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

Synthesis and Characterization of 2-(5-{(E)-[4-(dimethylamino)phenyl]diazenyl}-1,3,4-thiadiazol-2-yl)aniline.

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 2-(5-{(E)-[4-(dimethylamino)phenyl]diazenyl}-1,3,4-thiadiazol-2-yl)aniline. The compound was synthesized via diazotization and coupling reactions, with its structure confirmed by FT-IR and 1H-NMR, spectroscopy. This synthesis consists of two steps such as Reflux Cyclization from Anthranilic acid and Coupling with N, N-Dimethyl aniline.***

Keywords: Characterization, Anthranilic acid, Spectroscopy, Cyclization

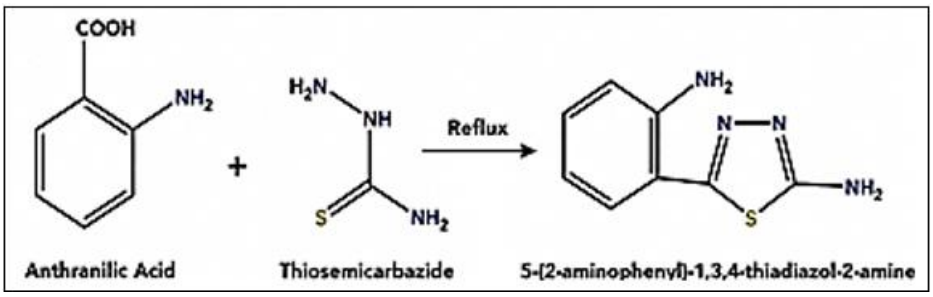
1. Introduction

A Thiadiazoles are five membered aromatic heterocyclic compounds consisting of one sulfur atom and two nitrogen atoms [1]. With molecular formula C2H2N2S, they exist in four constitutional isomers depending on the positions of the heteroatoms:1, 2, 3-, 1, 2, 4-, 1, 2, 5-, and 1,3,4-thiadiazole [2]. All thiadiazoles are aromatic in nature because of the ring system is stabilized by two double bonds and a lone pair of electrons from the sulfur atom [3]. Thiadiazole rings act as bioisosteres for pyrimidine and oxadiazole rings, allowing them to interact efficiently with biological targets [4]. 1, 3, 4-thiadiazole is the most important isomer in drug discovery, found in FDA-approved medications like acetazolamide (diuretic) and sulfamethizole (antimicrobial) [5]. 1, 2, 4-Thiadiazole is a commonly used in agricultural fungicides, antibacterial agents, and dyes [6]. 1, 2, 3 and 1, 2, 5-Thiadiazole is a valued building blocks in specialized pharmaceutical synthesis and materials science [7]. Thiadiazole- incorporated azo dyes are advanced synthetic colorants containing an azo group (-N=N-) linked to a thiadiazole heterocyclic ring. These specialized compounds offer deeps hues, enhanced thermal and photochemical stability and valuable biological activities, making them useful in textile, optics and pharmacology [8]. These dyes has coordination ability because of nitrogen and sulfur atoms act as chelating sites to form stable transition metal complexes. It has biological activities display notable antibacterial, antifungal and antioxidant properties. This incorporated azo dyes used as a textile dyeing act as reliable disperse dyes for synthetic fibers like polyster and it has some biological importance such as explored for pharmaceutical applications and targeted therapeutic evaluations.

