

Synthesis and Characterization of Salicylic acid-derived Thiadiazol coupled Resorcinol for Textile Application on Terrycloth, Nylon, and Cotton Fiber

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Abstract:

This study reports the synthesis, characterization, and application of a new azo-linked compound, 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol, for textile applications. The compound was synthesized via diazotization and coupling reactions, with its structure confirmed by FT-IR, ¹H-NMR, and ¹³C-NMR spectroscopy. The dye's 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.

1. Introduction:

Water pollution is a pressing environmental issue exacerbated by industrial effluents containing synthetic dye [1-2]. These dyes are extensively used in industries such as textiles, paper, leather, and plastics [3]. Their complex aromatic structures make them resistant to conventional wastewater treatments, leading to persistent pollution that poses significant ecological and health risks [4-5]. Many synthetic dyes are non-biodegradable, toxic, and carcinogenic, further complicating their environmental impact. When discharged into water bodies, these dyes degrade water quality by affecting aesthetics, limiting light penetration, and disrupting aquatic ecosystems, including photosynthesis and oxygen balance. Additionally, chemical transformations of these dyes can produce harmful byproducts, such as carcinogenic aromatic amines, which pose further health risks.

The textile industry, a major consumer of synthetic dyes, contributes substantially to this problem. Approximately 10-15% of the 700,000 tons of dyes produced annually are lost during dyeing processes and released as effluent [3, 6-7]. Azo dyes, the most widely used class of synthetic dyes, are valued for their vibrant colors and chemical stability. However, they resist biological degradation, and under anaerobic conditions, they can break down into toxic aromatic amines. Therefore, the development of novel, durable azo dyes is critical for enhancing textile performance while minimizing environmental hazards.

The fastness of dyes, which refers to their ability to resist fading or bleeding during exposure to various conditions, is a key performance metric in textiles. Factors such as washing, light exposure, and friction significantly influence the longevity and appearance of dyed fabrics. Different fabrics-natural fibers like cotton and wool or synthetic ones like polyester-exhibit distinct interactions with dyes due to variations in their chemical composition and structural properties.

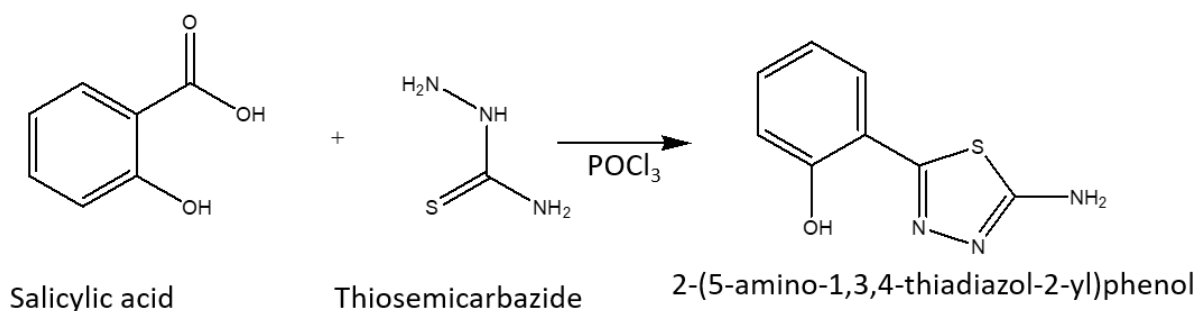
Azo dyes, characterized by one or more azo ($-N=N-$) groups, vary in complexity from monoazo to polyazo structures. Monoazo dyes, the simplest, are used on natural fibers like cotton and wool, offering moderate fastness [8-10]. Disazo and trisazo dyes, with more complex structures, produce vivid colors and exhibit better fastness properties, especially on synthetic fibers like polyester [11-14]. Polyazo dyes, containing multiple azo groups, provide deep shades with excellent fastness, particularly for synthetic textiles [15-17]. Reactive azo dyes, which chemically bond with cellulosic fibers, offer superior washing fastness, while acid azo dyes are preferred for protein-based fibers like wool and silk due to their ionic interactions. Despite their advantages, some azo dyes face challenges such as poor fastness under certain conditions or the energy-intensive processes required for dyeing synthetic fibers. These issues underscore the need for innovative dyes with improved properties. Compounds containing functional groups like azo ($-N=N-$) and thiadiazole are promising due to their unique electronic structures, strong visible-light absorption, and enhanced stability [18-20]. The addition of functional groups like aldehyde ($-CHO$) and hydroxyl ($-OH$) can further improve reactivity and molecular architecture [20].

