International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2025: 7.089

Synthesis and Characterization of 3- {[5-(2-aminophenyl)-1,3,4-thiadiazol-2-yl]diazenyl}pyridine-2,6-diamine

S. V. Jadhav

Indira Gandhi Kala Mahavidyalaya, Ralegaon, Yavatmal (M.S.), India
Email: *sj2451981[at]gmail.com*

Abstract: ***This study reports the synthesis, Characterization and application of new azo-linked compound, Synthesis and Characterization of 3- {[5-(2-aminophenyl)-1,3,4-thiadiazol-2-yl]diazenyl}pyridine-2,6-diamine for textile applications. The compound was synthesized via diazotization and coupling reactions, with its structure confirmed by FT-IR, 1H-NMR, and 13 C-NMR spectroscopy, The dyes fastness properties were assessed on Terrycloth, nylon, and Cotton Mesh under different conditions: neutral, alkaline (NaOH, and acidic (HCl) environments, Terrycloth exhibited excellent fastness properties across all tests, with minimal color fading. Nylon showed moderate resistance in neutral and acidic environments but was less stable under alkaline conditions. Cotton Mesh the lowest fastness, particularly under alkaline conditions, due to its cellulose-based structure, making it more prone to dye leaching. These results indicate the suitability of Terrycloth and Nylon for high-performance textile applications requiring color durability.***

Keywords: Terrycloth, Nylon, Characterization, Textile application and Heterocyclic compound

1. Introduction

Azo dyes dominate the textile industry, where they are used to color a wide array of fabrics, including cotton, and wool, silk, and synthetic fibers [1] Their popularity in textiles is due to their excellent colorfastness, cost-effectiveness, and the ability to produce a vast range of colors [2]. Beyond textiles, azo dyes are also used in the manufacturing of plastics, rubber products, and printing inks [3]. In the food industry, certain azo dyes are approved for use as food colorants, although their safety is subject to stringent regulatory controls. Additionally, they are found in cosmetics and personal care products, where they impart color to lipsticks, hair dyes, and other formulations. Thiadiazoles are a significant class of heterocyclic compounds that have garnered considerable attention in scientific research and industrial applications due to their unique chemical properties and broad spectrum of biological activities [4]. These compounds feature a five-membered ring structure containing two nitrogen atoms and one sulfur atom, which endows them with unique electronic and structural characteristics. The thiadiazole nucleus serves as a versatile scaffold for the development of various derivatives, each exhibiting distinct properties and functionalities. Thiadiazoles are characterized by a heterocyclic ring consisting of three carbon atoms, two nitrogen atoms, and one sulfur atom. The general formula for thiadiazoles is C2H2N2S, and they can exist in several isomeric forms, with the position of the nitrogen and sulfur atoms varying within the ring. The most common and studied isomers include 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,3,4-thiadiazole, and 1,2,5-thiadiazole. Each isomer exhibits unique electronic properties [5], making them suitable for different applications. Thiadiazole-incorporated azo dyes represent a fascinating intersection of two prominent classes of compounds, combining the vivid coloration properties of azo dyes with the unique chemical and biological characteristics of thiadiazoles. This hybrid approach leverages the structural versatility and functionality of both moieties, resulting in dyes with enhanced properties and expanded applications. These compounds are of significant interest in fields ranging from textile manufacturing to biomedical research, owing to their potential for improved stability, performance, and bioactivity.

Textile Industry: These dyes provide fabrics with vibrant and durable colors, with enhanced resistance to fading from light and washing. Their improved stability and potential for reduced environmental impact make them attractive for sustainable textile manufacturing [6].

Biomedical Field**:** The bioactive properties of thiadiazoles make these dyes promising candidates for medical applications, such as imaging, diagnostics, and therapeutic agents. For instance, their antimicrobial properties can be beneficial in developing antimicrobial fabrics and coatings [7].

