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Synthesis, Characterization and Antibacterial Activity of Some Schiff Bases Prepared from 3-Hydroxy-2-naphthaldehyde and Phenyl Methanamine Derivatives

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The synthesis of some new Schiff bases by condensing 3-hydroxy-2-naphthaldehyde and derivatives of phenyl methanamine *i.e.* 1-(4-chlorophenyl)methanamine, 1-(4-bromophenyl)methanamine, 1-(4-methylphenyl)methanamine and 1-(4-methoxyphenyl)methanamine is reported. These compounds are characterized on the basis of physical characteristics, micro-analytical data, ¹H NMR, FTIR spectrum and electronic spectrum data. The Schiff base ligands have also been tested *in vitro* for their antibacterial activity. The experimental results suggested that Schiff base ligands are more potent in antibacterial activities.

Keywords: Schiff base, Amine derivatives and aldehyde, Spectroscopic study, Biological activity.

INTRODUCTION

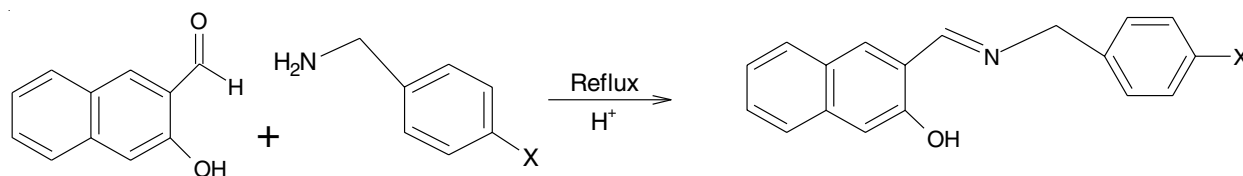
Schiff bases named after Hugo Schiff described the condensation between aldehydes and amines. Schiff bases are good ligands as they are able to coordinate with metals through imine nitrogen and another group usually linked with aldehydes. Schiff bases are important class of ligand in coordination chemistry [1,2]. Schiff bases are condensation products of primary amines with carbonyl compounds. The common structural feature of these compounds is the azomethine group with the general formula -HC=N- [3]. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (>C=O) is replaced by an imine or azomethine group. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral and antipyretic properties [4,5]. Imine or azomethine groups are present in various natural, naturally derived and non-natural compounds. The imine group present in such compounds has been shown to be critical to their biological activities [6-9]. Schiff bases are important compounds owing to their wide range of industrial applications [10].

In this research work, Schiff bases 3-[(4-chlorobenzyl)imino]methyl}-2-naphthol, 3-[(4-bromobenzyl)imino]methyl}-2-naphthol, 3-[(4-methylbenzyl)imino]methyl}-2-naphthol

and 3-[(4-methoxybenzyl)imino]methyl}-2-naphthol prepared by refluxing 3-hydroxy-2-naphthaldehyde with 1-(4-chlorophenyl)methanamine, 1-(4-bromophenyl)methanamine, 1-(4-methylphenyl)methanamine and 1-(4-methoxyphenyl)methanamine. The structure of ligands has been characterized by FTIR, ¹H NMR and UV spectroscopy. The biological activity was also studied against Gram-positive and Gram-negative bacteria for ligands. The structure of the Schiff base ligand in present work is shown in **Scheme-I**.

EXPERIMENTAL

All the chemical reagents used were of analytical grade and of highest purity available and used without further purification. All derivatives of phenyl methanamine were obtained from E. Merck. 3-Hydroxy-2-naphthaldehyde was obtained from Sigma-Aldrich. Solvents used were distilled and purified before used, these are obtained from Fluka and Sigma-Aldrich. Melting point of ligands were determined in capillary tube using melting point apparatus. Infrared spectra were measured as KBr pellets on FT-IR spectrometer Shimadzu Japan Model IR Prestige-21 in frequency range $4000\text{--}400\text{ cm}^{-1}$. The electronic spectra were measured using DMSO as a solvent on UV Spectrophotometer Shimadzu Japan model Pharmaspec-1700. ¹H NMR spectrum of ligands were recorded using NMR-spectrometer Bruker Germany 300 MHz. The elemental analysis was performed on Elemental Analyzer Leco USA model CHNS-932.



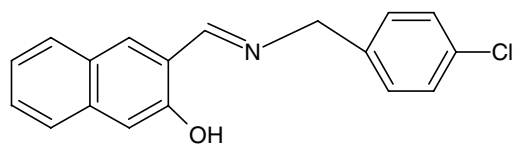
where X = -Br, -Cl, -CH₃ and -OCH₃

Scheme-I: Preparation of Ligands

Synthesis of Schiff base ligands

3-[(4-Chlorobenzyl)imino]methyl-2-naphthol (HL¹):

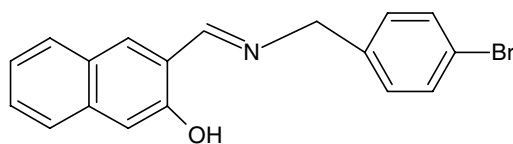
0.1 M solution of 1-(4-chlorophenyl)methanamine (25 mL) was added to 0.1 M solution of 3-hydroxy-2-naphthaldehyde (25 mL) in ethanol then few drops of conc. H₂SO₄ added to the reaction mixture. The reaction mixture is heated under reflux for about 3 h at 70-75 °C. The resulting solution is further concentrated by adding distilled water on water bath. The product obtained was precipitated, cooled and collected after filtration. The precipitate was purified by washing with distilled water and then with ethanol. The product again recrystallized in ethanol and dried in vacuum desiccator overnight.