In this study, we synthesized and characterized a novel azo-linked compound, 4- $\{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl\}$ benzene-1,3-diol, designed for textile applications. The compound was synthesized through a multi-step reaction involving the coupling of a thiadiazole derivative. Its unique structural features, including the electron-accepting thiadiazole moiety, enhance its molecular stability and dyeing performance.

To evaluate its applicability, we tested the color fastness of the synthesized dye on Terry cloth, Nylon, and Cotton mesh under various conditions, including washing with detergent, alkaline, and acidic solutions. These tests focused on three critical fastness properties like washing, light, and rubbing-highlighting the dye's potential for textile applications demanding durability and color retention. This approach aims to advance the development of sustainable dyes that meet both industrial and environmental standards.

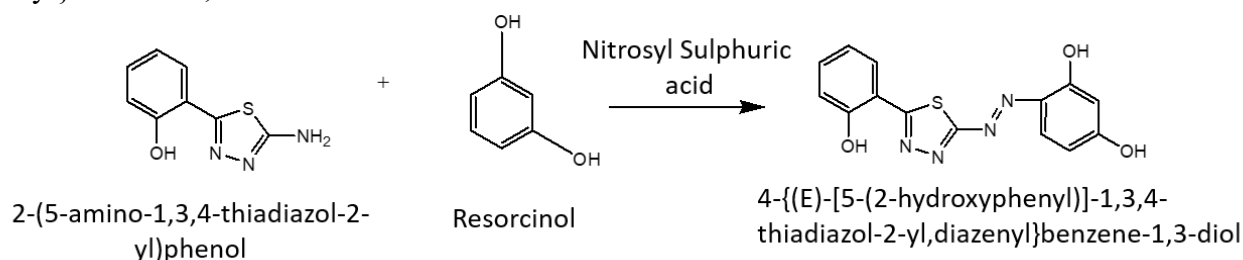
2. Synthesis:

Salicylic acid (1.38 g, 10 mmol) and thiosemicarbazide (0.91 g, 10 mmol) were combined in the presence of phosphorus oxychloride (10 mL) as a cyclization agent. The reaction mixture was refluxed at 110°C for 6 hours under constant stirring. During the reaction, the formation of a clear solution was observed, indicating progression. Upon completion, the reaction mixture was cooled to room temperature and carefully poured into crushed ice with stirring to precipitate the product. The crude 1,3,4-thiadiazole derivative was filtered, washed thoroughly with cold water to remove residual phosphorus-containing by-products, and dried under vacuum. The product was 2-(5-amino-1,3,4-thiadiazol-2-yl) phenol recrystallized from ethanol to yield pure as a white to pale yellow crystalline solid.



Scheme-1 Reaction of Salicylic acid and thiosemicarbazide

2-(5-amino-1,3,4-thiadiazol-2-yl) phenol (1 mol) was diazotized in the presence of nitrosyl sulfuric acid (prepared from sodium nitrite, 0.37 g, 5.4 mmol, and concentrated sulfuric acid, 2 mL) at 0-5°C. The diazonium salt was then coupled with resorcinol (0.77 g, 5.4 mmol) in an alkaline medium, using a cold aqueous sodium hydroxide solution (1.0 g NaOH in 10 mL water). The reaction mixture was stirred at 0-5°C for 2 hours, yielding a brightly colored azo compound. The crude product was filtered, washed with water, and recrystallized from ethanol to give pure 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl, diazenyl}benzene-1,3-diol



Scheme-2 Reaction of synthesized compound in first step with Resorcinol in the presence of nitrosyl sulphuric acid

4. Results and Discussion:

4.1. ¹H-NMR spectra:

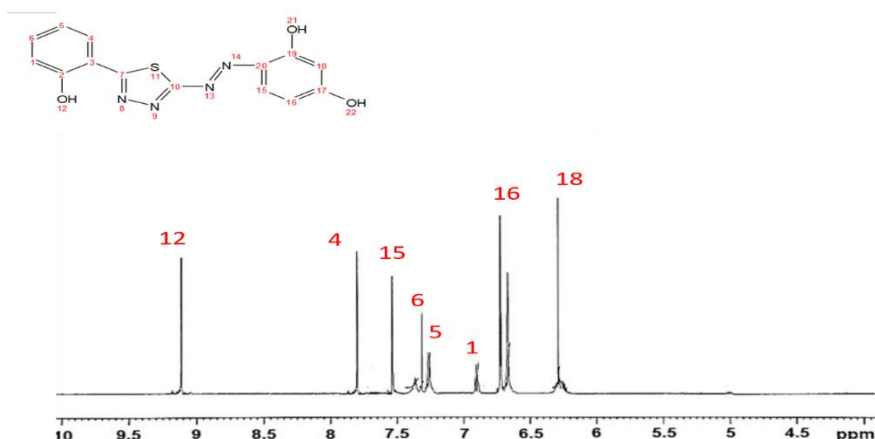


Figure-1: ¹H-NMR (DMSO-d₆, 400 MHz) for 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl, diazenyl}benzene-1,3-diol

δ 6.3 (1H, s, H-18): This singlet corresponds to the para-position proton of the benzene ring attached to the hydroxyphenyl group. The absence of splitting indicates no direct coupling with adjacent protons.

δ 6.7 (1H, d, H-16): This doublet arises from the proton at the 16-position of the benzoic acid ring. The lack of splitting confirms its isolated environment.

δ 6.89 (1H, s, H-1): This singlet is attributed to the proton at the 1st position of the 2-hydroxyphenyl ring.

δ 7.3 (1H, d, $J = 8.4$ Hz, H-5): A doublet that represents the proton at the 5th position of the hydroxyphenyl ring moiety. The coupling constant indicates an ortho-coupling interaction with the adjacent proton at position 5.

δ 7.35 (1H, s, H-6): A singlet corresponding to the proton at the 6th position of the compound, unaffected by neighboring protons.

δ 7.51 (1H, s, H-15): A singlet corresponding to the proton at the 15th position of the compound, unaffected by neighboring protons.

δ 7.7 (1H, d, $J = 8.4$ Hz, H-4): This doublet is attributed to the proton at the 4th position of the hydroxyphenyl moiety, coupled with the adjacent proton.

δ 9.2 (1H, d, $J = 8.4$ Hz, H-12): This doublet is attributed to the OH at attached to 2nd position of the hydroxyphenyl.

The ¹H-NMR spectrum of 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol provides a detailed account of the proton environment within the molecule. The singlet at δ 6.3 (1H, s, H-18) corresponds to the para-position proton on the benzene ring attached to the hydroxyphenyl group, indicating no coupling interactions with adjacent protons. A doublet observed at δ 6.7 (1H, d, H-16) arises from the proton at the 16th position of the benzoic acid ring, confirming an isolated proton environment. Similarly, δ 6.89 (1H, s, H-1) is attributed to the proton at the 1st position of the 2-hydroxyphenyl ring, with no observable coupling. The resonance at δ 7.3 (1H, d, $J = 8.4$ Hz, H-5) represents the proton at the 5th position of the hydroxyphenyl moiety, displaying ortho-coupling with an adjacent proton. A singlet at δ 7.35 (1H, s, H-6) corresponds to the proton at the 6th position, unaffected by neighboring protons. Another singlet is observed at δ 7.51 (1H, s, H-15) for the proton at the 15th position, further indicating the lack of coupling interactions. The doublet at δ 7.7 (1H, d, $J = 8.4$ Hz, H-4) is assigned to the proton at the 4th position of the hydroxyphenyl moiety, which shows coupling with an adjacent proton. A deshielded resonance at δ 9.2 (1H, d, $J = 8.4$ Hz, H-12) is attributed to the hydroxyl group at the 2nd position of the hydroxyphenyl ring. This downfield shift reflects the electron-withdrawing effects of the hydroxyl group and the associated hydrogen bonding interactions.