2. Method and Synthesis

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

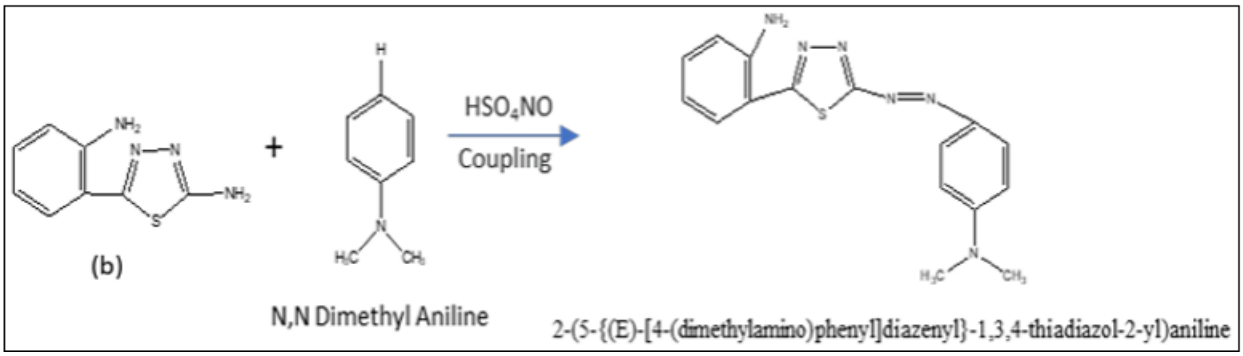
Step 1: Reflux Cyclization from Anthranilic Acid -
Anthranilic acid (0.01 mol) and thiosemicarbazide (0.01 mol) were mixed in $POCl_3$ (25 mL) and the reaction flask was equipped with a reflux condenser. The mixture was refluxed for 7 hours at 100°C, leading to intramolecular cyclization and formation of 2-amino-5-(2-aminophenyl)-1,3,4-thiadiazole. 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 N, N-Dimethyl Aniline-
A diazonium salt was freshly prepared by adding 0.01 mol (0.7 g) of sodium nitrite to 2.5 mL of concentrated sulfuric acid at 0–5 °C, forming nitrosyl sulfuric acid. This was slowly introduced into a chilled solution of 0.01 mol of the thiadiazole-based aryl amine in concentrated H_2SO_4, maintaining the temperature below 5 °C with continuous stirring. After 30 minutes, the cold diazonium solution was slowly added drop wise to a precooled basic solution of 0.01 mol (1.23 g) of N, N-dimethyl aniline dissolved in 10%

NaOH. A deep-colored azo dye began to precipitate immediately, indicating a successful electrophilic substitution at the Para-position of the dimethyl aniline ring. The reaction mixture was stirred for 1 hour, and the resulting product was filtered, washed with chilled water, dried, and recrystallized from ethanol to obtain pure 2-(5-{(E)[4-(dimethylamino) phenyl] diazenyl}-1,3,4-thiadiazol-2-yl) aniline in good yield.

M.W.: 324.41 g·mol^{-1}. Colour: Dark Brown



3. Characterization

1) CHNS analysis

Sr. No.	Name of Elements	Percentage (%)
1	Carbon (C)	59.24%
2	Hydrogen (H)	4.97%
3	Nitrogen (N)	25.91%

2) ^{1}H NMR spectrum

δ 8.48 ppm (1H): Strongly deshielded proton, probably at the ortho position to a –COOH group or within the azo-thiadiazole ring system. The deshielding suggests conjugation with electron withdrawing groups. δ 7.46 ppm (2H): Aromatic protons of Para-substituted benzoic acid ring, likely meta to both carboxyl and azo linkages. δ 7.22 ppm (2H): Aromatic protons on the azo-linked phenyl ring, potentially meta to the azo and hydroxyl groups, experiencing moderate deshielding. δ 7.00 ppm (1H): Aromatic proton in a more shielded environment, probably adjacent to an electron-donating –OH group, or at a position where resonance stabilization occurs. δ 6.91–6.90 ppm (1H): Isolated aromatic proton, close to –OH, likely shows slight multiplicity due to coupling with neighboring protons. δ 6.76 ppm (3H): Likely a set of overlapping aromatic protons, typically observed when the ring is highly substituted, such as in 2,4,6-trisubstituted phenyl rings. δ 6.33 ppm (1H): Highly shielded aromatic proton, likely between two electron-donating groups, such as –OH and –NH_2 or –OH and –OCH_3. δ 5.49–5.45 ppm (1H): This low-field broad signal may correspond to a phenolic –OH proton, often downfield due to strong intramolecular hydrogen bonding or solvent interactions in $DMSOd_6$.

