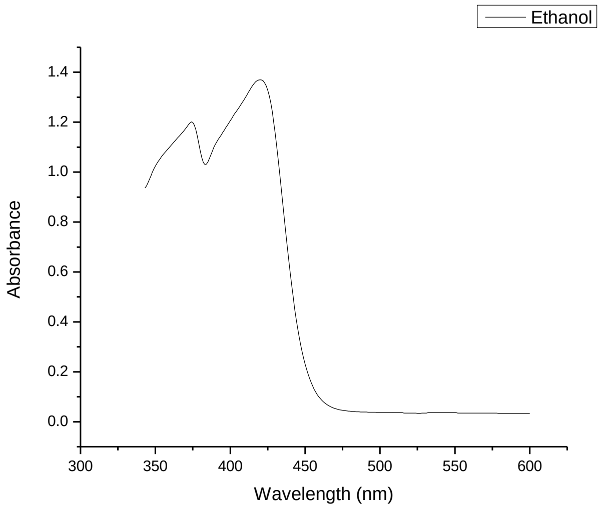
The UV absorption spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol is shown in **Figure 1.** The compound exhibited two intense bands at 375nm and 421nm. The band at 375nm indicates the n-π^* transition of the azo linkage (-N=N) due to the electron donating group (-OH group) present in a molecule and they have bathochromic effect with longer wavelength. The band at 421nm is attributed to the π-π^* transition of the azo linkage (-N=N-). Hence, the synthesized compound contains azo group as the chromophores.

FIGURE 2: UV Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol



The UV absorption spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol is shown in **Figure 2.** The broad band at 366nm is assigned to the n-π* transition of the azo linkage (-N=N-) due to the electron donating group (-OH group) present in a molecule and they have bathochromic effect with longer wavelength. Hence, the synthesized compound contains azo group as the chromophores.

FIGURE 3: UV Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol



The UV absorption spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol is shown in **Figure 3.** The two intensity bands are showed in 374nm and 420nm. The band at 374nm is observed as the n-π^* transition of the azo linkage (-N=N-) due to the electron donating group (-OH group) present in a molecule and they have longer wavelength in presence of bathochromic effect. The band at 420nm is attributed to the π-π^* transition of the azo linkage (-N=N-). Hence, the synthesized compound contains azo group as the chromophores.

4.1.2. FT-IR ANALYSIS

The IR spectrum of the synthesized compounds are given in **Figures 4, 5 & 6.**

I. (Z)-4-((5-(HYDROXY(PHENYL)METHYL)-1,3,4-THIADIAZOL-2-YL) DIAZENYL)BENZENE-1,3-DIOL

The FT-IR spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol **(Figure 4)** indicated a band at 1595 cm^{-1} that is attributed to the stretching vibration of azo group(-N=N-). A broad peak 3439 cm^{-1} indicates the -OH bond and 1649 cm^{-1} is the C=N bond. A peak at 1312 cm^{-1} denotes C-N bond. A peak at 3188 cm^{-1} indicates the C-H stretching vibration of the aromatic ring. A peak at 1076 cm^{-1} denotes the C-O stretching vibration due to tertiary alcohol in the aromatic ring. The C-S-C group of the 1,3,4-thiadiazole ring are observed at 692 cm^{-1}.

II. (Z)-6-((5-(HYDROXY(PHENYL)METHYL)-1,3,4-THIADIAZOL-2-YL) DIAZENYL)NAPHTHALEN-2-OL

The FT-IR spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol **(Figure 5)** indicated a band at 1622 cm^{-1} that is attributed to the stretching vibration of azo group(-N=N-). A broad peak at 3412 cm^{-1} indicates the -OH bond and 3078 cm^{-1} indicates the C-H stretching vibration of the aromatic ring. A peak at 1336 cm^{-1}

denotes C-N bond and 1527 cm^{-1} is due to C=N bond. A peak at 1220 cm^{-1} denotes the C-O stretching vibration due to tertiary alcohol in the aromatic ring. A peak at 831 cm^{-1} indicates the out of plane C-H bending vibration. The band appears at 831 cm^{-1} corresponding to a para disubstituted ring.

III. 4-((E)-(5-((E)-4-HYDROXYSTYRYL)-1,3,4-THIADIAZOL-2-YL)DIAZENYL) BENZENE-1,3-DIOL

The FT-IR spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol **(Figure 6)** indicated a band at 1598 cm^{-1} that is attributed to the stretching vibration of azo group(-N=N-). A broad peak 3449 cm^{-1} indicates the -OH bond and 1645 cm^{-1} is the C=N bond. A peak at 1312 cm^{-1} denotes C-N bond. A peak at 1207 cm^{-1} denotes the C-O stretching vibration due to tertiary alcohol in the aromatic ring. The C-S-C group of the 1,3,4-thiadiazole ring are observed at 692 cm^{-1}.

