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Synthesis and Characterization of Schiff Base Compounds Containing Mono and Disulfonic Groups

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Abstract

Aromatic mono- or diamine compounds containing sulfonic groups are extensively utilized in the production of textiles, dyes, and polymers. Schiff base compounds are synthesized through the condensation reactions of these types of compounds with aromatic aldehydes or ketones. Due to their multifunctional nature, these Schiff base compounds serve as precursors in the synthesis of poly(ester)s, poly(ether)s, poly(urethane)s, and poly(azomethine)s. The Schiff base compounds were 2,5-bis((E)-(2-hydroxybenzylidene)amino)benzene sulfonic acid (SCH1) and 4,4'-bis((E)-(2-hydroxybenzylidene)amino)-[1,1'-biphenyl]-2,2'-disulfonic acid (SCH2). The yields of SCH1 and SCH2 were calculated to be 85% and 80%, respectively. Structural confirmation was achieved using FT-IR, UV-Vis, ^{1}H NMR and ^{13}C NMR measurements. Further characterization through fluorescence spectroscopy (PL), thermogravimetric analysis (TGA) and cyclic voltammetry (CV) revealed high thermal stability of the compounds, attributed to the phenyl groups in their structures. TGA measurements indicated the initial decomposition temperatures for SCH1 and SCH2 at 298°C and 347 °C, respectively, with the residual masses of 34.64% and 41.24% at 1000 °C.

Keywords: Schiff base, Sulfo Group, Thermal properties, Optical properties, LOI

1. Introduction

Schiff base compounds were first synthesized by German chemist Hugo Schiff in 1864. Imines have been extensively studied for over a century due to their unique reactivity and physical properties. Monomers containing imine (-C=N-) bonds, which result from the condensation reaction between an active carbonyl group and a primary amine, are known as Schiff bases. Azomethines, with the general formula of RCH=NR, are produced through the condensation reactions between primary aliphatic or aromatic amines (R-NH$_2$) and aldehydes or ketones [1].
The synthesis of Schiff base monomers involves two main steps: first, an addition reaction occurs, resulting in the formation of an unstable intermediate compound called 'carbonyl amine' through the condensation of a carbonyl group with primary amines. In the second step, a dehydration reaction transforms the unstable carbonyl amine into the Schiff base [2]. Additionally, compounds containing sulfo groups and imine bonds are employed in textile dyeing and the production of conductive textile materials [3].

Imine compounds are extensively utilized in various fields, including biological systems, chemical catalysis reactions, medicine, pharmacy, chemical analysis, and technology. Due to their high chelating capacity, these compounds are also used for the removal of heavy metal ions in wastewater. The presence of a phenyl ring in their main chain contributes to their high thermal stability.

In this study, Schiff base monomer compounds incorporating mono and di sulfo groups were synthesized. The structural characterization of the compounds was conducted using FT-IR, UV-Vis, ^{1}H NMR and ^{13}C NMR spectroscopy. The electrochemical, optical, and thermal properties of SCH1 and SCH2 were investigated using CV, UV-Vis, and TG-DTA measurements, respectively. Analysis of the optical and electrochemical band gap values were calculated form the UV-Vis and CV measurements, respectively.

