CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE
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2.1. General

This chapter deals with the synthesis and characterization of the Schiff base. In general a Schiff base is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen. Schiff bases are of the general formula $\text{R}_1\text{R}_2\text{C}=\text{N-R}_3$, where $\text{R}_3$ is an aryl or alkyl group that makes the Schiff base a stable imine.

\begin{center}
\begin{tikzpicture}
  \draw (-0.5,-0.5) -- (0.5,0.5) node[right] {$\text{R}_3$};
  \draw (0.5,-0.5) -- (-0.5,0.5) node[above] {$\text{N}$};
  \draw (-0.8,-0.8) -- (0.8,0.8) node[left] {$\text{R}_1$};
  \draw (-0.8,0.8) -- (0.8,-0.8) node[below] {$\text{R}_2$};
  \node at (-1,0) {$\text{C}$};
\end{tikzpicture}
\end{center}

*General formula of Schiff’s base*

There are several reaction pathways to synthesize Schiff bases [1-8]. The most common is an acid catalyzed condensation reaction of amine and aldehyde or ketone under refluxing conditions. The first step in this reaction is nucleophilic attack by nitrogen atom of amine on the carbonyl carbon, resulting in a normally unstable carbinolamine intermediate. The reaction can reverse to the starting materials, or the elimination of $\text{H}_2\text{O}$ group result in formation of C=N bond [1, 9]. Many factors affect the condensation reaction, for example the pH of the solution as well as the steric and electronic effects of the carbonyl compound and amine. As
amino group is basic, it is mostly protonated in acidic conditions and thus cannot act as a nucleophile and the reaction cannot proceed. Furthermore, under very basic reaction conditions the reaction is hindered if sufficient protons are not available to catalyze the elimination of the carbinolamine hydroxyl group [10]. In general, aldehydes react faster than ketones in Schiff base formation reactions as the reaction centre of aldehyde is sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density and thus makes the ketone less electrophilic compared to aldehyde [9].

The broad band of –OH observed in range 3600-3100 cm\(^{-1}\) is reported in several research paper by researcher [11]. The sharp bands in the ranges 750–780 cm\(^{-1}\) and 1500-1550 cm\(^{-1}\) are due to aromatic \(\nu (C-H)\) and \(\nu (C=C)\), respectively [12, 13]. The Schiff base research article shows the C=N stretching band at 1640-1690 cm\(^{-1}\) reported in research articles [14, 15, 16].

2.2. Materials

All the chemicals used were of analytical grade. The 2,2’-Bipyridylamine was purchased from Lancaster England, 2-Hydroxy-1-naphthaldehyde and 2-Hydroxyacetophenone was purchased from National Chemicals, Vadodara-Gujarat, 4-Hydroxybenzaldehyde, o-Phenyldiamidine, p-Anisidine was purchased from S D fine-chem limited Mumbai, Salicylaldehyde, p-Chloroaniline, p-Nitroaniline, 4-Hydroxy-3-bromobenzaldehyde, 3-Ethoxy-4-hydroxybenzaldehyde and metal salts were purchased from Chiti-Chem Corporation Baroda-Gujarat. The solvents were dried and distilled before use according to standard procedures.
2.3. Synthesis and characterization of Schiff base

2.3.1. 2-Hydroxy-1-naphthylideneanisidine (Nap-H-Anisi)

An ethanolic solution of 2-Hydroxy-1-naphthaldehyde (1.72 g, 10 mmol) and p-Anisidine (1.23 g, 10 mmol) in the molar ratio of 1:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield: 74%, Melting point: 98 °C.

C\textsubscript{18}H\textsubscript{15}NO\textsubscript{2} (277);
Found (Calculated) (%): C-77.97 (77.95), H-5.42 (5.37), N-5.05 (5.04).

