

Synthesis and Characterization of Schiff bases Derived from 2-hydroxy-1-naphthaldehyde with Selected Primary Aromatic Amines

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Abstract

This study describes the synthesis of novel Schiff base compounds derived from 2-hydroxy-1-naphthaldehyde and various primary aromatic amines. A solvent-assisted mechanochemical approach was employed to produce these compounds efficiently. Characterization through IR spectroscopy, solubility testing, melting point determination, PXRD analysis, and elemental analysis confirmed the successful formation of the Schiff bases. The synthesized compounds exhibited high yields (>80%) and distinctive IR bands associated with the azomethine $\nu(\text{C}=\text{N})$ stretching vibration. Solubility studies revealed their preference for polar solvents. Melting points were relatively high, suggesting strong intermolecular interactions. PXRD analysis confirmed the formation of new crystalline products, distinct from the starting materials. Elemental analysis results aligned with the expected molecular compositions, supporting the proposed structures of the Schiff bases.

Keywords: Schiff base, azomethine, mechanochemistry, 2-hydroxy-1-naphthaldehyde, primary aromatic amines

1. Introduction

Schiff bases, a versatile class of organic compounds, have garnered significant attention due to their diverse applications in materials science and medicine (Echem, Oforka, and Abosode 2014; Emara 2010; Sani et al. 2022). These compounds, characterized by their azomethine group ($\text{C}=\text{N}$), are typically synthesized via the condensation of primary amines with aldehydes or ketones. Their structural diversity and tunable properties make them ideal building blocks for developing novel materials and bioactive molecules (Aliyu and Sani 2012; Emara 2010; Sani and Kurawa 2016).

In this study, we explored a sustainable and solvent-assisted approach to Schiff base synthesis using mechanochemical techniques. Mechanochemical synthesis utilizes mechanical energy, such as grinding or milling, to drive chemical reactions between solid materials. By eliminating the need for solvents, this

method offers a greener alternative to traditional solution-based approaches (Sani, Kurawa, and Siraj 2018).

In this context, 2-hydroxy-1-naphthaldehyde stands out as an intriguing precursor due to its naphthalene ring, which imparts unique electronic and steric properties to the resulting Schiff bases. By incorporating, we aimed to investigate the influence of its aromatic moiety on the chemical behavior and potential applications of these compounds.

A series of Schiff bases were synthesized and characterized by reacting with selected primary aromatic amines (4-iodoaniline, 4-aminobenzonitrile, 4-aminobenzoic acid, 3-aminobenzoic acid, and 2-aminobenzonitrile). The choice of these specific amines is motivated by their diverse functional groups and electronic effects, which are anticipated to significantly influence the properties of the resulting Schiff bases. For instance, the iodine atom in 4-iodoaniline introduces significant electronic effects due to its high electronegativity and potential for halogen bonding. In contrast, the nitrile and carboxyl groups in 4-aminobenzonitrile and 4-aminobenzoic acid, respectively, can create strong intermolecular interactions and modify the electronic environment of the Schiff bases. By systematically studying these variations, we sought to gain insights into how different functional groups influence the chemical and physical properties of Schiff bases.

2. Experimental

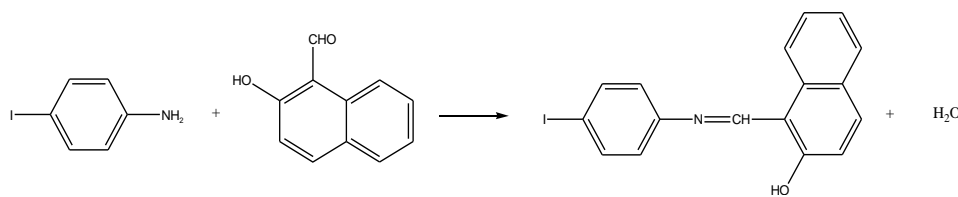
2.1 Materials and characterization

All reagents used in this study were purchased from Sigma Aldrich UK and were of >95% purity. The reagents were used as received without further purification. Infrared spectra were recorded using a Perkin-Elmer FT-IR Spectrum-400 spectrometer. Powdered X-ray diffraction (PXRD) patterns were obtained