4.2. ¹³C-NMR spectra:

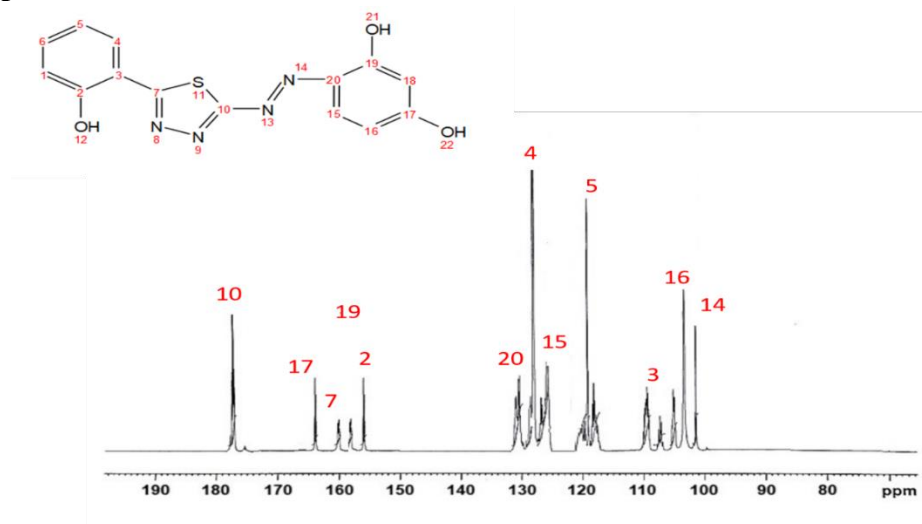


Figure-2: ^{13}C -NMR for 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol
 The ^{13}C NMR spectrum provides valuable insights into the carbon environments of the molecule, confirming the structure of 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol. Each signal was assigned as follows: The ^{13}C -NMR spectrum of the compound shows distinct peaks that are assigned to the carbons in the structure based on their chemical environments:

Peak at 179.3 ppm (C-10): This peak corresponds to the C-N carbon (thiocarbonyl group) of the thiadiazole ring. The high deshielding is due to the double bond to sulfur, which is highly electronegative.

Peak at 164.2 ppm (C-17): This signal is assigned to the phenolic carbon (C-OH) of the 2-hydroxyphenyl group. The downfield shift is caused by the attachment to the hydroxyl group and aromatic system.

Peak at 155.8 ppm (C-2): This peak corresponds to the phenolic carbon (C-OH) of the 1,3-dihydroxybenzene moiety. The chemical shift is influenced by the hydroxyl group and its position in the aromatic ring.

Peak at 160.2 ppm (C-7): This peak represents the diazenyl carbon (C=N) adjacent to the thiadiazole ring. The deshielding arises from the strong electronegative effect of the adjacent nitrogen atoms in the azo group.

Peaks at 128.7, 119.2 and 131.1 ppm (C-4, C-5, C-20): These peaks represent aromatic carbons in the benzene rings (both the 2-hydroxyphenyl and 1,3-dihydroxybenzene moieties). These carbons are influenced by their respective substituents, leading to slight variations in chemical shifts.

Peaks at 10.8, 118.2 and 103.1 ppm (C-3, C-15, C-16): These peaks are assigned to unsubstituted aromatic carbons within the benzene rings. They exhibit relatively upfield shifts due to the absence of electronegative substituents.

Peak at 101.8 ppm (C-14): This peak is associated with an aromatic carbon adjacent to the azo group in the 1,3-dihydroxybenzene moiety. The proximity to the diazenyl group causes mild deshielding.

Peaks at 157.9 ppm (C-19): This signal corresponds to an aromatic carbon adjacent to the phenolic group in the 2-hydroxyphenyl ring. The electron-donating effect of the hydroxyl group results in an upfield shift.

4.3.FT-IR Spectra:

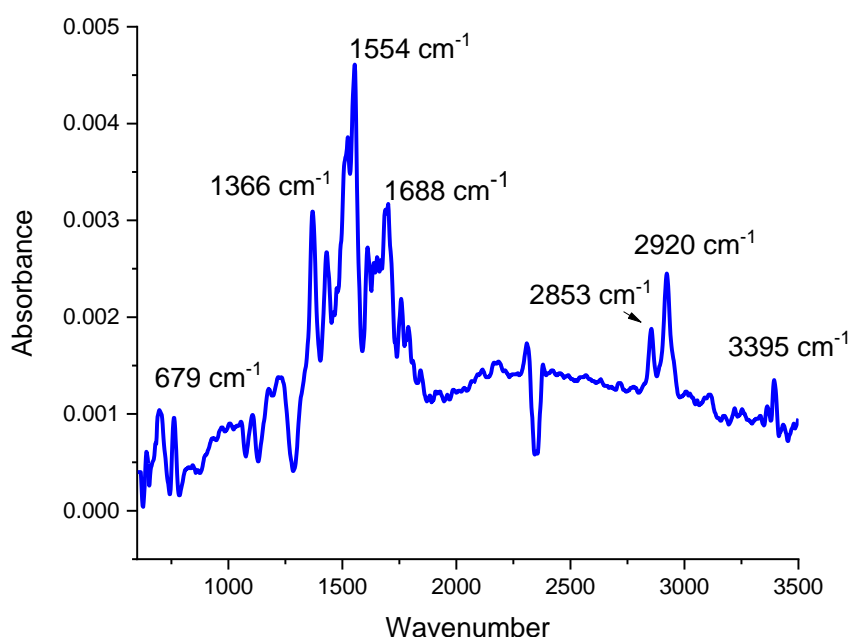


Figure-3: FT-IR spectra of 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol.

The FT-IR spectrum of 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol, reveals characteristic absorption bands corresponding to key functional groups present in the molecule. The observed peaks and their assignments are as follows:

1. 679 cm⁻¹ (C-S Stretch): The absorption at 679 cm⁻¹ is attributed to the C-S stretch vibration in the 1,3,4-thiadiazole ring. This peak is typically observed for sulfur-containing heterocycles.
2. 1366 cm⁻¹ (C-N Stretch): The peak at 1366 cm⁻¹ corresponds to the C-N stretching vibration of the diazenyl (-N=N-) group. This confirms the presence of the diazo group (-N=N-) in the structure.
3. 1554 cm⁻¹ (Aromatic C=C Stretch): The absorption at 1554 cm⁻¹ is attributed to the aromatic C=C stretching vibrations of the benzoic acid and 2,4-dihydroxyphenyl rings. This confirms the aromatic nature of the compound, reflecting the conjugation between the aromatic rings and the diazo group.
4. 1688 cm⁻¹ (C=O Stretch): The peak at 1688 cm⁻¹ is assigned to the C=O stretching vibration of the carboxyl group (-COOH) attached to the benzoic acid moiety. This indicates the presence of the carboxylic acid functional group in the compound.
5. 2853 cm⁻¹ (C-H Stretch, Aliphatic): The absorption at 2853 cm⁻¹ corresponds to the C-H stretching vibrations of the aliphatic CH₂ or CH₃ groups in the compound. This is typically seen in compounds with methyl or methylene groups attached to an aromatic ring.
6. 2920 cm⁻¹ (C-H Stretch, Aromatic): The absorption at 2920 cm⁻¹ is indicative of the C-H stretching vibrations of the aromatic C-H bonds, further confirming the presence of the aromatic rings in the structure.
7. 3395 cm⁻¹ (O-H Stretch): The broad absorption at 3395 cm⁻¹ is attributed to the O-H stretching vibration of the hydroxyl group (-OH) attached to the 2,4-dihydroxyphenyl ring. The broadness of the peak suggests the presence of strong hydrogen bonding, characteristic of hydroxyl groups.

The FT-IR spectrum of 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol, confirms the presence of several functional groups, including the hydroxyl group, diazenyl group, carboxyl group, and aromatic rings. The C=O stretch at 1688 cm⁻¹ and O-H stretch at 3395 cm⁻¹ are key features that confirm the carboxylic acid and hydroxyl functionalities, while the C-N stretch at 1366 cm⁻¹ and C-S stretch at 679 cm⁻¹ are distinctive for the diazenyl and thiadiazole components of the compound. These absorption peaks, in conjunction with the aromatic C=C stretches, provide conclusive evidence of the compound's structural integrity.

4.4. Dye fastening analysis:

The color fastness of the synthesized dye, 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol, was assessed separately under alkaline (NaOH) and acidic (HCl) conditions on three fabric types: Terry cloth, Nylon, and Cotton mesh. The performance was evaluated using a numerical scale ranging from 1 to 5, with 5 indicating excellent color retention and 1 representing severe fading. Additionally, the percentage of dye intensity retention was determined to quantify the extent of fading. The results are presented in Table 1 (for NaOH) and Table 2 (for HCl).