FIGURE 4: FT-IR Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol

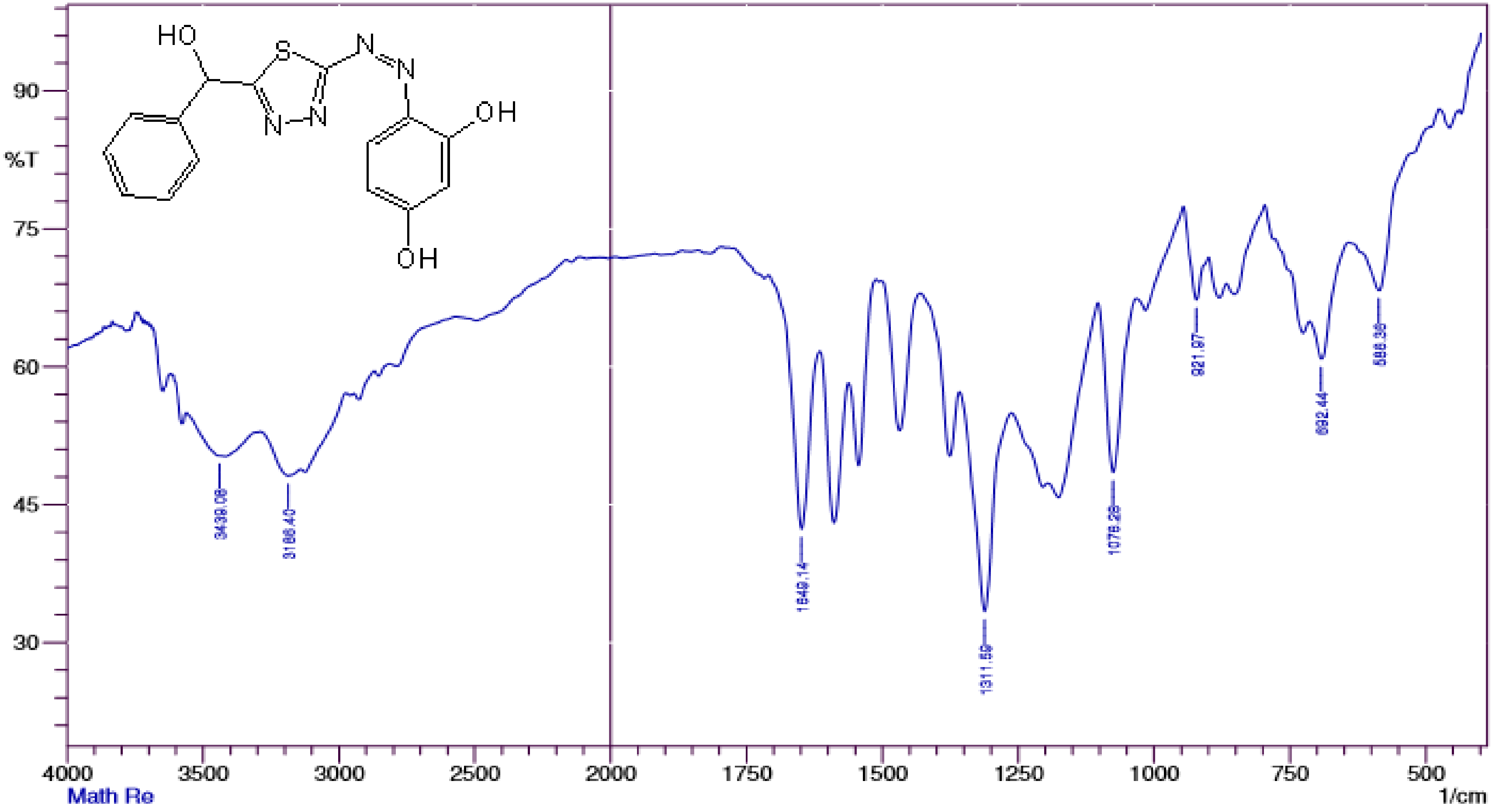


FIGURE 5: FT-IR Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol

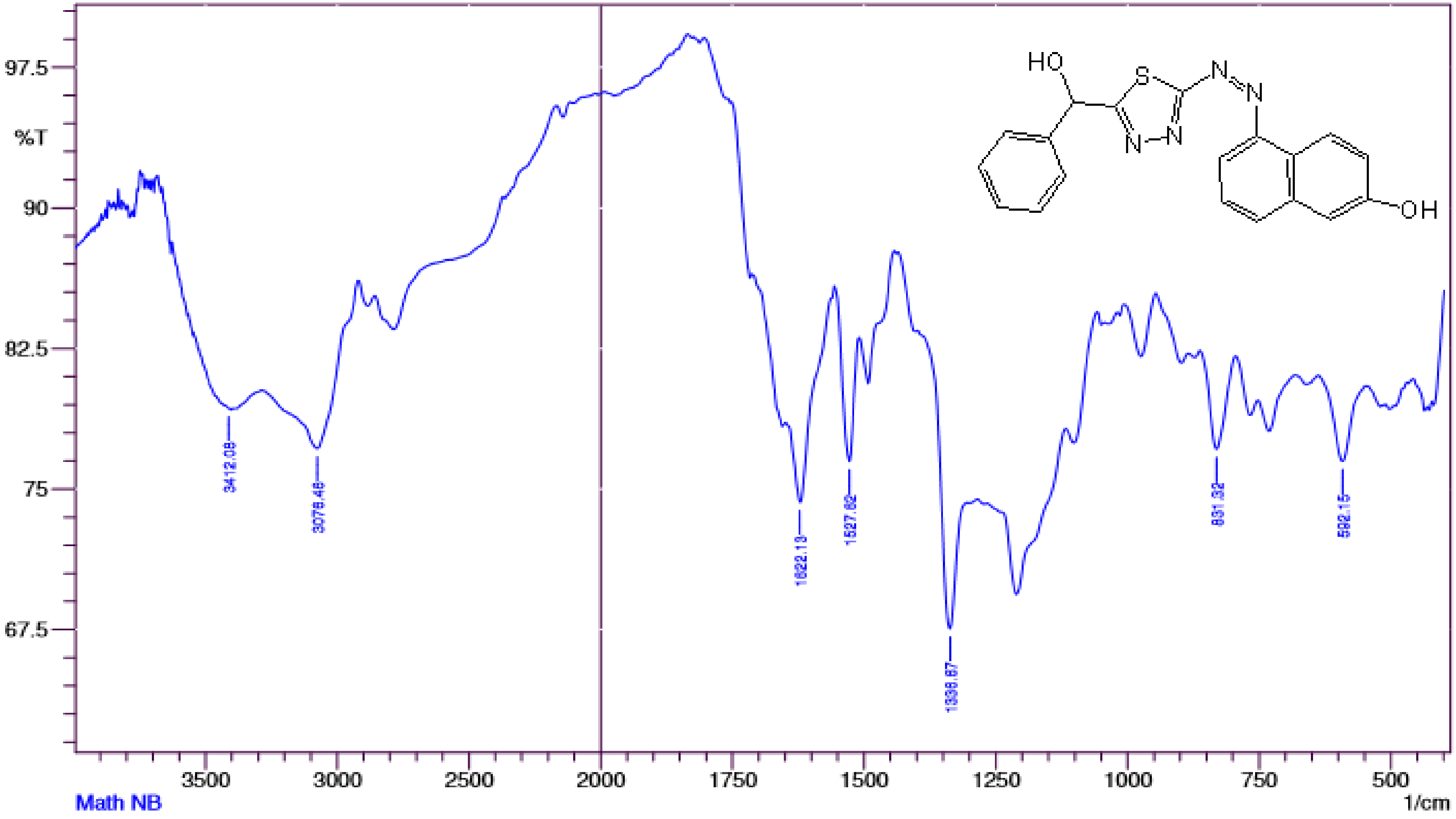
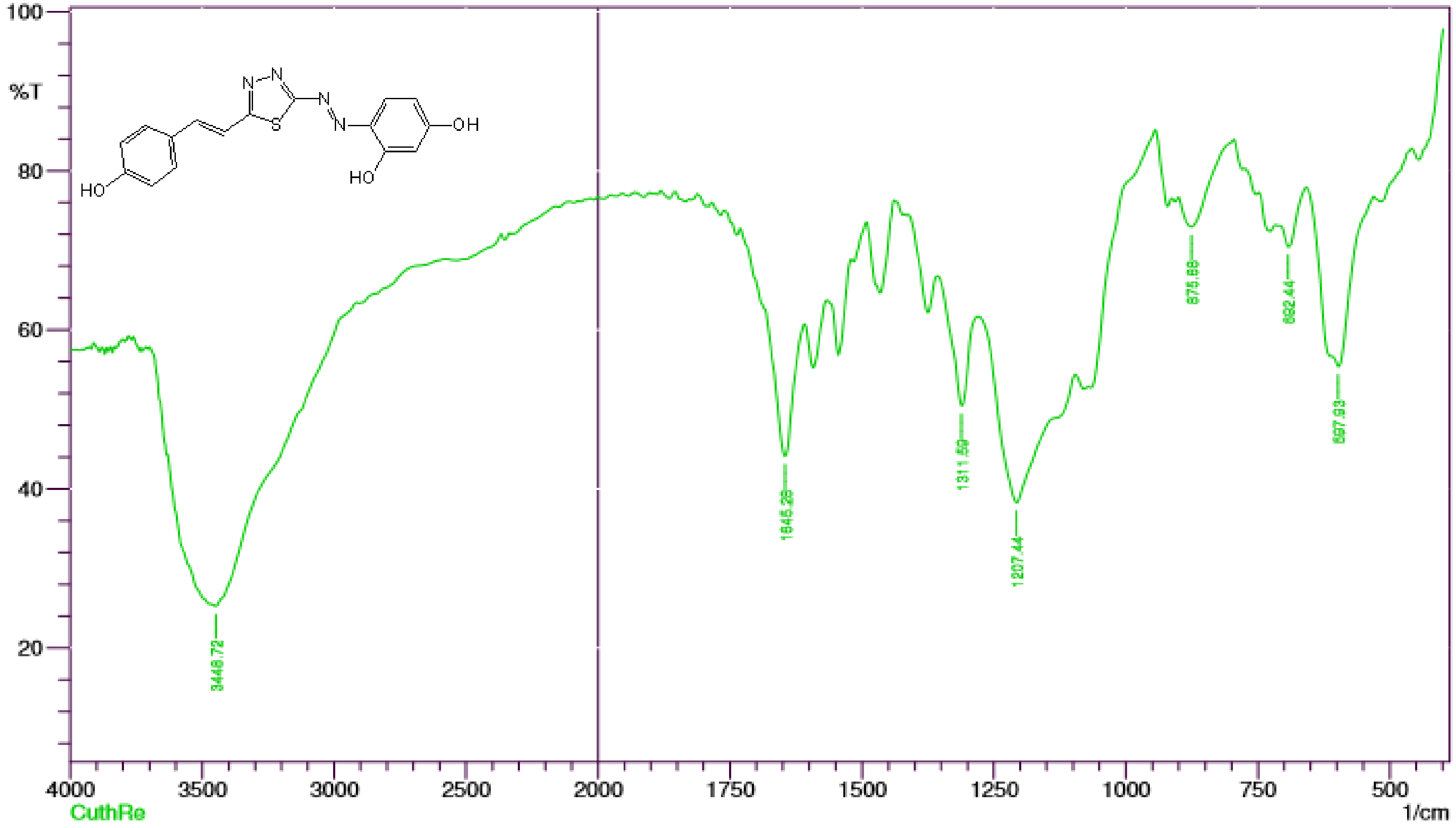