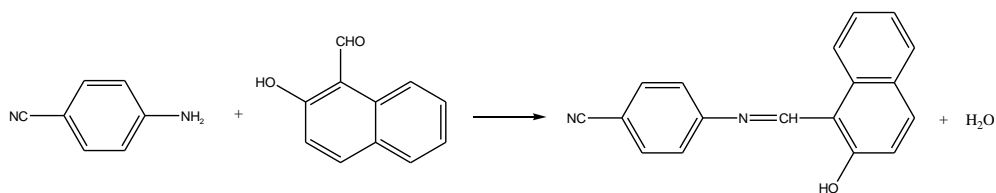
using a PANanalytical Empyrean X'Pert Pro X-ray diffractometer, with data collected from 5 to 60° at a step size of 0.0167° per second. The elemental composition of the samples was determined using a Perkin-Elmer CHNS/O 2400 series II elemental analyzer.

2.2.1 Synthesis of Schiff Bases

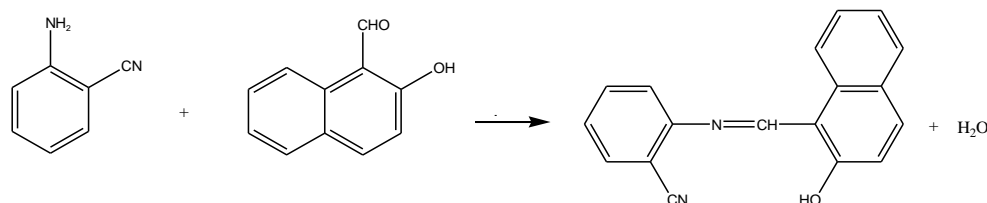
A total of 0.17218 g (1 mmol) of 2-hydroxy-1-naphthaldehyde and the desired primary aromatic amine (4-iodoaniline, 4-aminobenzonitrile, 4-aminobenzoic acid, 3-aminobenzoic acid, or 2-aminobenzonitrile) were accurately weighed into a mortar. The mixture was ground for 45 minutes using a mortar and pestle, resulting in different coloured products. The powdered products were transferred from the mortar and stored in sample bottles. The synthesized Schiff bases were labeled H₂L¹ to H₂L⁵ as shown in the provided schemes (Stilinović et al. 2012). The Schiff base compounds were also synthesized using solution-based method.



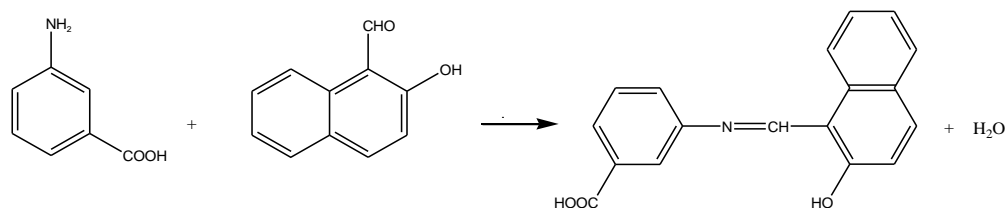
Scheme 1: Synthetic reaction of Schiff base (H₂L¹)



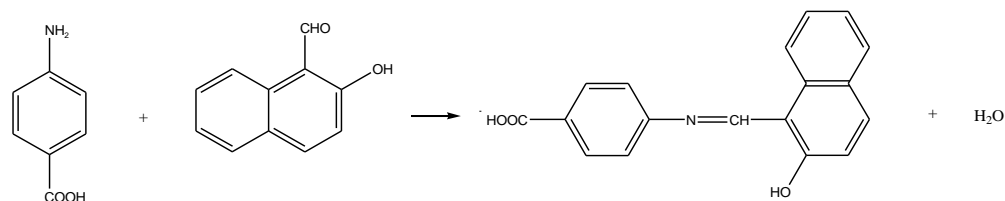
Scheme 2: Synthetic reaction of Schiff base (H₂L²)