![Reaction diagram](image)

IR Spectra of (Nap-H-Anisi)
IR (cm\(^{-1}\)):

\[ \nu (\text{OH}) : 3440 \quad \nu (\text{C}=\text{N}) : 1650 \]
\[ \nu (\text{C}=\text{C}) : 1550 \quad \nu (\text{C}-\text{H}) : 775 \]

2.3.2. 2-Hydroxyacetophenoneanisidine (AcPh\(\cdot\)H-Anisi)

An ethanolic solution of 2-Hydroxyacetophenone (1.36 g, 10 mmol) and p-Anisidine (1.23 g, 10 mmol) in the molar ratio of 1:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield: 52%, Melting point: 95 °C.

C\(_{15}\)H\(_{15}\)NO\(_2\) (241);

Found (Calculated) (%): C-74.69 (74.64), H-6.22 (6.18), N-5.81 (5.72)

2-Hydroxyacetophenone + p-Anisidine \(\rightarrow\) 2-Hydroxyacetophenoneanisidine
IR Spectra of (AcPh-H-Anisi)

IR (cm⁻¹):

\begin{align*}
\nu (\text{OH}) & : 3400 \\
\nu (\text{C} = \text{N}) & : 1640 \\
\nu (\text{C} = \text{C}) & : 1530 \\
\nu (\text{C-H}) & : 750
\end{align*}

2.3.3. Salicylidineanisidine (Sal·H-Anisi)

An ethanolic solution of Salicylaldehyde (1.22 g, 10 mmol) and p-Anisidine (1.23 g, 10 mmol) in the molar ratio of 1:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield: 72 %, Melting point: 78 °C.

\( \text{C}_{14}\text{H}_{13}\text{NO}_2 \) (227);

Found (Calculated) (%): C-74.01 (74.04), H-5.73 (5.65), N-6.17 (6.11).
Salicylaldehyde  p-Anisidine  Salicylidineanisidine

IR Spectra of (Sal·H-Anisi)

IR (cm\(^{-1}\)):

\(\nu\) (OH) : 3420  \hspace{1cm} \nu\) (C=N) : 1650
\(\nu\) (C=C) : 1520  \hspace{1cm} \nu\) (C-H) : 770

2.3.4. p-Chlorosalicylideneaniline (Sal·H-ClAnil)

An ethanolic solution of Salicylaldehyde (1.22 g, 10 mmol) and p-Chloroaniline (1.27 g, 10 mmol) in the molar ratio of 1:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield : 81 %, Melting point : 100 °C.
C_{13}H_{10}NOCl (231.5);
Found (Calculated) (%) : C-67.39 (67.34), H-4.32 (4.30), N-6.05 (6.01).

\[
\begin{align*}
\text{CHO} &+ \text{H}_2\text{N} &\rightarrow & \text{EtOH} &\rightarrow \\
\text{OH} & & & & \\
\text{Cl} & & & &
\end{align*}
\]

Salicylaldehyde  p-Chloroaniline  p-Chlorosalicylideneaniline

**IR Spectra of (Sal·H·ClAnil)**

IR (cm\(^{-1}\)) :

\[
\begin{align*}
\nu (\text{OH}) &: 3450 & \nu (\text{C=N}) & : 1650 \\
\nu (\text{C=C}) & : 1550 & \nu (\text{C-H}) & : 775
\end{align*}
\]

**2.3.5. p-Nitrosalicylideneaniline (Sal·H·NO}_2\text{Anil)**

An ethanolic solution of Salicylaldehyde (1.22 g, 10 mmol) and p-Nitroaniline (1.38 g, 10 mmol) in the molar ratio of 1:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at
room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield : 69 %, Melting point : 154 °C.

C_{13}H_{10}N_{2}O_{3} (242);
Found (Calculated) (%) : C-64.46 (64.39), H-4.13 (4.11), N-11.57 (11.54).