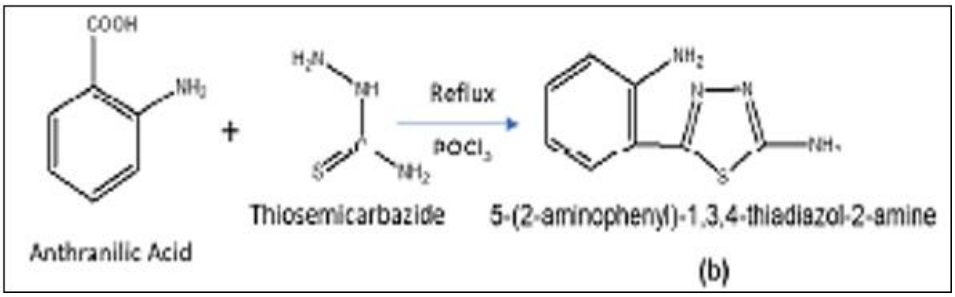
Material Science: Thiadiazole-incorporated azo dyes are used in the development of advanced materials, such as organic semiconductors, photodynamic therapy agents, and sensors. Their tunable optical properties are particularly useful in optoelectronic applications.

Agricultural Applications: These dyes can be utilized in the formulation of pesticides and herbicides, leveraging the bioactivity of thiadiazoles to enhance effectiveness while maintaining vibrant coloration for tracking and identification purposes.

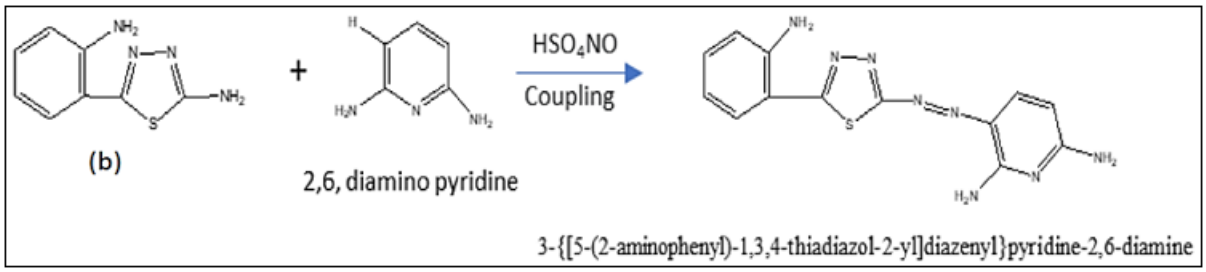
2. Method and Synthesis

The synthesis of 3- {[5-(2-aminophenyl)-1,3,4-thiadiazol-2-yl]diazenyl}pyridine-2,6-diamine achieved through a series of steps starting from basic materials like Anthranilic acid, thiosemicarbazide, 2,6 diamino pyridine and appropriate reagents for diazotization and coupling reactions.

Step 1: Reflux Cyclization from Anthranilic Acid -
Anthranilic acid (0.01 mol) and thiosemicarbazide (0.01 mol) were mixed in $POCl_3$ (25 mL) and the reaction flask was equipped with a reflux condenser. The mixture was refluxed for 7 hours at 100°C, leading to intra molecular cyclization and formation of 5-(2-aminophenyl)-1,3,4-thiadiazole- 2-amine. The mixture was cooled and quenched with ice, followed by neutralization with saturated Na_2CO_3. The solid was filtered, washed, and dried.



Step 2: Coupling with 2,6 diamino pyridine-
The diazotization of the thiadiazole intermediate was carried out at 0–5°C using NS acid. The freshly formed diazonium salt was then slowly added to a chilled ethanolic solution of 2,6 diamino pyridine (0.01 mol) adjusted to pH 5. The product separated gradually as a deep yellow-orange solid, which was washed with cold ethanol and recrystallized.



M.W: 312.36 $g.mol^{-1}$
Color- Yellow

3. Characterization

3.1 Elemental Analysis

Sr. No.	Name of Elements	Percentage (%)
1	Carbon (C)	49.99
2	Hydrogen (H)	3.87
3	Nitrogen (N)	35.87

3.2 ^{1}H NMR Spectra of 3- {[5-(2-aminophenyl)-1,3,4-thiadiazol-2-yl]diazenyl}pyridine-2,6-diamine