2. Materials and Methods

2.1. Materials

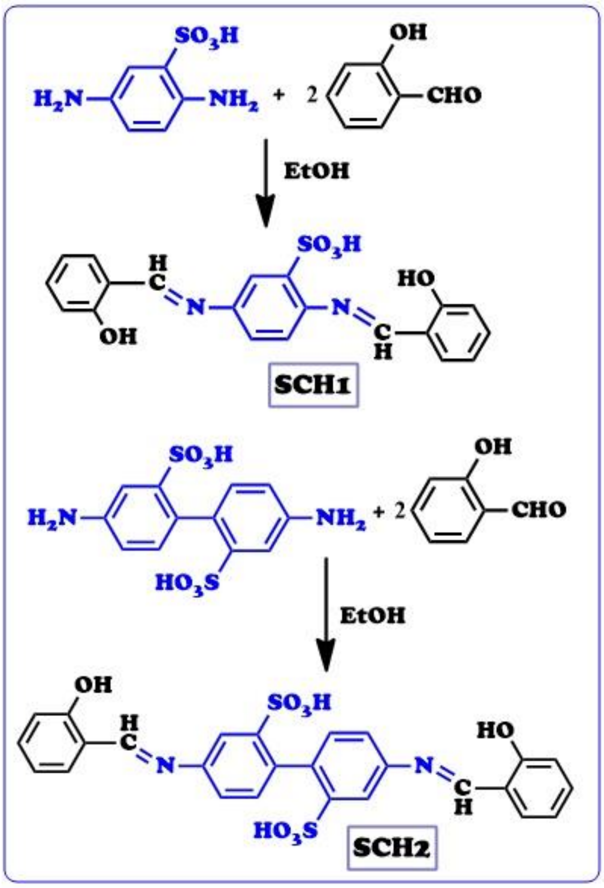
2-Hydroxybenzaldehyde, 2,5-diamino benzene sulfonic acid, 4,4'-diamino-2,2'-biphenyl sulfonic acid, N, N'-dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol (Et-OH), tetrahydrofuran, methanol, hexane, acetonitrile, toluene, dichloromethane, chloroform, were procured from Merck Chemical Co. (Germany). Tetrabutylammoniumhexafluorophosphate (Bu_4AF_6P, 98%) was sourced from Sigma-Aldrich Chem. Co. (Germany). All reagents were used without further purification.

2.2. Synthesis of Schiff bases

2,5-bis((E)-(2-hydroxybenzylidene)amino)benzene sulfonic acid (SCH1) was synthesized using 2-hydroxybenzaldehyde (2.0 mmol) dissolved in 5 mL of ethanol, followed by the addition of 2,5-di amino benzene sulfonic acid (1.0 mmol) to this solution. The mixture was refluxed at 70 °C for 5 h.
4,4'-bis((E)-(2-hydroxybenzylidene)amino)-[1,1'-biphenyl]-2,2'-disulfonic acid (SCH2) was synthesized using 2-hydroxy benzaldehyde (2.0 mmol) dissolved in ethanol (5 mL), and then 4,4'-diamino-2,2'-biphenyl sulfonic acid (1.0 mmol) was added to this solution. The mixture was refluxed at 70 °C for 5 h [4]. The products (SCH1 and SCH2) were purified via crystallization in ethanol. The yields of SCH1 and SCH2 were calculated to be 85% and 80%, respectively. The synthesis pathways of SCH1 and SCH2 are given in **Scheme 1**.

2.3. Characterization Methods

The infrared spectra of SCH1 and SCH2 compounds were recorded using a PerkinElmer Frontier FT-IR-FIR Spectrometer. Functional groups analysis of the compounds was conducted through FT-IR spectroscopy, employing a PIKE technologies GladiATR sampling accessory (4000-400 cm^{-1}). ^1H and ^{13}C NMR spectra were obtained using an Agilent 600 MHz and 150 MHz Premium COMPACT NMR Magnet, with DMSO-d_6 as the solvent and TMS as the internal standard at room temperature. Analytikjena Specord 210 spectrometer was utilized to assess the optical properties of SCH1 and SCH2 in the range of 250-700 nm, using DMSO as the solvent. PerkinElmer Diamond Thermal Analyzer was employed to perform TG-DTA analyses from 20 °C to 1000 °Cat a heating rate of 10 °C min^{-1} under N_2 atmosphere (200 mL min^{-1}). CHI 660C Electrochemical Analyzer was employed to process cyclic voltammetry analyses at a scan rate of 25 mV s^{-1}, to investigate the electrochemical features of SCH1 and SCH2. The electrochemical study utilized, a cell comprising a reference electrode (silver wire), a working electrode (glassy carbon electrode; GCE; d= 0.3 cm in diameter) and an auxiliary electrode (platinum wire), in a 0.1 M NBu_4PF_6 in acetonitrile solution as the supporting electrolyte. The system was purged with argon for five minutes before measurements taken at room temperature. The electrochemical HOMO-LUMO energy levels and the electrochemical band gaps (E'_g) were estimated from the onset values of oxidation (E_{ox}) and the reduction (E_{red}) [5].



