



SYNTHESIS AND STRUCTURAL STUDIES OF SOME BIS-BIDENTATE SCHIFF BASES

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ABSTRACT:

The salen-type Schiff base ligand condensation of 4,4'-bis[(salicylaldehyde-5)azo]biphenyl with 1,3-diaminopropane, 1,4-diaminobutane, 1,2-diaminopropane and 1,2-diaminoethane were investigated and characterized by physical and spectral techniques namely, elemental analysis, melting point, ¹H NMR, IR UV-Vis spectra and mass spectroscopy measurement. The Schiff base were screened for antibacterial activity in vitro against Gram positive and Gram negative bacteria viz. Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa and Klebsiella pneumoniae using standard agar cup plate or well diffusion method. The ligands BNPSAP, BNBSAP, BIPSAP and BNESAP were found to be active against all bacterial strain.

KEYWORDS: Schiff base and Antibacterial activity.

INTRODUCTION:

The schiff base ligands provide the opportunity to design the new systems selective to specific metals ions. These ligands are widely used for analytical purposes, such as their use as extracting agents in liquid-liquid, solid-phase and cloud-point extraction techniqueⁱ. The complexes make these compounds efficient and stereospecific catalysts for oxidation, reduction and hydrolysisⁱⁱ⁻ⁱⁱⁱ. These show biological activity and other transformations of organic and inorganic chemistry. Polymeric coordinating reagents are novel types of ligands giving complexes having a mixture of the physical properties of polymer and the chemical properties of the ligand^{iv}. Coordination polymers derived from polymeric schiffbase have been studied extensively. However, little systematic works have been done on the preparation of polychelates derived from the Schiffbase of bisalicylaldehyde^{v-vi}. In such symmetric bis-bifunctioning terminally metallizable Schiff bases the donor atoms on the rings are widely separated, so that the ligand can coordinate with two metal atoms from the both ends giving chelate polymers. Moreover, polymeric metal complexes derived from simple or polymeric coordinating ligands are generally insoluble in common solvents, have several active sites available within the molecule and are thermally stable^{viii}.

EXPERIMENTAL:**GENERAL PROCEDURE:**

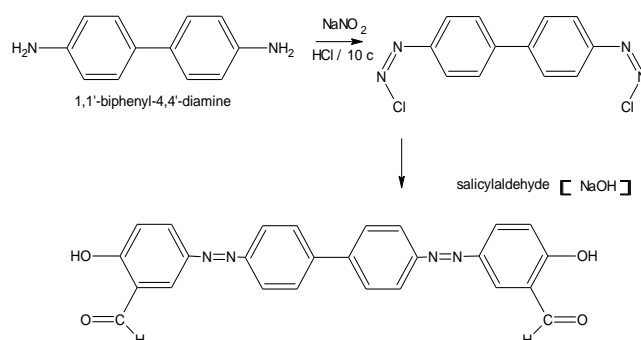
All the chemicals and solvents used were of Analytical Grade (AR) and purchased commercially. All the solvents were purified by standard method and used^{ix}. The compound Terephthalaldehyde and metalacetate were purchased from E.MerckLtd.(India), Isoniazid was purchased from Himedia, India and used without further purification.

Microanalysis of carbon, hydrogen and nitrogen of the ligands were carried out on a Perkin Elmer CHN2400 elemental analyser.¹HNMR species of the ligands were recorded in DMSO-d₆ solution on EM-360,60MHz spectrometer. The electronic spectra of the ligands were recorded on a Shimadzu UV/Vis spectrometer in the region 200-1000nm. The Fourier-transform infrared (FTIR) spectra of ligands were recorded as KBr pellets using Shimadzu spectrometer (IR Affinity-1S). The antibacterial activities of the compounds were assessed against E.coli, s. aureus, paeruginosa and K. pneumoniate using standard agar cup plate or well diffusion method^x.