HL¹: 3-[(4-Chlorobenzyl)imino]methyl-2-naphthol

3-[(4-Bromobenzyl)imino]methyl-2-naphthol (HL²):

0.1 M solution of 1-(4-bromophenyl)methanamine (25 mL) was added to 0.1 M solution of 3-hydroxy-2-naphthaldehyde (25 mL) in ethanol then few drops of conc. H₂SO₄ added to the reaction mixture, after addition reaction mixture is heated under reflux for about 4 h at 70-75 °C. The resulting solution is further concentrated by adding distilled water on water bath. The product obtained was precipitated, cooled and collected after filtration. The precipitate was purified by washing with distilled water and then with ethanol. The product again recrystallized in ethanol and dried in vacuum desiccator overnight.

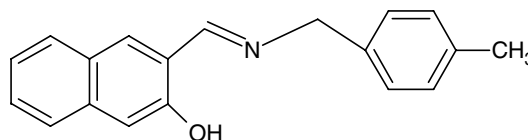


HL²: 3-[(4-Bromobenzyl)imino]methyl-2-naphthol

3-[(4-Methylbenzyl)imino]methyl-2-naphthol (HL³):

0.1 M solution of 1-(4-methylphenyl)methanamine (25 mL) was added to 0.1 M solution of 3-hydroxy-2-naphthaldehyde (25 mL) in ethanol then few drops of conc. H₂SO₄ added to the reaction mixture. The reaction mixture is heated under reflux for about 4 h at 70-75 °C. The resulting solution is further concentrated by adding distilled water on water bath. The product obtained was precipitated, cooled and collected after filtration. The precipitate was purified by washing with distilled

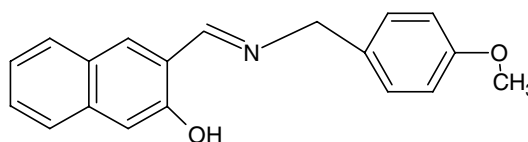
water and then with ethanol. The product again recrystallized in ethanol and dried in vacuum desiccator overnight.



HL³: 3-[(4-Methylbenzyl)imino]methyl-2-naphthol

3-[(4-Methoxybenzyl)imino]methyl-2-naphthol (HL⁴):

0.1 M solution of 1-(4-methoxyphenyl)methanamine (25 mL) was added to 0.1 M solution of 3-hydroxy-2-naphthaldehyde (25 mL) in ethanol then few drops of conc. H₂SO₄ added to the reaction mixture. The reaction mixture is heated under reflux for about 5 h at 70-75 °C. The resulting solution is further concentrated by adding distilled water on water bath. The product obtained was precipitated, cooled and collected after filtration. The precipitate was purified by washing with distilled water and then with ethanol. The product again recrystallized in ethanol and dried in vacuum desiccator overnight.



HL⁴: 3-[(4-Methoxybenzyl)imino]methyl-2-naphthol

After completion of reaction processes precipitate of all the Schiff base are formed as coloured solids. The purity of ligand was checked by m.p. and TLC. The ligands are soluble in methanol, ethanol, DMF and DMSO.

RESULTS AND DISCUSSION

The Schiff base is synthesized by using equimolar quantities of 4-bromobenzenesulfonamide and 4-chlorobenzenesulfonamide with 7-methylquinoline-3-carbaldehyde. The physical characteristics and analytical data of ligands are given in Tables 1 and 2.

Infrared spectroscopy: The infrared spectra of ligands were recorded to confirm their structures. The infrared spectral data of Schiff base ligands and are listed in Table-3. A sharp band observed for ligands at 1575 to 1620 cm⁻¹, is due to azomethine >C=N linkage assigned to stretching vibration of the imines group [11,12]. All the ligands displayed a band at 1310-1322 cm⁻¹ which is assigned to -C-O stretching vibration and the aromatic C-H band has the region 3010-2950 cm⁻¹ [13].