[Chemical reaction and structures]

Salicylaldehyde  p-Nitroaniline  p-Nitrosalicylideneaniline

*IR Spectra of (Sal-H-NO₂Anil)*

IR (cm⁻¹):

\[ \nu (\text{OH}) : 3450 \quad \nu (\text{C} = \text{N}) : 1650 \]

\[ \nu (\text{C} = \text{C}) : 1550 \quad \nu (\text{C-H}) : 750 \]
2.3.6. 4-Hydroxybenzylidene-o-phenylediamine (Ben-H-Phdia)

An ethanolic solution of 4-Hydroxybenzaldehyde (2.44 g, 20 mmol) and o-Phenylenediamine (1.08 g, 10 mmol) in the molar ratio of 2:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield: 65 %, Melting point: 212 °C.

C_{20}H_{16}N_{2}O_{2} (316);
Found (Calculated) (%): C - 75.94 (75.88), H - 5.06 (5.01), N - 8.86 (8.87).
IR Spectra of (Ben-H-Phdia)

IR (cm\(^{-1}\)):

\[ \nu (\text{OH}) : 3400 \quad \nu (\text{C=N}) : 1680 \]
\[ \nu (\text{C=C}) : 1520 \quad \nu (\text{C-H}) : 780 \]

2.3.7. 2-Hydroxyacetophenone-o-phenylenediamine (AcPh-H-Phdia)

An ethanolic solution of 2-Hydroxyacetophenone (2.72 g, 20 mmol) and o-Phenylenediamine (1.08 g, 10 mmol) in the molar ratio of 2:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield : 57 %, Melting point : 156 °C.

C\(_{22}\)H\(_{20}\)N\(_2\)O\(_2\) (344);
Found (Calculated) (%) : C-76.74 (76.66), H-5.81 (5.74), N-8.14 (8.11).
2-Hydroxyacetophenone  o-Phenyline-diamine  2-Hydroxyacetophenone-o-phenyldiamine

IR Spectra of (AcPh-H-Phdia)

IR (cm$^{-1}$):

$\nu$ (OH) : 3450  \quad \nu$ (C=N) : 1670

$\nu$ (C=C) : 1520  \quad \nu$ (C-H) : 775

2.3.8. 3-Bromo-4-hydroxybenzylidene-o-phenyldiamine (BrBen-H-Phdia)

An ethanolic solution of 3-Bromo-4-hydroxybenzaldehyde (4.04 g, 20 mmol) and o-Phenylenediamine (1.08 g, 10 mmol) in in the molar ratio of 2:1 were mixed with constant stirring. Refluxing was carried out
for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield: 64 %, Melting point: 242 °C.

C_{20}H_{14}N_{2}O_{2}Br_{2} (473.8);
Found (Calculated) (%): C-56.65 (56.54), H-2.95 (2.97), N-5.91 (5.89).

IR Spectra of (BrBen·H·Phdia)
IR (cm⁻¹):

\[ \nu (\text{OH}) : 3400 \quad \nu (\text{C=N}) : 1690 \]
\[ \nu (\text{C=C}) : 1510 \quad \nu (\text{C-H}) : 775 \]

2.3.9. 3-Ethoxy-4-hydroxybenzylidene-o-phenylenediamine (EtBen-H-Phdia)

An ethanolic solution of 3-Ethoxy-4-hydroxybenzaldehyde (3.32 g, 20 mmol) and o-Phenylenediamine (1.08 g, 10 mmol) in in the molar ratio of 2:1 were mixed with constant stirring. Refluxing was carried out for an hour and was cooled at room temperature. The obtained product was filtered, recrystallized in ethanol and dried in air.

Yield : 63 %, Melting point : 157 °C.

C₂₄H₂₄N₂O₄ (404);
Found (Calculated) (%) : C-71.29 (71.21), H-5.94 (5.88), N-6.93 (6.96).
IR Spectra of (EtBen-H-Phdia)

IR (cm\(^{-1}\)):

\[
\begin{align*}
\nu (\text{OH}) & : 3350 \\
\nu (\text{C=H}) & : 1500 \\
\nu (\text{C=N}) & : 1640 \\
\nu (\text{C-H}) & : 750
\end{align*}
\]
REFERENCES
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