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Research Article

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Synthesis and biological properties of N_2O_2 Schiff bases derived from *o*-phenylenediamine and substituted salicylaldehydes

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ABSTRACT

Three symmetrical and two unsymmetrical N_2O_2 Schiff bases obtained from the condensation of o-phenylenediamine with various salicylaldehydes namely salicylaldehyde, 5-nitrosalicylaldehyde and 5-bromosalicylaldehyde were synthesized and characterized based on elemental analysis, IR, ^1H NMR and electronic absorption spectroscopy. The antimicrobial activity of the compounds tested against the microorganisms E. coli (ATCC 25922), E. feacalis (ATCC 29212) and S. aureus (ATCC 25923) using the agar ditch method showed a dependence on the substituent present in order H>NO_2>Br. The unsymmetrical compounds exhibited higher activity compared to the symmetrical compounds.

Key words: *o*-phenylenediamine, symmetrical Schiff base, unsymmetrical Schiff base, antimicrobial activity

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INTRODUCTION

There has been renewed interest in the Chemistry of Schiff bases as a result of the wide variety of potential applications reported for this class of compounds. These compounds can be used in photochemical, catalytic, biological and electrochemical applications [1-3]. Schiff bases are also used as ligands to obtain metal complexes that can serve as models in the understanding of biological systems. The preparative ease and variable geometries of the metal complexes obtained makes them important stereochemical models in main group and transition metal coordination Chemistry. Thus, these compounds play an important role in advancement of inorganic biochemistry [4].

Schiff bases composed of N_2O_2 donor atoms are important chelating ligands for designing supramolecular synthons, medicinal and catalytically useful metal complexes [5-6]. Symmetrical Schiff bases derived from aromatic 1,2-diamines such as *o*-phenylenediamine have received attention due to their synthetic flexibility, rich coordination chemistry and application in catalysis [7]. Related unsymmetrical Schiff bases have received less attention, The unsymmetrical Schiff bases of 1,2-diamines may be of more practical importance due to presence of the different reactive centres located in the compounds. Unsymmetrical Schiff bases are important in understanding the process of metal binding in metalloproteins and metalloenzymes in the body [8-9].

We have been interested in understanding the effects of subtle changes in electronic properties of Schiff bases and metal complexes through substituent and solvent variation [10-11] and metal complex formation [12]. In this paper, we report the effect of change in substituent on the biological properties of symmetrical and unsymmetrical Schiff bases derived from *o*-phenylenediammine and substituted salicyaldehydes.

EXPERIMENTAL SECTION

Chemicals and solvents were of reagent or analytical grade and used without further purification.

o-phenylenediamine, salicylaldehyde, 5-nitrosalicylaldehyde and 5-bromosalicylaldehyde, were purchased from Aldrich Sigma Company Ltd and used as supplied.

Elemental analysis data were obtained on a Perkin Elmer model 2400 series II CHNS/O analyzer. Infrared (IR) spectra of the compounds were recorded as KBr discs on a Perkin-Elmer Spectrum RX1 spectrophotometer in the range 4000 to 400 cm^{-1}.

^1H NMR spectrum of the ligand was recorded in $CDCl_3$ solutions on a Bruker Avance III 400 MHz spectrometer with chemical shifts reported in ppm relative to TMS as internal standard. The electronic absorption spectra of all the complexes were recorded in DMSO on a PGT80/T80$^+$ UV-VIS spectrophotometer in 1cm quartz cell at room temperature immediately after preparing the solution. Melting points (^oC) were determined with aid of Gallenkamp melting-point apparatus and are uncorrected. The symmetric Schiff bases **(L1 - L3)** were prepared using literature method [12].

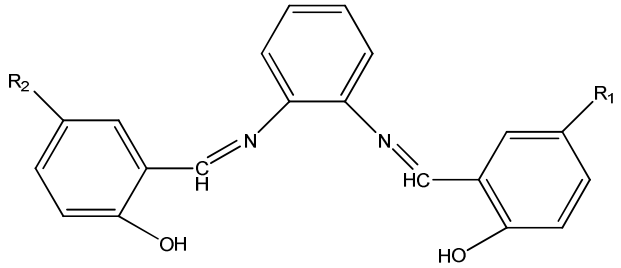
Synthesis of Unsymmetrical Schiff Bases (L4 –L5)

To a cold stirred solution of o-phenylenediamine (10 mmol.) in absolute ethanol (10 ml) were added ethanolic solutions (10 ml) of salicylaldehyde (10 mmol.) and the corresponding substituted salicylaldehyde (10 mmol.). The mixture was refluxed at 70 ^oC for 3 h and cooled to room temperature. The yellow solid obtained collected by filtration dried and re-crystallized from ethanol.

RESULTS AND DISCUSSION

Synthesis

Symmetrical and unsymmetrical Schiff bases (Figure 1) were prepared in good yields from the condensation reaction of *o*-phenylenediamine with corresponding aldehydes in 1:2 ratio for the symmetrical compounds **L1-L3** and 1:1:1 ratio for the unsymmetrical compounds **L4-L5**. All the compounds obtained are stable at room temperature and are non-hygroscopic. The analytical data and physical properties of the compounds are presented in table 1. The elemental analysis data conform to expected values.