A) PREPARATION OF AZODYES:**FOR THE PREPARATION of 4,4'-bis[(salicylaldehyde-5)azo] biphenyl (BSAB)**

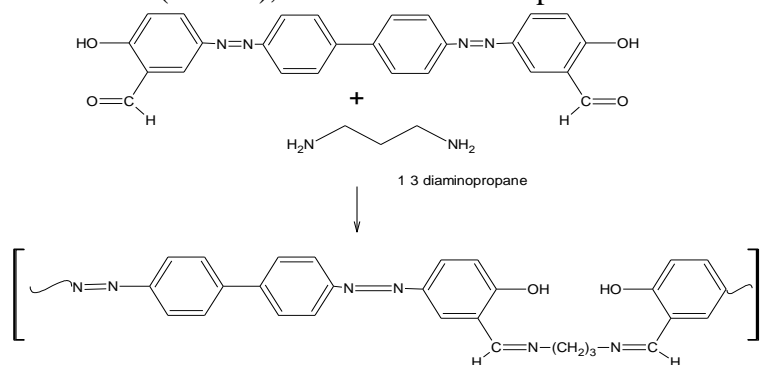
A paste of 9.52gms (0.05 mol) of finely powdered benzidine in 150 ml water was made in a beaker. To this 5ml conc. HCl was added and warmed until dissolved. Then solution was cooled to 10⁰C in ice bath and stirred mechanically and further 5 ml conc. HCl was added. To this, a cold solution of sodium nitrite 3.5gm (0.05mol) in 15 ml water was added rapidly as possible keeping the temperature below 10⁰C. A clear orange yellow diazonium solution was obtained.

To this tetraazotized solution of Benzidine a cold solution of salicylaldehyde (0.025mol) and sodium carbonate (15gm) in 50ml. water were added with constant stirring. The mixture was then stirred for further 3-4h in an ice bath maintaining the temperature below 10⁰C. When the coupling of one mole of salicylaldehyde was complete a second mole of salicylaldehyde (0.025mol 3 gm) dissolved in minimum quantity of sodium hydroxide was added and stirring was continued until the reaction was complete. The precipitated dye (BSAB) obtained was filtered off, washed and dried. Yield=70% and m.p. = 260⁰C.

**Scheme-I****B) PREPARATION OF SCHIFF BASE LIGANDS****FOR THE PREPARATION 4,4'-bis[(N-Propansalicylaldehydediamine-5)azo]biphenyl (BNPSAP)**

The Schiff base (BNPSAP) was prepared by the condensation of dye (BSAB) with 1,3-diaminopropane as described below. The dye BSAB 4.25g (0.01mol) was dissolved in DMF (25ml). A solution of 1,3-diaminopropane (0.071 ml 0.01mol) in ethanol (25ml) was added to the above solution(1:1) a followed by (1:1) a drop of concentrated H₂SO₄ as a catalysis. The reaction mixture was refluxed on an oil bath for about 3h. The Schiff base ligand 4,4'-bis [(N-Propane salicylaldehydediamine-5)azo] biphenyl (BNPSAP) was separated out as a dark

brown coloured product, which was filtered, washed with DMF, Et-OH and recrystallised from DMF–alcohol mixture (1:1 v/v), Yield=65% and m.p. =270⁰C



Scheme II

The newly synthesized ligand was characterized with the help of elemental analysis, IR and ¹H NMR studies. The elemental analysis for carbon, hydrogen and nitrogen is given in table 1. The elemental analysis suggests the empirical formula C₂₉H₂₆N₆O₂ for ligand BNPSAP.

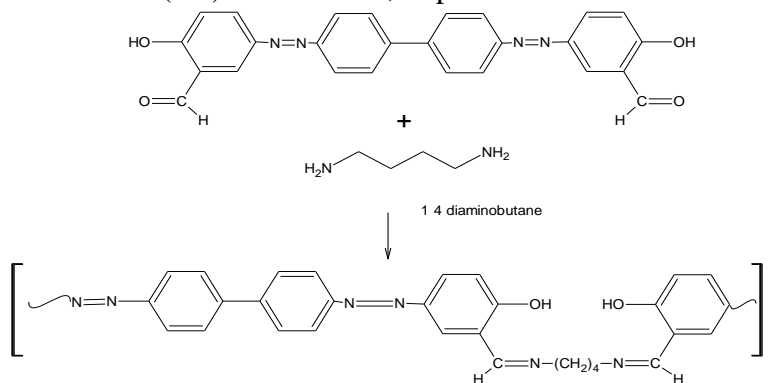
IR spectrum of ligand BNPSAP shows a medium broad band at 2925cm⁻¹, due to intramolecular hydrogen bonded phenolic ν(OH) stretching. The strong band at 1615cm⁻¹ is assigned to ν(C=N) stretching frequency. A medium band observed at 1585cm⁻¹ is may be due to ν(N=N) (azo) stretching. A band at 1290cm⁻¹ is due to ν(C-O) phenolic stretching frequency. The important IR bands of BNPSAP are tabulated in table 2.