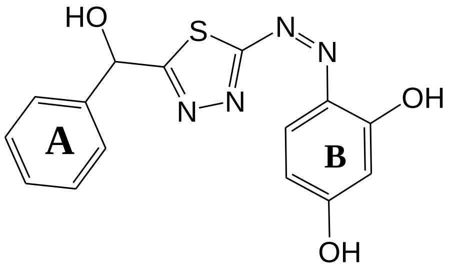
FIGURE 6: FT-IR Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol



4.2.3. NMR ANALYSIS

The structure of all the synthesized compounds are confirmed by NMR spectrum analysis and the NMR is recorded using DMSO-d_6 solvent.

I. (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol



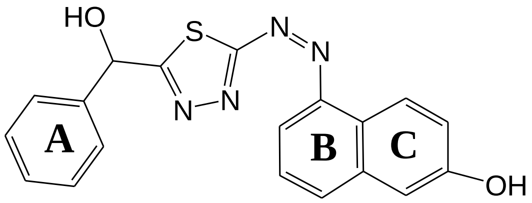
The H^1 NMR spectrum of the synthesized compound (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol is shown in **Figure 7**. The signal at δ 2.45 is assigned to the aliphatic -OH of the one proton.

The high intense peak at δ 5.80 is attributed to the two -OH protons in the aromatic ring(B).

The three peaks at δ 7.27, δ 7.10 and δ 6.94 are observed for the aromatic rings(A and B) of eight protons. The peak at δ 8.62 is attributed to the aliphatic -CH of one proton due to the aromatic ring(A). **(Mahmut Gür., 2019)**

Hence the structure of the synthesized compound of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol is confirmed by H^1 NMR spectrum.

II. (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol



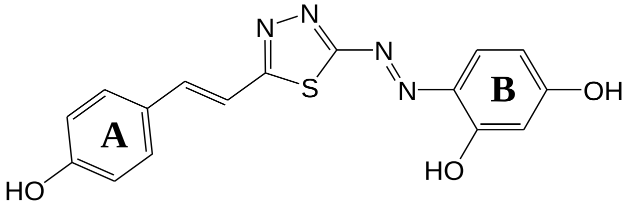
The H^1 NMR spectrum of the synthesized compound (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol is shown in **Figure 8**. The singlet peak at δ 2.74 and δ 5.03 integrating to one -OH proton and one -CH proton is assigned to the aliphatic group respectively.

The broad peak at δ 3.52 indicates the -OH proton present in the aromatic ring(C).

The multiplet at δ 7.33 – 7.67 is attributed to the aromatic ring (A) of five protons and two aromatic rings(B and C) of six protons, which was denoted as naphthalene ring. **(Mahmut Gür., 2019)**

Hence the structure of the synthesized compound of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol is confirmed by H^1 NMR spectrum.

III. 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol



The H^1 NMR spectrum of the synthesized compound 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol is shown in **Figure 10.**

The broad peak at δ 4.17 is attributed to the three -OH protons assigned to the two aromatic rings (A and B).

The quartet at δ 6.50 – δ 6.35 was observed as aliphatic two -CH protons which was near to the aromatic ring(A).

The triplet at δ 7.85 – δ 7.77 denotes the four protons in the aromatic ring(A). The three singlet peak at δ 7.28, δ 7.11 and δ 6.94 integrating for three protons assigned to the aromatic ring(B). **(Mahmut Gür., 2019)**

Hence the structure of the synthesized compound of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol is confirmed by H^1 NMR spectrum.