Scheme 3: Synthetic reaction of Schiff base (H_2L^3)



Scheme 4: Synthetic reaction of Schiff base (H_2L^4)



Scheme 5: Synthetic reaction of Schiff base (H_2L^5)

3. Results and discussion

Table 1: Physical properties of the synthesized Schiff bases

Compound	Molecular Formula	Colour	Melting Point($^{\circ}C$)	Yield (%)
H_2L^1	($C_{17}H_{12}NOI$)	Yellow	180	90.4
H_2L^2	($C_{18}H_{12}N_2O$)	Yellow Orange	197	89.6
H_2L^3	($C_{18}H_{12}N_2O$)	Dirty Yellow	195	82.3
H_2L^4	($C_{18}H_{12}NO_3$)	Yellow	190	92.5
H_2L^5	($C_{18}H_{13}NO_3$)	Pale brown	198	87.5

Key: H_2L^1 = Schiff base derived from 2-hydroxy-1-naphthaldehyde and 4-nitroaniline
 H_2L^2 = Schiff base derived from 2-hydroxy-1-naphthaldehyde and 4-aminobenzonitrile
 H_2L^3 = Schiff base derived from 2-hydroxy-1-naphthaldehyde and 2-aminobenzonitrile
 H_2L^4 = Schiff base derived from 2-hydroxy-1-naphthaldehyde and 3-aminobenzoic acid
 H_2L^5 = Schiff base derived from 2-hydroxy-1-naphthaldehyde and 4-aminobenzoic acid

Table 1 presents the physical properties of five Schiff bases (H_2L^1 - H_2L^5) synthesized from 2-hydroxy-1-naphthaldehyde and different S primary aromatic amines. The data includes the molecular formula, colour, melting point, and yield of each compound. All compounds have the general structure $R-C=N-Ar$, where R is derived from 2-hydroxy-1-naphthaldehyde and Ar is the aromatic amine. The molecular formulas vary based on the specific amine used, leading to differences in molecular weight and potential intermolecular interactions. Some compounds exhibit shades of yellow, suggesting conjugation within the molecular structure. H_2L^3 has a "dirty yellow" colour, which might indicate little variations in the reaction conditions (Sani 2022). The melting points are relatively high, ranging from 180°C to 198°C . This suggests strong intermolecular forces (Hussaini et al. 2023). There is a general trend of higher melting points with increasing molecular weight (H_2L^1 to H_2L^5), which is consistent with the increased van der Waals forces between larger molecules (Siraj and Kurawa 2020). The yields are generally good, ranging from 82.3% to 92.5%. This indicates efficient conversion of the starting materials to the desired Schiff bases. H_2L^3 has the lowest yield, which might be related to its "dirty yellow" colouration or other factors affecting the reaction efficiency. The physical properties of these Schiff bases might influence their potential applications. For example, compounds with high melting points and good thermal stability could be suitable for materials applications (Shaker, Aziz, and Salleh 2009).

Table 2: Solubility test of the synthesized Schiff bases

Compound	DMF	DMSO	Acetonitrile	Diethyl ether	Chloroform	Acetone	N-hexane
H ₂ L ¹	S	S	SS	IS	S	SS	IS
H ₂ L ²	SS	S	S	SS	S	S	IS
H ₂ L ³	S	S	S	SS	S	S	IS
H ₂ L ⁴	S	S	SS	IS	SS	SS	IS
H ₂ L ⁵	S	S	SS	SS	SS	SS	IS