Scheme 1. Mechanism of the Schiff base synthesis

3. Results and Discussion

FT-IR spectra of SCH1 and SCH2 compounds are given in Figure 1. As shown in Figure 1A, the stretching vibration bands of -C=N-, -C=C- and -C-O of SCH1 were observed at 1639, 1608 and 1246 cm^{-1}, respectively. As seen in Figure 1B, the stretching vibration bands of -C=N-, -C=C- and -C-O of SCH2 were observed at 1639, 1608 and 1234 cm^{-1}, respectively. The vibrations observed at 3354 cm^{-1} and 3353 cm^{-1} are attributed to O-H stretching, while those at 3053 cm^{-1} and 3081 cm^{-1} are attributed to aromatic C-H stretching for SCH1 and SCH2, respectively. The asymmetric and symmetric O=S=O stretching vibrations of the sulfonic acid group are assigned to the peaks at 1380 cm^{-1} and 1161 cm^{-1} for

SCH1, and at 1382 cm⁻¹ and 1164 cm⁻¹ for SCH2, respectively [6].

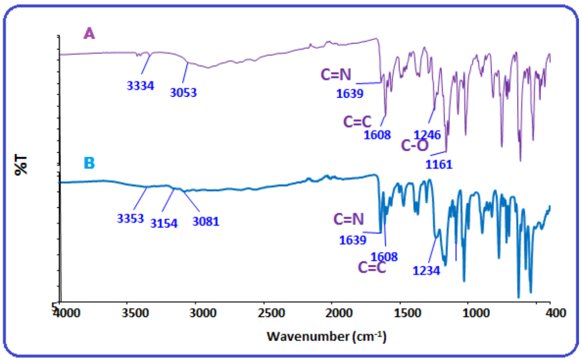


Figure 1. FT-IR spectra of SCH1 (A) and SCH2 (B).

As illustrated in Figure 2, the maximum absorption wavelength corresponding to the $\pi \rightarrow \pi^*$ transitions induced by phenyl rings in SCH1 and SCH2 were observed at 320 and 326 nm, respectively. Additionally, transitions associated with $n \rightarrow \pi^*$ involving electron pairs on oxygen atoms and imine bonds appeared at 360 and 385 nm, respectively. The optical band gap values (E_g) of SCH1 and SCH2 compounds were calculated by the following equation:

$$E_g = \frac{1242}{\lambda_{onset}} \tag{1}$$

where λ_{onset} represents the onset wavelength for the electronic transition which can be obtained from the absorption edges of the UV-Vis spectra [7]. The λ_{onset} values for SCH1 and SCH2, derived from their UV-Vis absorption bands, were found to be 438 nm and 400 nm, respectively. The optical band gap (E_g) values for the SCH1 and SCH2 compounds were determined from their λ_{onset} values, yielding 2.84 eV and 3.11 eV, respectively.

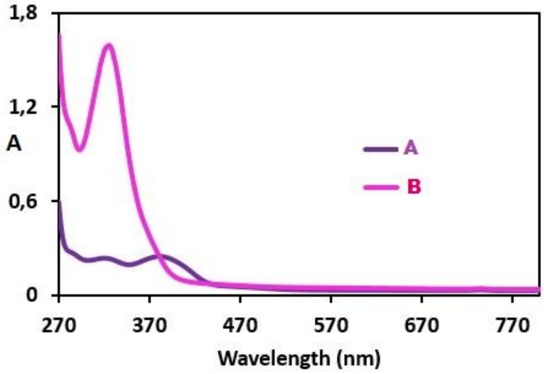
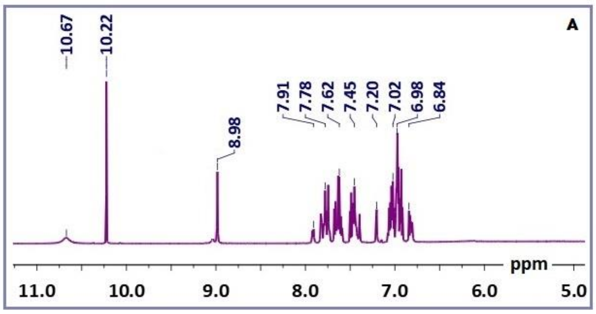


Figure 2. UV-Vis spectra of SCH1 (A) and SCH2 (B).