Sr. No.	Fabric used	Colour Fastness ratings	Intensity retention
1	Nylon	3	72%
2	Terry cloth	4	86%
3	Cotton mesh	2	55%

Table 1: Color Fastness Ratings and Intensity Retention Under NaOH Conditions

a. Observations for NaOH Washing:

Terrycloth: Exhibited good fastness (Rating 4), retaining 86% of its dye intensity. The dye’s stability in the alkaline environment indicates strong binding with synthetic tericot fibers.

Nylon: Demonstrated moderate fastness (Rating 3) with 72% intensity retention. The polymeric structure of nylon supports some level of dye adhesion but is less robust than tericot.

Cotton Mesh: Showed poor fastness (Rating 2), retaining only 55% of the dye intensity. The weak interactions between the dye and cotton fibers likely caused significant fading.

Sr. No.	Fabric used	Colour Fastness ratings	Intensity retention
1	Nylon	4	84%
2	Terrycloth	5	92%
3	Cotton mesh	2	57%

Table 2: Color Fastness Ratings and Intensity Retention Under HCl Conditions

b. Observations for HCl Washing:

Terrycloth: Maintained good fastness (Rating 5) with 92% intensity retention under acidic conditions, confirming the dye’s high affinity for synthetic fibers even in acidic environments.

Nylon: Registered moderate fastness (Rating 4) with 84% retention, similar to its performance in alkaline washing. This suggests that nylon’s dye adherence is not significantly affected by P^H changes.

Cotton Mesh: Performed poorly (Rating 2), retaining only 57% of dye intensity. The lack of chemical affinity between the dye and cotton fibers led to considerable fading.