FIGURE 7: H^1 NMR Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol

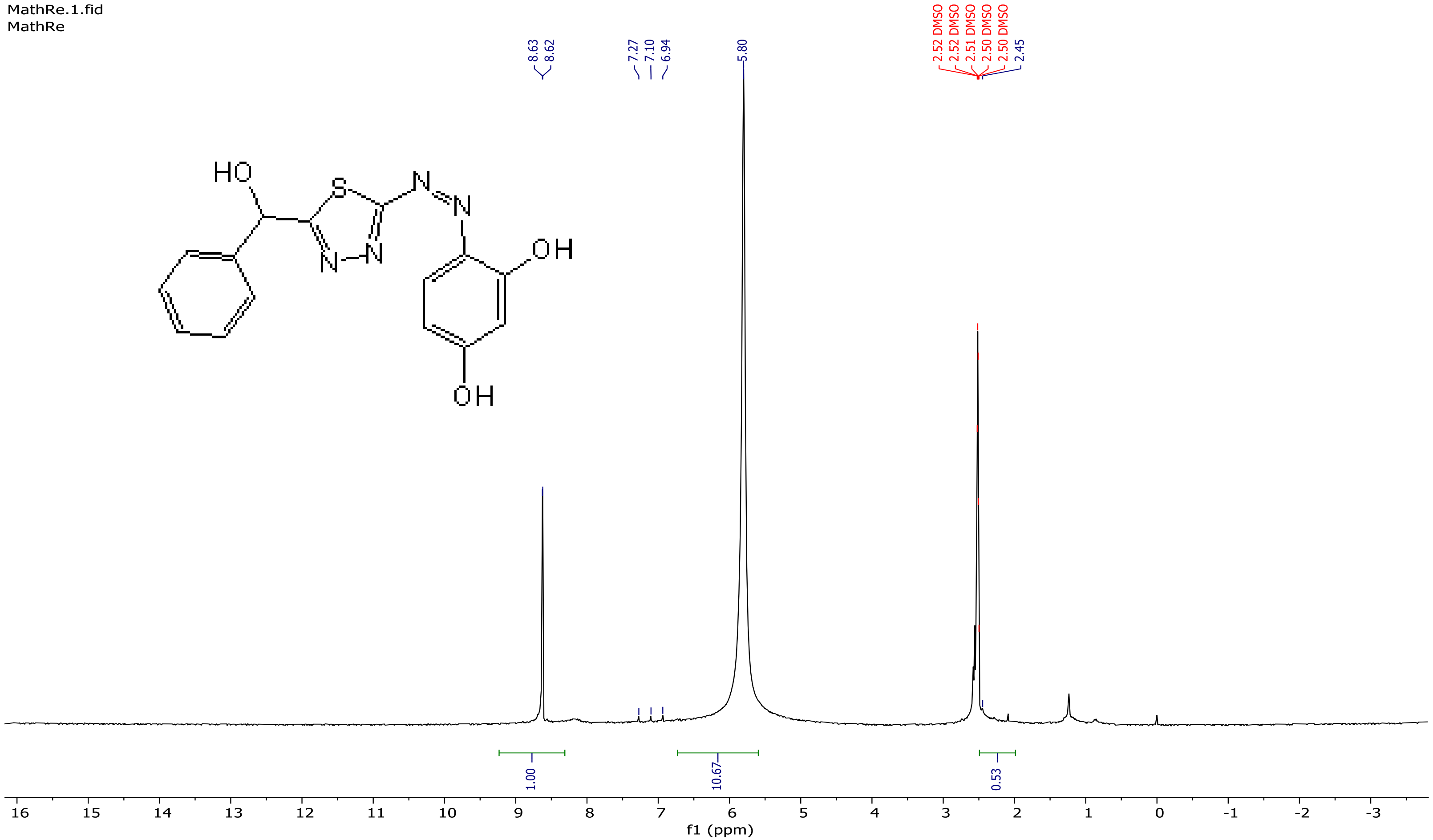


FIGURE 8: H^1 NMR Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol

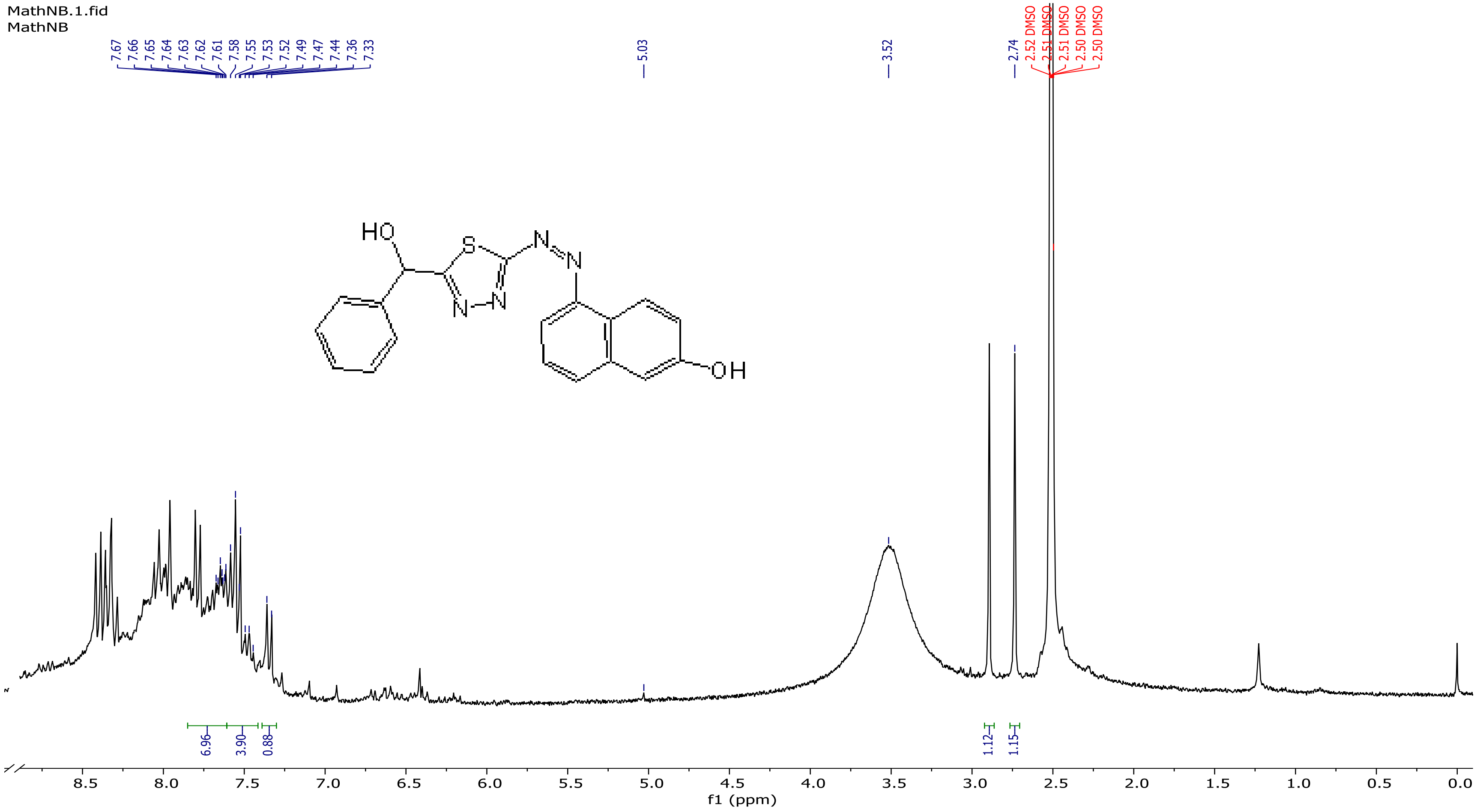


FIGURE 9: Expanded H^1 NMR Spectrum of (Z)-6-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)naphthalen-2-ol