¹H NMR spectrum of ligand shows signals at 10.80, 7.89 and 7.10-7.55 δ ppm due to the phenolic, azomethine and aromatic protons respectively. ¹H NMR spectrum clearly indicates the presence of OH and azomethine groups. This down field phenomena of OH proton is attributed to the existence of the hydrogen bonding in the ligand. The multiplets at δ(7.10-7.55) ppm showed aromatic protons.

FOR THE PREPARATION 4, 4'-bis[(N-Butanesalicylaldehydediamine-5)azo]biphenyl (BNBSAP)

The Schiff base (BNBSAP) was prepared by the condensation of BSAB with 1,4-diaminobutane as described below.

4.25g (0.01mol) of the dye (BSAB) was dissolved in 25ml, DMF. A solution of 1,4-diaminobutane 0.08ml. (0.01mol) in 25ml ethanol was added to this solution. A drop of concentrated H₂SO₄ was added as catalysts in the reaction and mixture was further refluxed on a water bath for about 3h. The Schiff base ligand 4,4'-bis [(N-Butanesalicylaldehydediamine-5)azo]biphenyl. The ligand (BNBSAP) was separated out as a dark brown product, which was filtered, washed with Et-OH and DMF and recrystallised from DMF- alcohol mixture (1:1) Yield=60% , m.p. =255⁰C.



Scheme-III

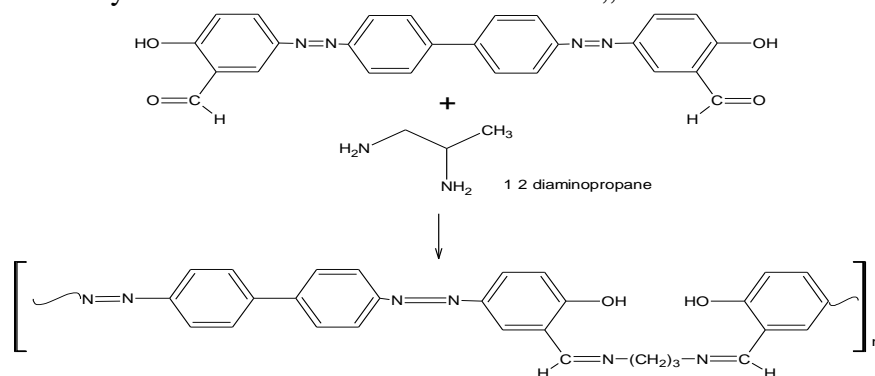
The ligand BNBSAP was characterized by elemental analysis, IR and ^1H NMR studies. The elemental analysis of carbon, hydrogen and nitrogen is given in table 1. on the basis of elemental analysis empirical formula $\text{C}_{30}\text{H}_{28}\text{N}_6\text{O}_2$ can be suggested to BNBSAP.

The IR spectrum of ligand shows a medium broad band at 2925cm^{-1} which can be assigned to hydrogen bonded phenolic $\nu(\text{OH})$ stretch. The strong band at 1634cm^{-1} is assigned to $\nu(\text{C}=\text{N})$ group, while band at 1585cm^{-1} is assigned to $\nu(\text{N}=\text{N})$ stretch. A strong and sharp band at 1281cm^{-1} is due to $\nu(\text{C}-\text{O})$ stretching frequency. The assignments of important IR bands are tabulated in table 2.

^1H NMR spectrum of BNBSAP shows expected signals at 10.59 and 8.10 δ ppm for OH and H-C=N proton, respectively. Multiplet signals in the region 7.05 - 8.05 δ ppm is due to aromatic protons.

FOR THE PREPARATION 4,4'-bis[(1-Propanesalicylaldehydediamine-5)azo]biphenyl (BIPSAP)

4.25g (0.01mol) of the dye (BSAB) was dissolved in 25ml. DMF. A solution of 1, 2-diaminopropane 0.08ml (0.01mol) in 25 ml ethanol was added to this solution. A drop of concentrated H_2SO_4 was added as a catalysts the reaction mixture was refluxed on a oil bath for about 3h. The Schiff base 4,4'-bis[(1 Propane salicylaldehydediamine-5) azo] biphenyl (BIPSAP) was separated out as a dark brown product, which was filtered, washed with Et-OH and DMF and crystallized from DMF- alcohol mixture,, Yields=75% and m.p. =267 $^\circ\text{C}$.