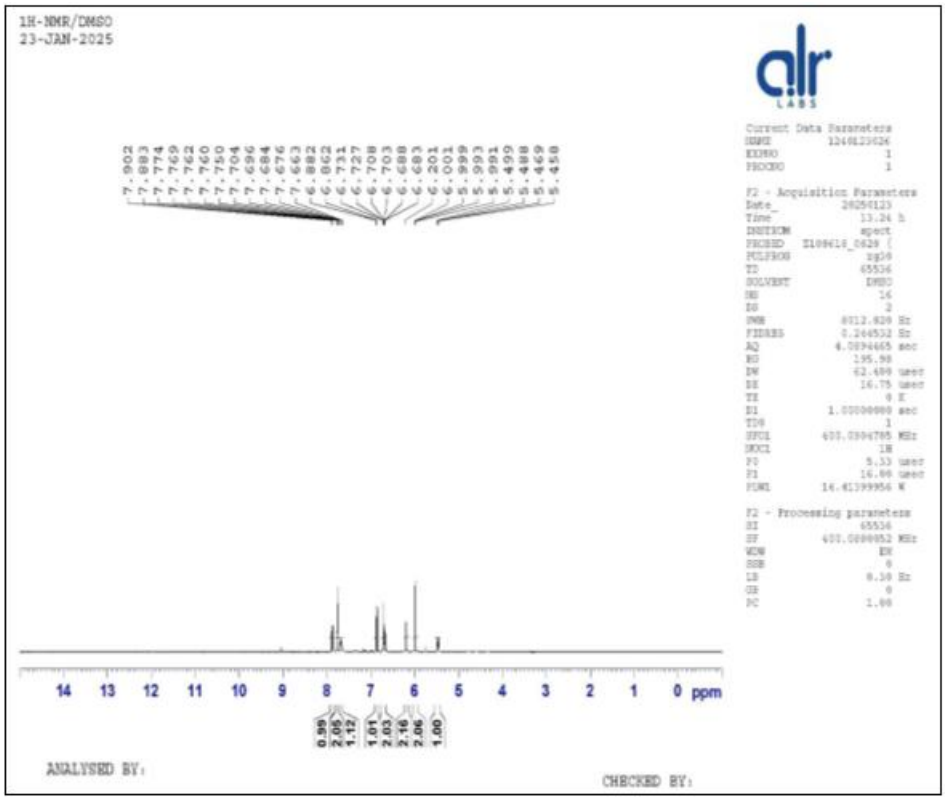


Figure 1: ^{1}H NMR spectrum

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):
δ 7.90–7.77 (m, 1H) – Aromatic proton, likely from the thiadiazole-substituted phenyl ring
δ 7.76–7.70 (m, 2H) – Aromatic protons on the substituted pyridine ring
δ 7.69–7.66 (m, 1H) – Another pyridine ring proton
δ 6.88–6.86 (m, 1H) – Aromatic proton adjacent to NH_2
δ 6.73–6.68 (m, 2H) – Aromatic protons on the aminophenyl ring
δ 6.20 (s, 2H) – Amino protons (–NH_2), sharp due to less exchange
δ 6.00–5.99 (br s, 2H) – Second –NH_2 group, possibly broadened due to hydrogen bonding
δ 5.49–5.45 (br s, 1H) – Likely a labile proton (possibly hydroxyl or another amino if present)
1. δ 7.90–7.77 (multiplet, 1H) This signal corresponds to an aromatic proton of the aminophenyl ring (probably ortho to the –NH_2 group).

13C NMR spectra of 3-{[5-(2-aminophenyl)-1,3,4-thiadiazol-2-yl]diazenyl}pyridine-2,6-diamine