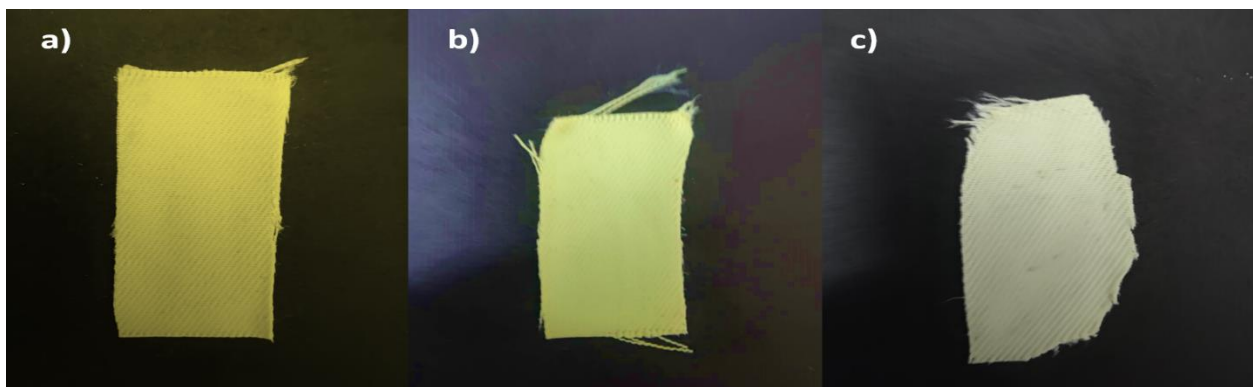


Figure 4: Cotton Mesh a) before washing, b) washed with NaOH c) Washed with HCl

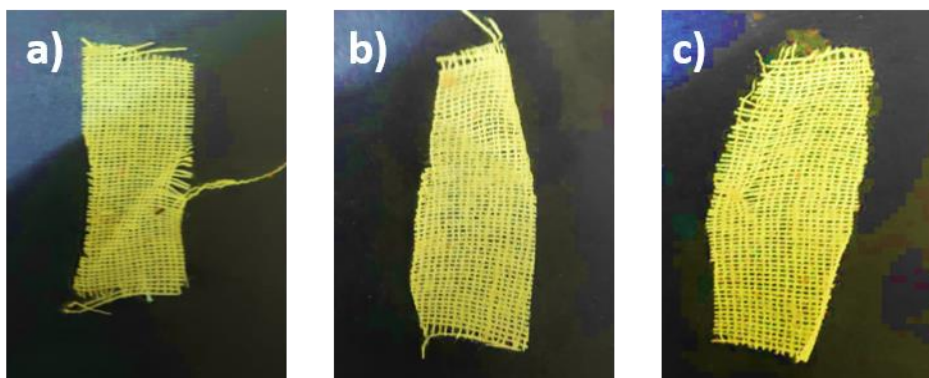


Figure 5: Terrycloth a) before washing b) washed with NaOH c) Washed with HCl

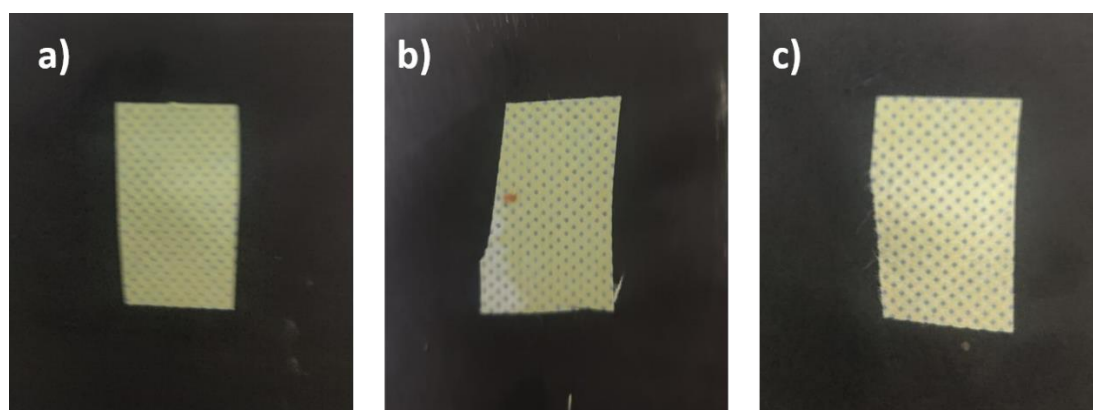


Figure 6: Nylon a) before washing b) washed with NaOH c) Washed with HCl

The dye showed consistent performance on synthetic fabrics (terrycloth and nylon) under both alkaline and acidic conditions, making it suitable for synthetic textile applications. Its excellent fastness on terrycloth (Rating 5) and moderate fastness on nylon (Rating 4) highlight its potential for durable coloration in synthetic fibers. However, its performance on cotton mesh (Rating 2) was inadequate, reflecting the dye's limited applicability to natural fibers. The separate evaluations under NaOH and HCl conditions provide a detailed understanding of the dye's stability and affinity across varying P^H levels.

4.5. Conclusion:

In this study, we successfully synthesized and characterized 4-{(E)-[5-(2-hydroxyphenyl)]-1,3,4-thiadiazol-2-yl,diazenyl}benzene-1,3-diol, a novel azo-based dye with potential applications in textile dyeing. The structural elucidation of the compound was confirmed using spectroscopic techniques, including 1H -NMR, ^{13}C -NMR, and FT-IR, which provided detailed insights into its chemical structure and functional groups. The dye demonstrated vibrant coloration and tunable absorption properties, attributable to its extended π -conjugation and electronic interactions between the azo and thiadiazole moieties.

The fastness properties of the dye were systematically evaluated on different fabrics under varying P^H conditions (alkaline and acidic). The results revealed excellent color retention on terrycloth, moderate retention on nylon, and poor performance on cotton mesh under acidic conditions. This disparity underscores the dye's higher affinity for synthetic fibers due to stronger interactions between the dye molecule and polymeric substrates, as opposed to natural fibers like cotton. The dye showed consistent stability in both acidic (HCl) and alkaline (NaOH) washing environments, maintaining its structural integrity and chromatic intensity in terrycloth and nylon, which further highlights its suitability for synthetic textile applications.

The investigation into the fastness properties, including quantitative assessments of dye intensity retention, provided a comprehensive understanding of the dye's performance under acidic conditions. The good fastness on terrycloth (92%) and moderate fastness on nylon (84%) make this dye a promising candidate for industrial applications in synthetic textiles, where durability and P^H resistance are essential. However, the lower fastness observed in cotton mesh (57%) suggests that further modifications to the dye's structure may be required to enhance its affinity for natural fibers. Overall, the study demonstrates the potential of the synthesized dye as a valuable addition to the azo dye family, particularly for use in durable synthetic textile coloration.

5. References:

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