Key: S-Soluble, SS- Slightly soluble, IS- Insoluble

Table 2 presents the solubility data of the five Schiff bases (H₂L¹ to H₂L⁵) in various organic solvents. The key used in the table indicates the solubility of each compound in each solvent. All Schiff bases are soluble or slightly soluble in polar solvents like DMF, DMSO, acetonitrile, and acetone. This suggests that the polar nature of the Schiff bases, arising from the presence of the imine (C=N) group and the aromatic rings, contributes to their solubility in these solvents (Hussaini et al. 2023). The slight solubility of some compounds in these solvents might be due to factors like steric hindrance or intermolecular interactions within the solid state. The Schiff bases are insoluble in n-hexane, a nonpolar solvent. This indicates that the polar nature of the Schiff bases is not compatible with nonpolar environments. The solubility of the Schiff bases varies to some extent depending on the specific solvent. For example, H₂L¹, H₂L⁴ and H₂L⁵ are slightly soluble in acetonitrile and acetone, while H₂L² and H₂L³ are soluble in these solvents. This suggests that factors like molecular structure, intermolecular forces, and solvent-solute interactions play a role in determining solubility. The solubility properties of these Schiff bases might be relevant for various applications. For example, compounds with good solubility in polar solvents could be

suitable for biological or pharmaceutical applications, while those with limited solubility in nonpolar solvents might be useful for materials or coatings (Khalil et al. 2012).

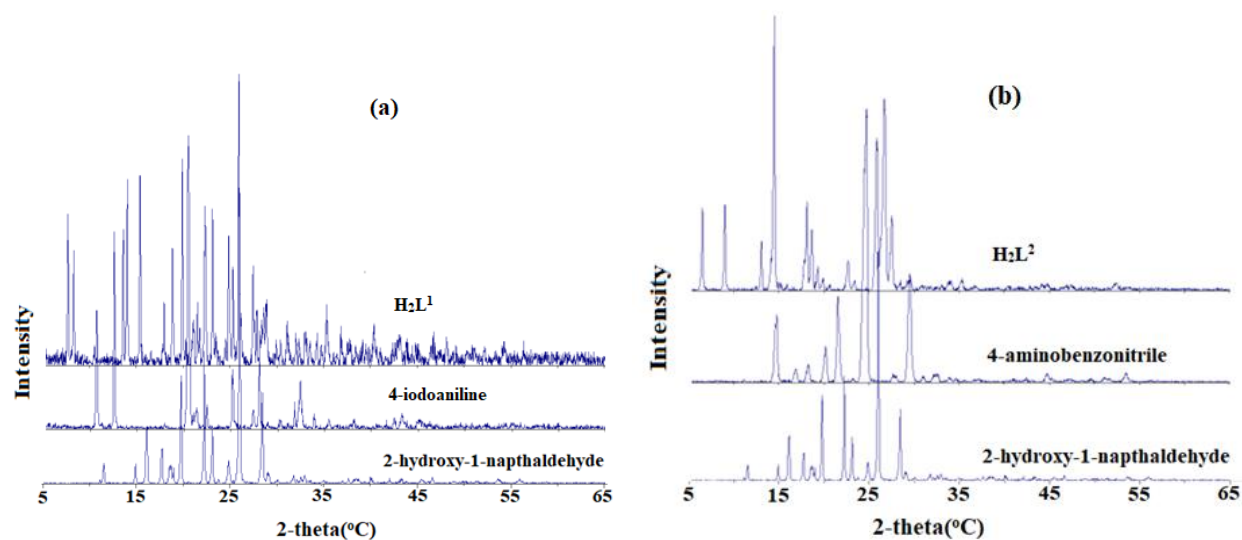
Table 3: Infrared spectra result of the synthesized Schiff bases

Compound	$\nu(\text{OH}) \text{ cm}^{-1}$	$\nu(\text{C}=\text{N}) \text{ cm}^{-1}$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{C})$
H_2L^1	3382	1603	1208	1453
H_2L^2	3692	1577	1203	1455
H_2L^3	3350	1607	1215	1419
H_2L^4	3633	1622	1259	1424
H_2L^5	3335	1626	1213	1427