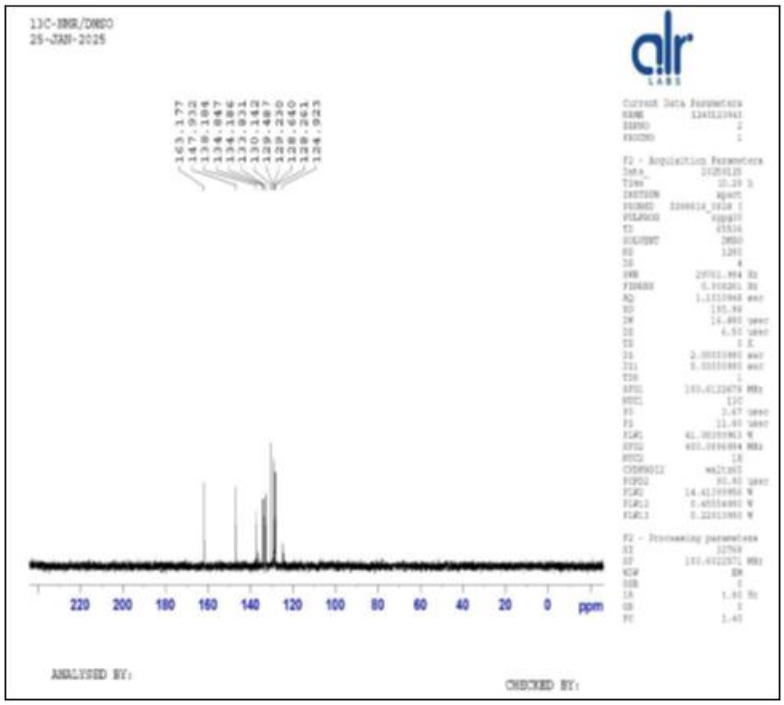


Figure 2: ^{13}C NMR

The ^{13}C NMR spectrum of 3-{[5-(2-aminophenyl)-1,3,4-thiadiazol-2-yl]diazenyl}pyridine-2,6-diamine, recorded in DMSO-d_6, reveals a total of 12 distinct signals, all within the aromatic and heteroaromatic region, confirming the expected structural framework. A highly deshielded signal at δ 163.17 ppm is attributed to the C-2 or C-6 carbon of the pyridine ring, which is directly bonded to an electron-donating $–NH_2$ group, causing significant downfield shift due to resonance and inductive effects. The resonance at δ 147.93 ppm corresponds likely to a quaternary carbon adjacent to the azo (–N=N–) linkage or to the C=N carbon in the thiadiazole ring, both typically appearing in this region due to their electron-deficient nature.

Signals at δ 134.84 and 134.18 ppm are assigned to quaternary aromatic carbons, particularly within the 1,3,4-thiadiazole and azo-connected rings, while δ 133.18, 130.81, 129.48, and 129.42 ppm are attributed to aromatic CH carbons of the phenyl and pyridine rings. These values indicate substitution by electron-donating and electron-withdrawing groups across the aromatic rings, resulting in closely spaced chemical shifts. The peaks at δ 128.63, 128.41, and 128.09 ppm correspond to inner-ring CH carbons, possibly those positioned between the azo and amine functionalities, where conjugation causes overlapping resonance patterns. Finally, the signal at δ 124.92 ppm can be assigned to an aromatic CH carbon adjacent to an amino or nitrogen center, indicative of strong ring current effects and π-conjugation.

Overall, the ^{13}C NMR spectrum strongly supports the proposed molecular structure, confirming the presence of a conjugated system comprising pyridine, thiadiazole, phenyl, azo, and amino groups. The lack of aliphatic carbon signals and the complete aromatic coverage align well with the structural features of the molecule.

δ (ppm)	Probable Carbon Environment
163.17	Pyridine ring C-2 or C-6, directly bonded to $–NH_2$, highly deshielded
147.93	Quaternary carbon adjacent to azo linkage or C=N in thiadiazole
134.84	Quaternary carbon in thiadiazole ring
134.18	Azo-substituted quaternary carbon on phenyl/pyridine ring
133.18	Aromatic carbon in phenyl ring, ortho to amino
130.81	Aromatic CH carbon on phenyl ring
129.48	CH carbon in pyridine ring, meta to amino

FTIR Spectra of 3-{[5-(2-Aminophenyl)-1,3,4-thiadiazol-2-yl]diazenyl}pyridine-2,6-diamine

This molecule contains the following key functional groups: Azo linkage (–N=N–), 1,3,4-Thiadiazole heterocycle, Primary aromatic amines ($–NH_2$), Substituted pyridine ring

Key Absorption Bands:

1) Broad band around 3400–3300 cm^{-1}. Assignment: N–H asymmetric and symmetric stretching of primary amine, Interpretation: Confirms presence of $–NH_2$ on both pyridine and phenyl rings
2) Peaks in 3100–3000 cm^{-1} - Assignment: Aromatic C–H stretching, Interpretation: Due to pyridine and phenyl rings
3) Strong band at ~1600–1550 cm^{-1} - Assignment: N=N stretching (azo linkage) and aromatic C=C stretching, Interpretation: Indicates successful diazo coupling
4) Peaks near 1480–1350 cm^{-1}- Assignment: C–N stretching (amines) and aromatic ring vibrations, Interpretation: Correlates with aromatic amino groups and heterocycles
5) Medium peaks in 1250–1050 cm^{-1}- Assignment: C–N or N–N bending and pyridine ring deformation, Interpretation: Matches with substituted pyridine and thiadiazole features
6) Fingerprint region (900–700 cm^{-1}) - Assignment: Out-of-plane bending of aromatic C–H bonds, Interpretation: Substitution pattern of aromatic rings

The FTIR spectrum confirms the following: Primary aromatic amine groups ($–NH_2$), Azo functionality (–N=N–) clearly indicated, Presence of both pyridine and phenyl aromatic rings

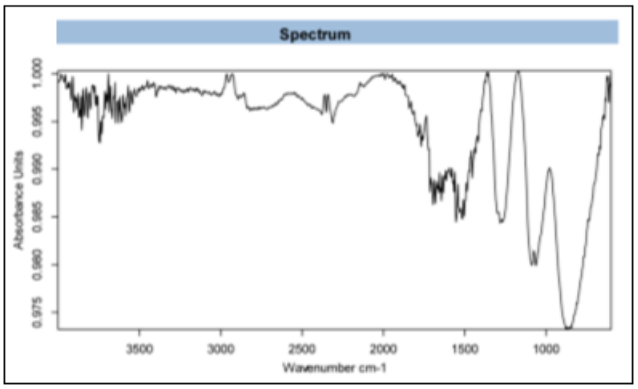


Figure 3: FTIR Spectrum

References

[1] ShrabanaSarkar, Aparna Banerjee:Degradation of synthetic Azo dyes of Textile industry, a Sustainable Approach using microbial Enzymes:Water Conserv Scieng; 2017, 2; pp-121-131.
[2] 2.Shrikrishna Digamber Tupare:Versality of Azodyes: Ashort review:International Journal of Scientific Research in Chemistry; Feb 2024; 9(7); pp-292-297.
[3] 3.Sneha Saad Abdullahi, Haruna Mush, Sneha Habibu: Comparative study and dyeing performance of as-synthesized azo heterocyclic monomeric, polymeric and commercial disperse dyes: Turk j chem: July2022,3;46(6), pp-1841-1852.
[4] Sanjay Belowar, Md. Abdul Jalil; Recent Advancements in the chemistry of 1,3,4-thiadiazole ring containing azo dyes: Elsevier: March 2026, pp-1-24.
[5] Nikita S. Gudim, Ekaterina A. Khyazeva: Benzo thiadiazole vs. iso Benzothiadiazole: Synthesis, Elearochemical, and optical properties of D-A-D Conjugated molecules based on them: Journals molecules: Aug 2021, 14; 26(16), 4931.
[6] Hamada Abdelwahab, Fatima A. M. Al- Zahrani: New thiadiazole azo disperse dyes derivatives and their application as a coloredmaterial for silk screen-printing ink for printing on polyster fabric:Pigment and Resin Tech; Sept.2022;53(3),pp-294-305.
[7] Jiaajiao Guo, Zhouling Xie,: Thiadiazole-based analogues as potential antibacterial agents against

methicillin- resistant Staphylococcus aureus(MRSA) and their SAR elucidation: European journals of medicinal Chemistry: Nov-2023, Vol-259, Article-5689.
[8] Shui-Lin Yan, Ming-Yan Yang, Zhao-Hhi Sun, Li-jing Min: Synthesis and Antifungal Activity of 1,2,3-thiadiazole derivatives containing 1,3,4-thiadiazole Moiety: Drug Design & Discovery: Aug 2014, 11(7), pp-940-943.