As illustrated in the ^{1}H NMR spectrum of the SCH1 compound shown in Figure 3A, the proton signals of -C<u>H</u>=N-, -O<u>H</u>, and -SO$_3$<u>H</u> groups were observed at 10.67, 10.22, and 8.98 ppm, respectively. For SCH1, the aromatic protons appeared between 6.84 and 7.91 ppm. In the case of SCH2, the proton signals of -C<u>H</u>=N, -O<u>H</u>, and -SO$_3$<u>H</u> groups were observed at 10.69, 10.22 and 9.09 ppm, respectively, with aromatic protons appearing between 6.92 and 7.92 ppm. Observation of signals of imine protons at 10.22 ppm in the ^{1}H NMR spectra of SCH1 and SCH2 compounds confirms the formation of Schiff base structure.



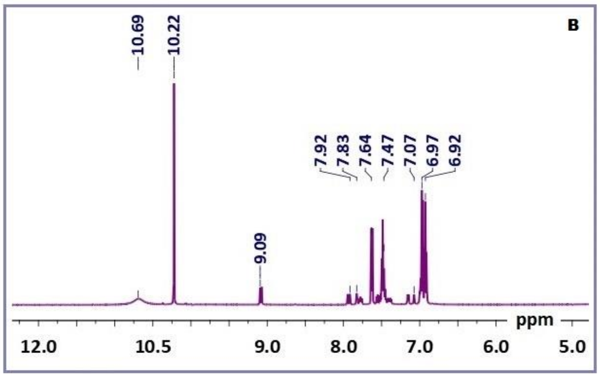


Figure 3. ^{1}H NMR spectra of SCH1 (A) and SCH2 (B).

As depicted in the ^{13}C NMR spectrum of the SCH1 compound in Figure 4A, the carbon atoms of -<u>C</u>H=N- and -<u>C</u>-OH were observed at 162.20 and 161.12 ppm, respectively. The aromatic carbon atoms in SCH1 were detected between 117.00 and 141.44 ppm. For SCH2, the -<u>C</u>H=N- and -<u>C</u>-OH carbon signals were observed at 163.24 and 161.13 ppm, respectively, while the aromatic carbon signals were detected between 117.24 and 146.33 ppm in Figure 4B. The detection of imine carbon signals at 162.20 and 163.24 ppm in the ^{13}C NMR spectra of SCH1 and SCH2 compounds confirms the successful formation of these compounds.

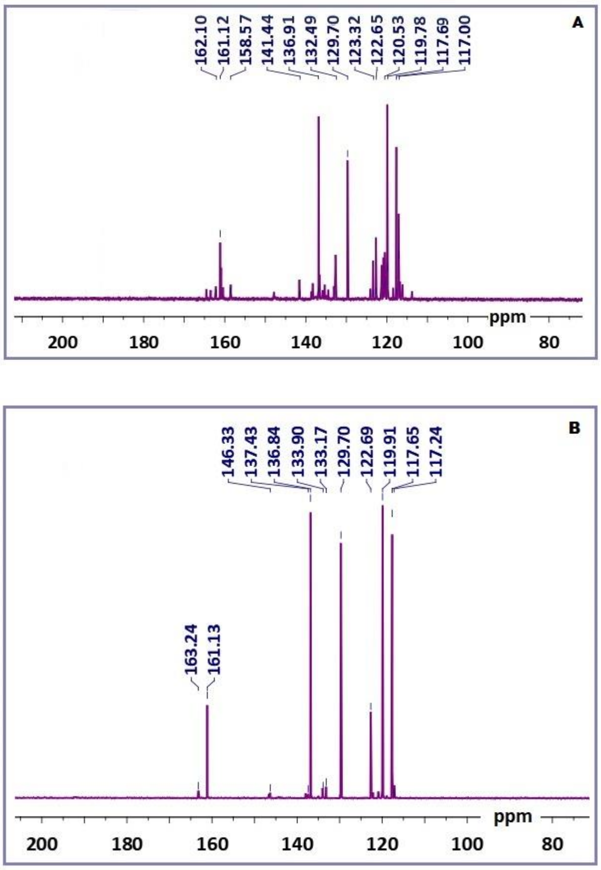


Figure 4. ^{13}C NMR spectra of SCH1 (A) and SCH2 (B).