Table 3 presents the infrared (IR) spectra results for the synthesized Schiff bases (H_2L^1 to H_2L^5). IR spectroscopy is a technique used to identify functional groups based on their characteristic absorption bands. In this case, the table focuses on the stretching vibrations of the hydroxyl (OH) and imine (C=N) groups. The OH stretching bands for all the compounds are broad, indicating the presence of hydrogen bonding. This is likely due to intermolecular hydrogen bonding between the hydroxyl groups of neighboring Schiff base molecules. The specific wavenumber of the OH stretching band varies slightly among the compounds (3335–3692 cm^{-1}). This could be attributed to differences in the strength of hydrogen bonding or the influence of other functional groups (Vadivel and Dhamodaran 2016). The compounds exhibit a strong absorption band in the 1577-1626 cm^{-1} region, which is characteristic of the imine (C=N) stretching vibration. This confirms the presence of the Schiff base functional group in all synthesized compounds (Joseyphus, Dhanaraj, and Nair 2006). The exact wavenumber of the C=N stretching band also varies slightly among the compounds. This could be due to factors such as electron-donating or electron-withdrawing effects of the aromatic substituents, or the influence of hydrogen

bonding. The presence of the characteristic C=N stretching band in all compounds confirms the successful formation of the Schiff base functional group (Joseyphus et al. 2006).

Powder X-ray diffraction (PXRD) analysis of the synthesized Schiff bases, prepared via solvent-assisted mechanochemical synthesis, exhibited significant differences compared to the starting materials, 2-hydroxy-1-naphthaldehyde and primary aromatic amines (Figure 1). This marked disparity strongly suggests the successful conversion of the reactants into the desired Schiff base products (Cinčić, Brekalo, and Kaitner 2011). The absence of characteristic peaks from the starting materials, coupled with the emergence of new, intense peaks at distinct angles, provides compelling evidence for the formation of these Schiff bases. Moreover, the sharp reflections observed in the PXRD patterns indicate the crystalline nature of the synthesized compounds, suggesting a well-defined molecular arrangement and potential for high purity and desirable properties (Cinčić and Kaitner 2011).