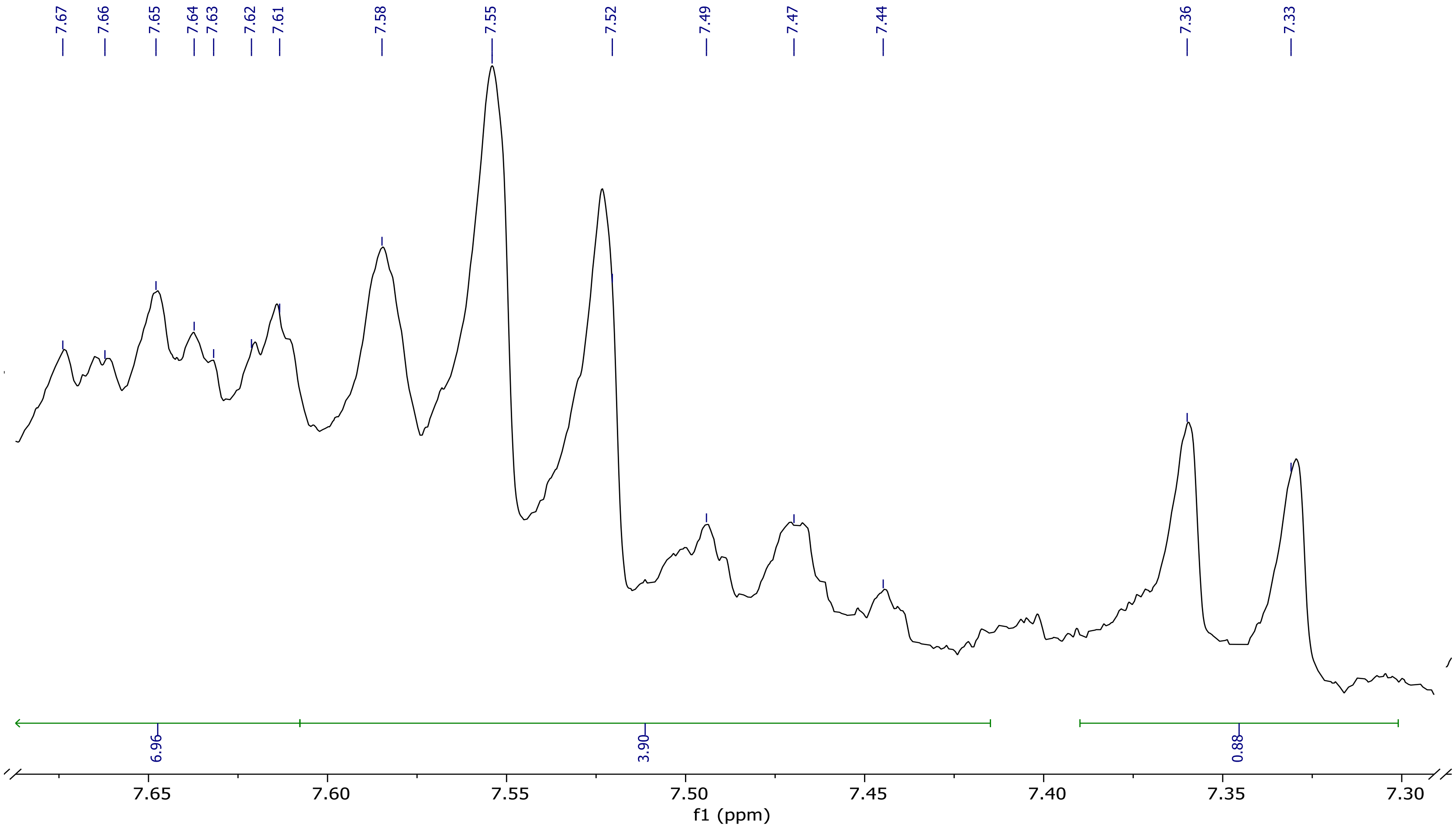


FIGURE 10: H^1 NMR Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol

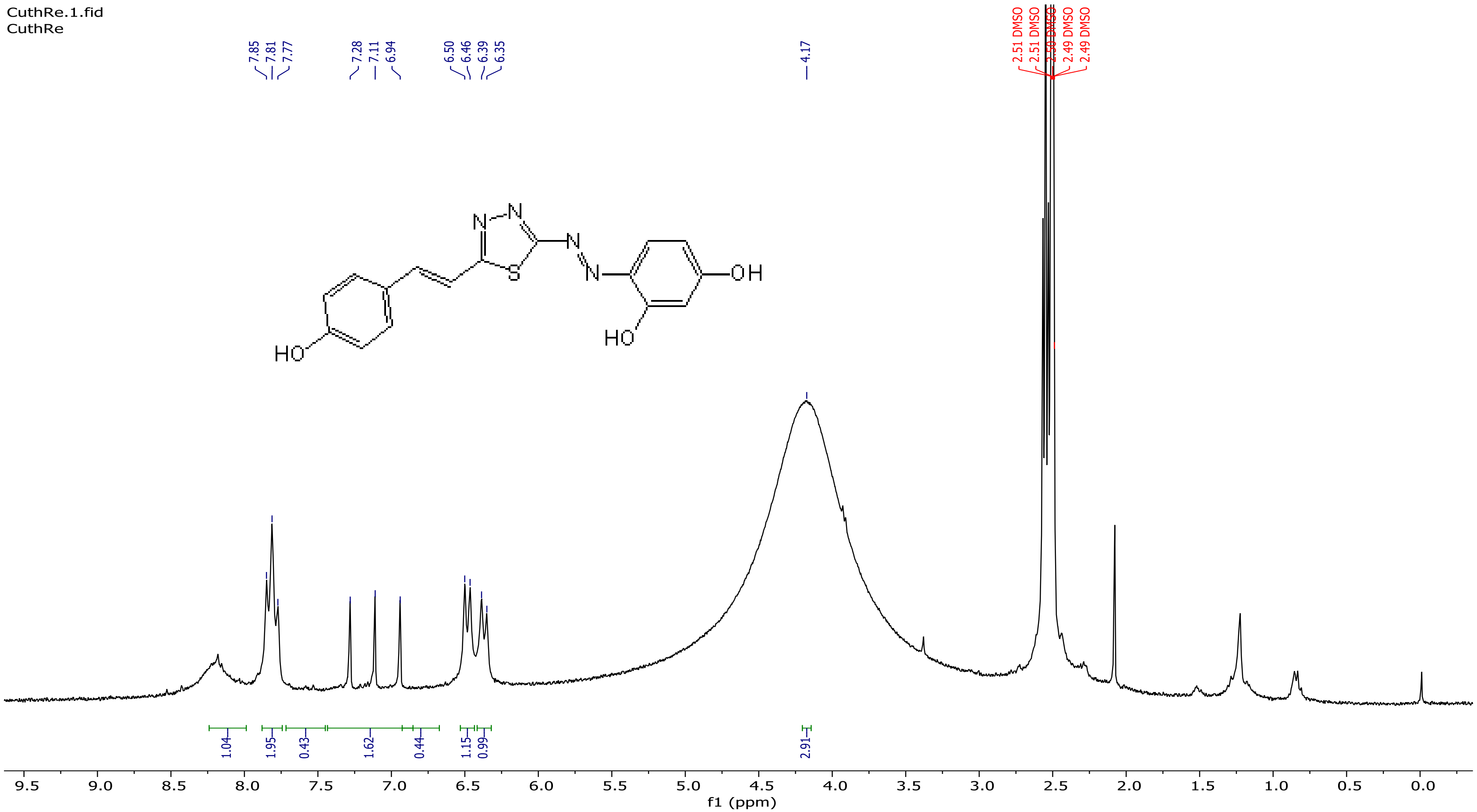
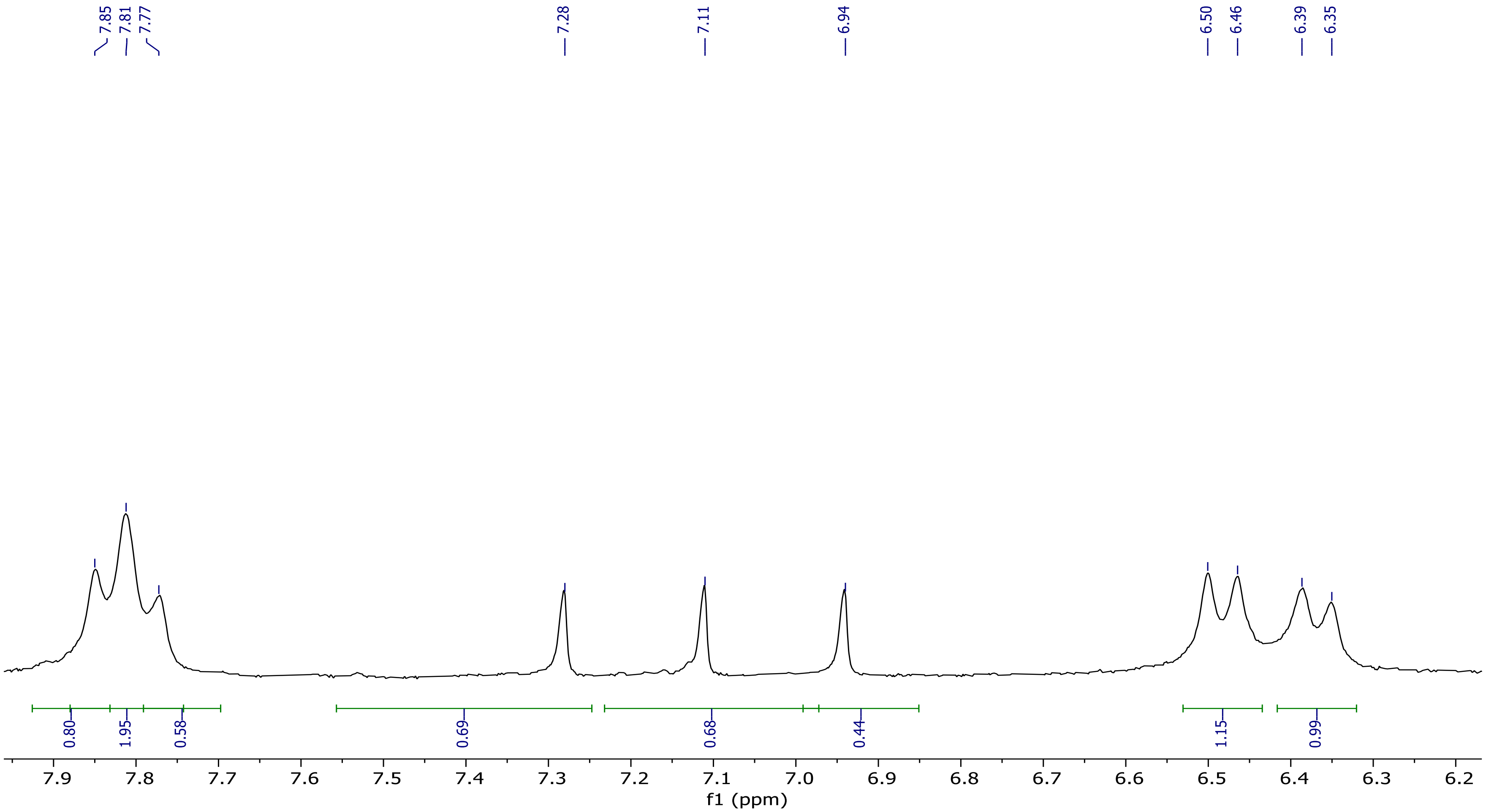