L1 $R_1=R_2=H$
L2 $R_1=R_2=Br$
L3 $R_1=R_2=NO_2$
L4 $R_1=H$ $R_1=Br$
L5 $R_1=H$ $R_1=NO_2$

Figure 1: Molecular Fomula Schiff bases L1-L5

The infrared spectral bands of all the Schiff bases show a band in the region 1602-1619 cm^{-1} due to azomethine (HC=N) group. The occurrence of this band along with disappearance of the band at *ca* 1700 cm^{-1} for the carbonyl group and appearance of a band in 1391-1392 cm^{-1} for the phenolic oxygen in all compounds confirms the formation of the Schiff base. The ^{1}HNMR spectra for each compound gave a peak at 8.89-9.24 attributed to the azomethine protons which further confirms formation of desired product.

TABLE 1. Physical and Analytical Data of Schiff bases L1-L5

Compound	Empirical Formular	Yield (%)	M.P ^{0}C	Colour	Microanalysis, cald(found) %C	%H	%N
L1	$C_{20}H_{16}N_2O_2$	79.0	153-154	yellow	75.93 (75.31)	5.10 (5.00)	8.86 (8.75)
L2	$C_{20}H_{14}Br_2N_2O_2$	83.3	118-199	yellow	50.66 (50.51)	2.98 (2.86)	5.91 (5.86)
L3	$C_{20}H_{14}N_4O_6$	87.0	>230	yellow	59.12 (58.79)	3.47 (3.48)	13.79 (13.55)
L4	$C_{20}H_{15}N_2O_2Br$	73.3	186-188	yellow	60.78 (59.65)	3.83 (3.42)	7.09 (6.79)
L5	$C_{20}H_{15}N_3O_4$	86.1	192-194	yellow	66.48 (65.80)	4.17 (3.96)	11.63 (11.49)

TABLE 2. Important IR, UV-vis and ^{1}HNMR Bands in Schiff bases L1-L5

Compound	ν (OH) cm^{-1}	ν (C=N) cm^{-1}	ν (C-O) cm^{-1}	δ HC=N	λ max nm
L1	3674	1606	1373	8.85	269,324
L2	3677	1602	1373	8.89	269,324
L3	3692	1619	1350	9.01	265,332
L4	3567	1608	1371	9.24	329
L5	3624	1611	1349	9.13	336

Electronic Absorption Spectra

The electronic absorption spectra of the ligands were recorded in the range 200-600 nm and are reported in table 2.

Earlier reports indicate that the electronic absorption bands of the salicylaldehyde type Schiff base comprises of three bands [13]. The band located in the range 230-260 nm in the spectra is assigned to the excitation of the π-electrons of the aromatic system since these bonds are quite sensitive to substitution at this part of the molecule. The band observed within the wavelength range 260-310 nm is due to n- π* transition between the π-orbital largely localized on the central C=N bond, influenced by the charge within the entire molecule.

The third band observed within the wavelength of 320-400 nm is attributed to an intermolecular charge transfer for interaction based on expected strong intermolecular hydrogen bonding between the hydroxyl group of the salicylidene part and azomethine nitrogen.

The electronic absorption bands the symmetric compounds exhibit two bands a high energy band between 265-269 nm attributed to n- π* and a low energy band 305-360 nm due to charge transfer transitions. The presence of electron withdrawing nitro groups results in shift of charge transfer band to higher wavelengths in the compounds. This suggests that the nitro group is a good charge-transfer acceptor centre as a result of its strong electron withdrawing power.

Antimicrobial Activity

The antimicrobial activity of the investigated compounds was tested at a concentration of 5 mg mL^{-1} using the agar ditch method against the microorganisms *E. coli*, *E. feacalis* and *S. aureus* The diameter of growth inhibition zones were measured (mm) and results summarized in table 3.

TABLE 3.

Compound	Diameter of inhibition zone of bacteria (mm)		
	S. aureus	***E.Feacalis***	***E. coli***
L1	20	0	20
L2	15	-	-
L3	12	-	16
L4	10	14	11
L5	15	20	11
Streptomycin	**12**	**25**	**18**

All the compounds were active against *S. aureus* in varying degrees. The *bis*-salicylaldehyde imine **L1** exhibited highest activity comparable to the reference compound against *S. aureus* and *E. coli* but no activity against *E. feacalis*. Comparison of the results with those of Schiff bases derived from aniline and the corresponding aldehydes [10] revealed that the presence of N2O2 donor group enhanced activity of the compounds. The bromo substituted compound **L2** was only active against *S.aureus*. Thus, activity of the symmetric compounds is in order **L1**>**L3**>**L2**. This reflects a dependence on the substituent present in order H>NO_2>Br.

The unsymmetrical compounds **L4** and **L5**, were active against all the bacterial strains studied with highest activity recorded against E. *feacalis*. The nitro compound **L5** exhibited highest activity, thus the presence of the electron withdrawing nitro group enhanced antimicrobial activity of the compounds.

CONCLUSION

Three symmetrical and two unsymmetrical Schiff bases containing the N2O2 unit derived from condensation reaction of *o*-phenylenediamine with substituted salicyaldehydes have been synthesized and characterized. The antimicrobial activity of the compounds varied with the nature of substituent in order H>NO_2>Br. The symmetrical Schiff basses exhibited narrow spectrum antimicrobial activity. The unsymmerical compounds compounds can be further investigated for design of broad spectrum antibiotic compounds.

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