Figure 5 presents the cyclic voltammograms (CVs) of the synthesized compounds, used to calculate their HOMO and LUMO energies as well as the electrochemical band gap (E'_g) depending on the following equations [8]:

$$E_{\mathrm{HOMO}} = -(4.39 + E_{ox}) \quad (2)$$

$$E_{\mathrm{LUMO}} = -(4.39 + E_{red}) \quad (3)$$

$$E'_g = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \quad (4)$$

E_{HOMO} and E_{LUMO} represent the energies of the HOMO and LUMO levels of the compounds, respectively. According to Figure 5, two cathodic peak potentials signify the oxidation of two phenolic -OH groups, leading to the formation of a phenoxy polaron structures for SCH1 and SCH2 [9]. The anodic reduction peak potentials were related to the imine bond for the compounds. The electrochemical E_g values of SCH1 and SCH2 were calculated as 2.28 eV and 2.42 eV, respectively, which were consistent with the optically measured energy gap (E_g) values.

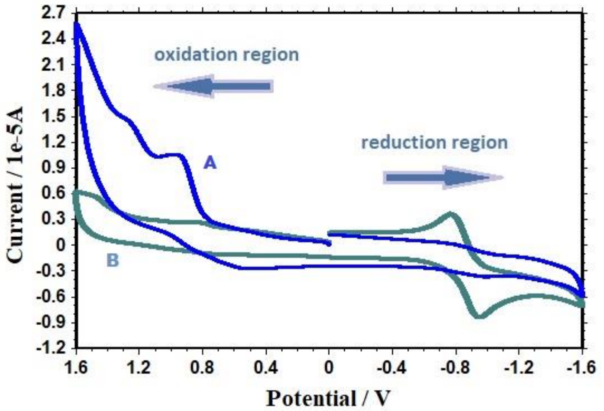


Figure 5. CV voltammograms of SCH1 (A) and SCH2 (B).

Figure 6 displays the thermal analysis curves for the Schiff bases. The initial degradation temperatures (T_{on}) for SCH1 and SCH2 were recorded at 298 °C and 347 °C, respectively. The T_{max} values, obtained from the DTG curves, were 330 °C and 716 °C for SCH1, and 368 °C and 732 °C for SCH2. Based on TG curves, the temperatures corresponding to 5%, 10%, 20%, 30 %, and 50% weight losses for SCH1 and SCH2 were calculated to be 306 °C, 317 °C, 340 °C, 381 °C, and 721 °C, and 354 °C, 363 °C, 375 °C, 410°C, and 807 °C, respectively. The T_{on} values suggest that the compound containing a phenyl group exhibits higher thermal stability. This enhanced stability is attributed to the presence of multiple phenyl groups in the main chain, which contribute to increased thermal resistance. The residual amounts of SCH1 and SCH2 at 1000 °C were calculated to be 34.64% and 41.24%, respectively.

Both compounds underwent degradation in two steps. For SCH1, the mass loss values were 39.37% in the temperature range of 261-513 °C and 25.98% in the range of 513-1000 °C. For SCH2, the mass loss values were 39.54% between 260 °C and 527 °C and 19.22% in the temperature range of 527-1000 °C. As displayed in Figure 6B, a 7% loss due to water and organic solvent was observed up to 150 °C. Additionally, endothermic peaks were observed in the DTA curves of SCH1 and SCH2 at 296 and 365 °C, respectively.

The flame retardancy values of the synthesized Schiff bases can be obtained by following the Van Krevelen’s calculation, utilizing the percentage of residue at 1000 °C. The formation of carbon residue during thermal decomposition restricts the emission of organic volatile compounds. This carbonaceous layer, produced in the process, impedes the propagation of flammable gases by diminishing heat transfer to the material. In this regard, Van Krevelen proposed a formula of $LOI = 17.5 + 0.4\,(s)$ where LOI represents the limiting oxygen index and (s) denotes the percentage of residue in the organic compounds, respectively [10]. According to Van Krevelen's theory, an increase in residue formation correlates with the flammability of organic compounds.

For compounds to be self-extinguishing, their *LOI* values must be at least 26 or higher [11]. The *LOI* values for SCH1 and SCH2 were calculated as 31.36 and 34.00, respectively, concluding with the fact that high *LOI* values render them self-extinguishing and qualify them for various applications requiring good flame resistance [12]. SCH2 includes an additional aromatic ring, resulting in increased material flammability.

Additionally, the Heat Resistance Index (T_{HRI}) was calculated following the method outlined in the literature [13] using the temperatures corresponding to 5% and 30% weight loss. The calculated T_{HRI} values for SCH1 and SCH2 were 171.99 °C and 189.92 °C, respectively. The incorporation of an additional aromatic ring as in SCH2 is evident in the enhanced *LOI* and T_{HRI}, indicating a significant improvement in both the thermal stability and flame retardancy of SCH2. Therefore, SCH1 and SCH2, characterized by high thermal stability and substantial char yield, show potential for use in the fabrication of heat-resistant materials.

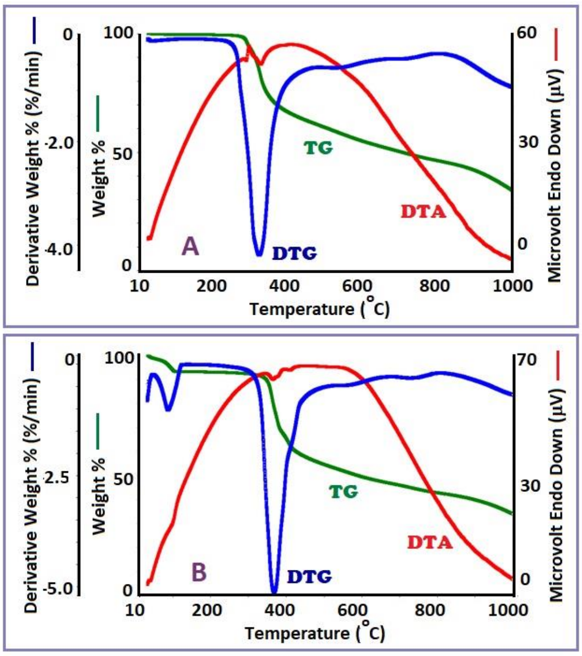


Figure 6. TG-DTA-DTG curves of SCH1 (A) and SCH2 (B).

4. Conclusion

Two Schiff bases were synthesized through the reactions of aromatic diamine compounds containing mono and di sulfo units in their structure with salicylaldehyde. The yields of the compounds were obtained to be high. The structures of the synthesized Schiff bases were confirmed using FT-IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy. The synthesized compounds exhibited significant thermal stability, with initial decomposition temperatures for SCH1 and SCH2 determined to be 298 °C and 347 °C, respectively, based on the TG measurements. The optical band gap values (E_g) of SCH1 and SCH2 were calculated to be 2.84 eV and 3.11 eV, respectively. The onset degradation temperatures of SCH1 and SCH2 were recorded at 298 °C and 347 °C, respectively. The thermal stability of these compounds was notably influenced by an additional aromatic ring, enhancing thermal stability and increasing the onset degradation temperature T_{on}.

The presence of dihydroxy groups in the synthesized Schiff bases facilitates the synthesis and characterization of poly(ether) and poly(urethane) macromolecules. This investigation will provide valuable insights for future research in this field.

Author's Contributions

İsmet Kaya: He performed FT-IR, TG and NMR measurements and data analysis of the compounds.

Feyza Kolcu: She performed UV-Vis, CV and Fluorescence measurements and data analyses of the compounds.

Sude Süel: She synthesized the Schiff base compounds.

Ethics

There are no ethical issues after the publication of this manuscript.

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