TABLE-1
PHYSICAL CHARACTERISTICS OF SCHIFF BASES

S. No.	Schiff base	Colour	m.f.	Molecular mass (g mol ⁻¹)	m.p. (°C)	Yield (%)
1	HL ¹	Brown	C ₁₈ H ₁₄ NOCl	295.76	145	78
2	HL ²	Dark maroon	C ₁₈ H ₁₄ NOBr	340.21	155	80
3	HL ³	Yellowish green	C ₁₉ H ₁₇ NO	275.34	190	79
4	HL ⁴	Dark green	C ₁₉ H ₁₇ NO ₂	291.34	180	77

TABLE-2
MICRO-ANALYTICAL DATA OF SCHIFF BASES

S. No.	Schiff base	Elemental analysis (%): Calcd. (Found)			
		C	H	N	X (X = Br & Cl)
1	HL ¹	(73.10) 73.00	(4.77) 4.66	(4.74) 4.60	(11.99) 11.86
2	HL ²	(63.55) 63.44	(4.15) 4.02	(4.12) 4.00	(23.49) 23.35
3	HL ³	(82.88) 82.76	(6.22) 6.10	(5.09) 4.95	—
4	HL ⁴	(78.33) 78.20	(5.88) 5.75	(4.81) 4.69	—

TABLE-3
IR SPECTRA (cm⁻¹) OF SCHIFF BASES

S. No.	Ligands	C=N	C=O	Ar. C-H
1	HL ¹	1590	1310	3010
2	HL ²	1585	1312	3000
3	HL ³	1615	1320	2960
4	HL ⁴	1620	1322	2950

Electronic spectra: The ultraviolet-visible spectrophotometry techniques used to characterize Schiff bases DMSO as a solvent. The ultraviolet-visible electronic spectra of the prepared Schiff's bases showed absorption bands that could be attributed to $\pi \rightarrow \pi^*$ electronic transitions; these transitions are assigned in relevance to the structures of the compounds [14]. The lower wavelength for the Schiff base has been assigned between 270-300 nm, these values are for $n \rightarrow \pi^*$ transition of $-C=N-$ linkage and aromatic nature of the Schiff base, while the longer wavelength lies in the range 340-350 nm (Table-4).

TABLE-4
UV SPECTRA (nm) OF SCHIFF BASES

S. No.	Schiff base	$n \rightarrow \pi^*$ transition	$\pi \rightarrow \pi^*$ transition
1	HL ¹	277	340
2	HL ²	270	342
3	HL ³	294	350
4	HL ⁴	300	348

¹H NMR spectra: ¹H NMR Spectra of Schiff bases were recorded in DMSO solution and TMS used as internal standard. The singlet signal at $\delta = 2.29$ and 3.79 ppm suggested the attribution of the protons of the $-CH_3$ group for Schiff base HL³ and HL⁴, respectively while at 4.80 ppm for halogen group for Schiff base HL¹ and HL², respectively. The singlet signal at $\delta = 7.09$ ppm suggested the attribution of the proton of $-CH$ of the ring in Schiff bases HL¹ and HL² and at $\delta = 7.09$ ppm

for HL¹ and HL² respectively (Table-5). Multiplet signal at $\delta = 7.09$ to 7.30 ppm suggested the attribution of the protons of two aromatic benzene rings, the singlet signal at $\delta = 8.764$ ppm suggested the attribution of the proton of the $CH=N$ group, the singlet signal at $\delta = 8.92$ ppm suggested the attribution of the proton of the $-NH$ group [15].

Antimicrobial activity: The antibacterial activity data is presented in Table-6, which revealed that the ligand was bacteriostatic against all bacterial strains. The antibacterial activity of ligands were screened on Gram-positive bacteria: *S. epidermidis* and *B. subtilis* and Gram-negative bacteria: *E. coli* and *P. vulgaris* by disc diffusion technique [16]. Filter paper disc were used for the incubation period of 24 h at 35 °C and results were recorded. The antibacterial activities of ligands were tested by measuring inhibition zone observed around material. All the synthesized Ligands showed significant range of activity on growth of all selected bacterial stain. [17].

TABLE-6
ANTIBACTERIAL ACTIVITY OF SCHIFF BASES (INHIBITION ZONE, mm)

Compound	Gram-positive		Gram-negative	
	<i>S. epidermidis</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. vulgaris</i>
Ciprofloxacin/ Clarithromycin	16	18	15	15
HL ¹	15	16	12	10
HL ²	13	17	11	11
HL ³	13	13	13	13
HL ⁴	14	15	12	12

Conclusion

New four Schiff based have been prepared by the condensation of 3-hydroxy-2-naphthaldehyde and derivatives of phenyl methanamine *i.e.* 1-(4-chlorophenyl)methanamine, 1-(4-bromophenyl)methanamine, 1-(4-methylphenyl)-

TABLE-5
¹H NMR SPECTRAL DATA (ppm) OF SCHIFF BASES

S. No.	Schiff base	Cl, Br, CH ₃ & OCH ₃	C-H	Aromatic ring	Imine	-NH
1	HL ¹	4.80	7.09	7.09 to 7.30	8.10	8.92
2	HL ²	4.80	7.09	7.09 to 7.30	8.10	8.92
3	HL ³	2.29	7.03	7.09 to 7.13	8.10	8.92
4	HL ⁴	3.79	6.89	7.09 to 7.13	8.10	8.92

methanamine and 1-(4-methoxyphenyl)methanamine. The structure of Schiff bases has been reported by physical characteristics, micro-analytical data, ^1H NMR, FTIR and UV spectrum data. The prepared Schiff bases have been biologically screened *i.e.* studying their effects against two Gram-positive, two Gram-negative bacteria. The results show that their activities against microbes.

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