FIGURE 11: Expanded H^1 NMR Spectrum of 4-((E)-(5-((E)-4-hydroxystyryl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol



4.2.4. FLUORESCENCE ANALYSIS

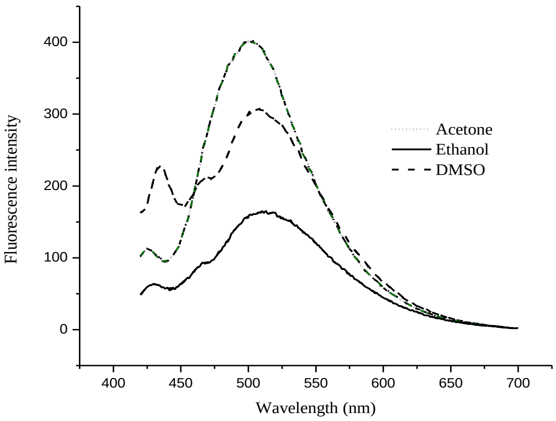
Fluorescence dyes are essential role in biological research because they combine very high sensitivity and selectivity in target detection with low toxicity.

The most intense and the most useful fluorescence is found in compounds containing aromatic functional groups with low energy transition levels. Compounds containing azo dyes structures and highly conjugation double bond may also fluorescence, but the number of these is highly compared with the number in the aromatic systems. The substitution on the benzene ring causes shift in the wavelength of the absorption maxima and changes in the fluorescence peaks. **(Mohammed G *et al.*, 2020)**

The fluorescence is more commonly associated with π-π^* transitions because such transitions exhibit shorter average life times and the deactivation processes are less likely to occur. In addition to, it is found empirically that azo dyes as fluorescent molecules is particularly favoured due to rigidity structures by the bridging azo group.

The fluorescence spectrum of the synthesized compound of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol is shown in **Figure 12** and the fluorescence are recorded in the concentration of 3.8×10^{-6} M at different solvents such as ethanol, acetone and DMSO. The compound are exhibited single distinct emission peak at 500-520nm at a room temperature. Hence, the compound have a higher fluorescence intensity due to the electron donating group(-OH group) are directly attached to the benzene ring of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol.

FIGURE 12: Fluorescence Spectrum of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol



Summary & Conclusion

5. SUMMARY AND CONCLUSION

The results of the synthesis and characterization of 2-amino-1,3,4-thiadiazole based azo dyes are summarized below,

- The reaction of diazotization of 2-amino-1,3,4-thiadiazole derivatives in DMF and concentrated sulphuric acid with coupling components such as resorcinol and β-naphthol in NaOH and water proceeded smoothly to give the corresponding 2-amino-1,3,4-thiadiazole based azo dyes under ice cold condition(-5^o C).
- The presence of chromophores(-N=N-) in a molecule was confirmed by UV spectrum at 360 – 450nm.
- The presence of -N=N-, C=N-, C-N, -OH, C-H, C-O and C-S-C bonds in a molecule was confirmed by FT-IR spectrum.
- The structure of the synthesized compound was confirmed by H^1 NMR spectrum.
- The synthesized compound of (Z)-4-((5-(hydroxy(phenyl)methyl)-1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol showed high fluorescence properties are confirmed by Fluorescence spectrum at 500-520nm.
- In drug discovery and development, organic dyes play an important role in fluorescent labelling of biomolecules and cells in order to investigate the in vivo or in vitro mechanism in living cells and tissues due to their commercial availability and ease of use by incorporating fluorescence properties. Hence, the research may be continued on fluorescence properties of 2-amino-1,3,4-thiadiazole based azo dyes in future.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Thank you