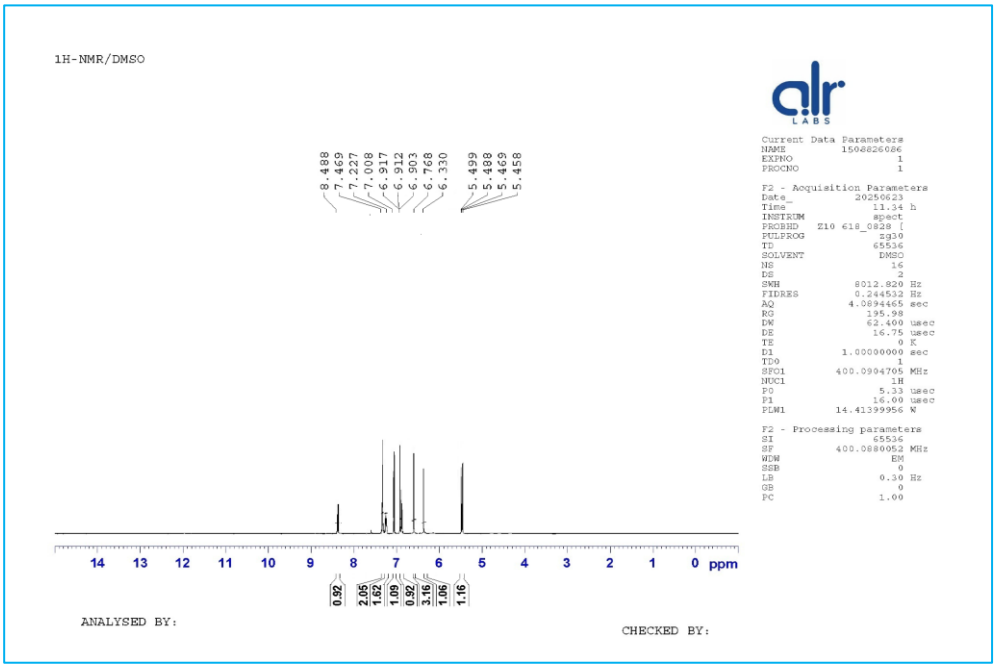


Figure 1: ^{1}H NMR spectra of 2-(5-{(E)-[4-(dimethyl amino) phenyl] diazenyl}-1,3,4-thiadiazol-2-yl)aniline

3) FTIR Spectra

The FTIR spectrum of 2-(5-{(E)-[4-(dimethylamino)phenyl] diazenyl}-1,3,4-thiadiazol-2yl) aniline displays distinct absorption bands corresponding to its functional groups, confirming the structural features of the synthesized azo dye. A broad band observed around 3300–3400 cm^{-1} is characteristic of N–H stretching vibrations from the primary amine group attached to the aromatic ring. This peak

indicates the presence of a free –NH_2 group which plays a key role in hydrogen bonding and solubility characteristics of the dye. A strong absorption peak around 1570–1600 cm^{-1} corresponds to azo (–N=N–) group stretching, validating successful diazo coupling between the dimethyl amino phenyl and thiadiazole units. Additionally, aromatic C=C stretching vibrations appear in the range of 1450–1600 cm^{-1}, which are associated with the benzene ring vibrations in both aromatic moieties. The presence of a C–N stretching vibration, arising from the dimethyl amino group, is evident in the range of 1200–1350 cm^{-1}, confirming the substitution on the Para-position of the phenyl ring. Absorptions observed near 1100–1000 cm^{-1} are due to C–S and C–N vibrations from the thiadiazole ring, which is integral to the electron-rich heterocyclic core of the molecule. Furthermore, weak bands around 2900 cm^{-1} may be attributed to C–H stretching from aliphatic methyl groups of the dimethyl amino substituent.