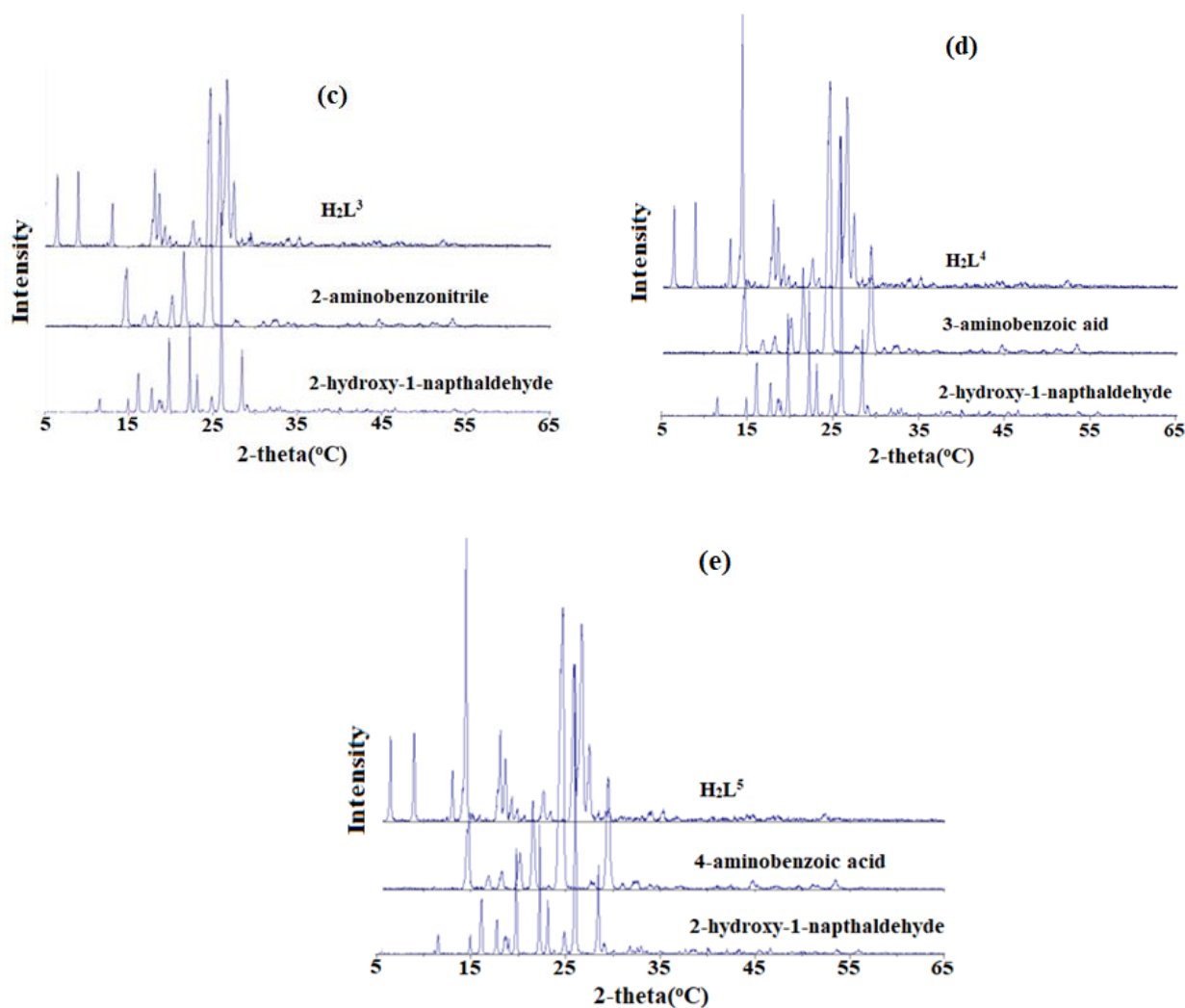


Figure 1. PXRD Patterns of H_2L^1 (a), H_2L^2 (b), H_2L^3 (c), H_2L^4 (d), H_2L^5 (e) Schiff bases showing different reflection peaks compares with different starting materials

Table 4: Elemental analysis result of the synthesized Schiff bases

Compound	C (%)	H (%)	N (%)
	Found(Calculated)	Found(Calculated)	Found(Calculated)
H_2L^1	55.93 (54.71)	3.89 (3.24)	4.48 (3.75)
H_2L^2	79.97 (79.39)	4.92 (4.44)	11.02 (10.29)
H_2L^3	80.91 (79.39)	4.52 (4.44)	11.13 (10.29)
H_2L^4	75.39 (74.22)	4.72 (4.50)	5.25 (4.81)
H_2L^5	74.99 (74.22)	4.89 (4.50)	5.02 (4.81)

Table 4 presents the elemental analysis results for the five synthesized Schiff bases (H_2L^1 to H_2L^5). Elemental analysis is a technique used to determine the percentage composition of elements (carbon, hydrogen, nitrogen) in a compound. The found values are compared to the calculated values based on the molecular formulas. For each compound, the found percentages of carbon, hydrogen, and nitrogen are generally in good agreement with the calculated values based on their molecular formulas. This suggests that the synthesized compounds have the expected elemental compositions (Sani et al. 2019). The close agreement between found and calculated values indicates that the synthesized compounds are reasonably pure. There are slight discrepancies between the found and calculated values of elements in the compounds. These discrepancies could be due to variations in the purity of the starting materials. The elemental analysis results provide strong evidence supporting the proposed structures of the Schiff bases (Aiyelabola et al. 2012).

4. Conclusion

This study successfully synthesized a series of novel Schiff base compounds derived from 2-hydroxy-1-naphthaldehyde and various primary aromatic amines. The solvent-assisted mechanochemical approach employed in this research proved to be an efficient and effective method for the synthesis of these compounds. The synthesized Schiff bases exhibited high yields, demonstrating the efficacy of the synthetic strategy. The synthesized compounds were characteristic by IR spectra, and distinct solubility profiles. These findings provide valuable insights into the properties and potential applications of these Schiff bases in diverse fields, such as materials science and medicinal chemistry. Future studies will investigate the potential of these synthesized Schiff bases as chemosensors for the selective detection of hazardous metal ions.

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