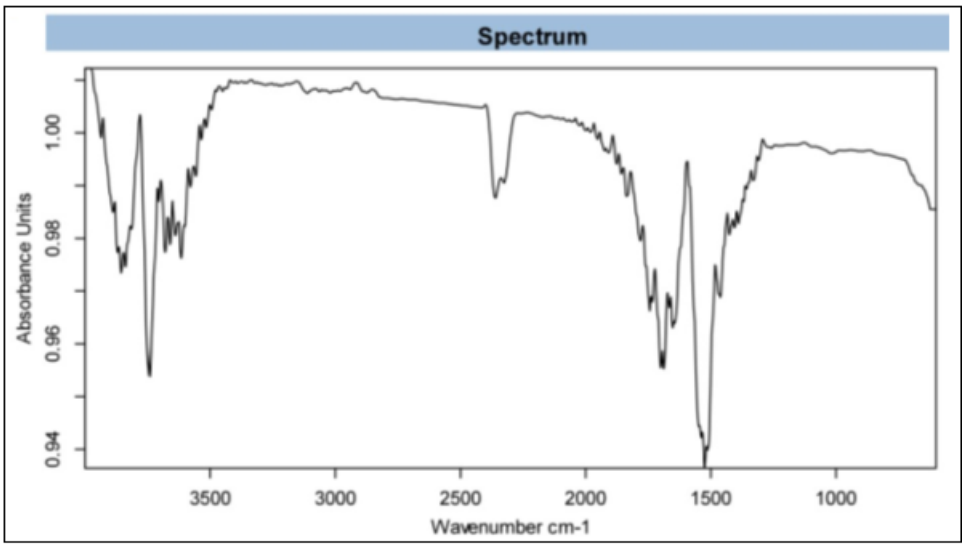


Figure 2: FTIR Spectra of 2-(5-{(E)-[4-(dimethylamino) phenyl]diazenyl}-1,3,4-thiadiazol-2-yl)aniline

4. Conclusion

The study successfully reports the synthesis and characterization of the novel azo-linked compound 2-(5-{(E)-[4-(dimethylamino)phenyl]diazenyl}-1,3,4-thiadiazol-2-yl) aniline. The compound was obtained through a simple two-step synthetic route involving reflux cyclization of anthranilic acid followed by diazotization and coupling with N, N-dimethylaniline. The formation of the desired azo-thiadiazole framework was confirmed by FTIR and ^{1}H-NMR spectroscopy. Overall, the study demonstrates an effective approach for synthesizing a new heterocyclic azo compound with potential relevance for further chemical and functional investigations.

References

[1] Yijing Li, Jingkum Geng: Thiadiazole-a promising structure in medicinal chemistry: Chemistry Europe: Dec-2012; Volume-8; Issue-1; pp-27-41.
[2] Kantabathina Hemantha, Kaviarasan Lakshmanan : A Review of Biological Activities-1,3,4- Thiadiazole and its derivatives: Rasayan Journal of Chemistry; January 2022;15(02); pp-1573-1587.
[3] Daniel Glassman Mitrik: A Theoretical study on the Aromaticity of Thiadiazoles and related compounds: Journal of Molecular structure THEOCHEM; August-2001;549(3),pp-285-288.
[4] Rana M El-Masry, Hanan H Kadry, Azza T Taher: Comparative Study of the Synthetic Approaches and Biological Activities of the Bioisosteres of 1,3,4-Oxadiazoles and 1,3,4-thiadiazoles over the Past Decade:Molecules:Apr-2022;22;27(9):2709.
[5] Sara Janowska, Dmytro Khylyuk, Anna Bielawska:New 1,3,4-Thiadiazole Derivatives with Anticancer Activity:Journal Molecules:March-2022;27(6),1814.
[6] Zhijiang Fan, Jun Shi, Na Luo: Synthesis, Crystal Structure and Agriculture Antimicrobial Evaluation of Novel Quinazoline Thioether Derivatives incorporating the 1,2,4-Triazolo[4,3-a]pyridine Moiety:Journal of Agriculture and food Chemistry: Sept.2019;
[7] Vaibhav Saxena: Synthesis and analgesic, anti-inflammatory activities of some novel thiadiazole derivatives: International Journals of Pharmaceutical Sciences and Drug Research, 2021, Vol. 13, issue-1.
[8] Harish Chowhan, Human Health and Dyes for Textiles. Journal of Textile Science & Engineering, 2024. 14(4): p.1-2.