Scheme IV

The newly prepared ligand BIPSAP was characterized by elemental analysis, IR and ^1H NMR data. The elemental analysis for carbon, hydrogen and nitrogen is given table 1.1 from the percentage composition of BIPSAP the empirical formula, which comes out to as $\text{C}_{29}\text{H}_{26}\text{N}_6\text{O}_2$

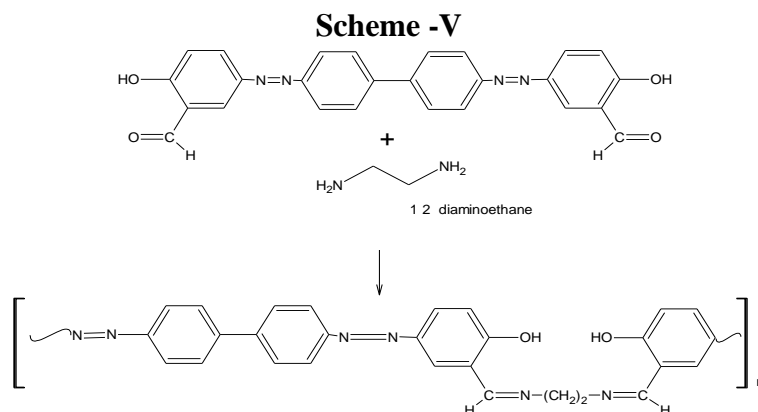
The IR spectrum of ligand BIPSAP shows broad band at 3035cm^{-1} due to intramolecular hydrogen bonded phenolic $\nu(\text{OH})$ stretching. A strong band at 1630cm^{-1} indicates the presence of $\nu(\text{C}=\text{N})$ group and sharp band 1281cm^{-1} may be due to $\nu(\text{C}-\text{O})$ stretching vibration. A medium band at 1585 may be assigned to azo $\nu(\text{N}=\text{N})$ stretching. The assignments of important IR bands are tabulated in table 2.

^1H NMR spectrum of BIPSAP exhibits Signals at 10.99, 8.06 and 6.80-7.31 δ ppm respectively corresponding to phenolic, azomethine and aromatic protons respectively.

FOR THE PREPARATION 4,4'-bis[(N-Ethanesalicylaldehydediamine-5)azo] biphenyl (BNESAP)

4.25g (0.01mol) of the dye (BSAB) was dissolved in 25 ml DMF. A solution of 1,2 diaminoethane 0.08ml. (0.01mol) in 25ml ethanol was added to this solution (1:1). A drop of concentrated H_2SO_4 was added and the reaction and mixture was refluxed on a oil bath for about 3 hours on cooling. The Schiff base ligand 4,4'-bis[(N ethanesalicylaldehydediamine-5) azo] biphenyl. (BNESAP) was separated out as a dark brown product, which was filtered, and

recrystallised from DMF and alcohol mixture and dried at room temperature, Yields=78% and m.p. =264⁰



The Ligand BNESAP was characterized by elemental analysis, IR and, ¹H NMR studies. The elemental analysis of carbon, hydrogen and nitrogen is given table 1. on the basis of elemental analysis empirical formula C₂₈H₂₄N₆O₂, can be suggested to BNESAP.

The IR spectrum of ligand shows a medium broad at 3048cm⁻¹ due hydrogen bonded phenolic υ(OH) stretch. The strong band at 1632 and 1279cm⁻¹ indicates presence of υ(-C=N) and υ(C-O) groups respectively. A sharp band at 1585cm⁻¹ is assigned to υ(N=N) stretch. The assignment of important IR bands are tabulated in table 2.

¹H NMR spectrum of BNESAP show singlet at 10.77 which may be attributed to phenolic υ(OH) proton. A singlet at 7.99 δppm may be due to υ(C=N) proton multiplexes are the range of 7.17 - 8.15 δppm is the characteristics feature of aromatic proton.

RESULTS AND DISCUSION:

In the presnets study, schiff base ligands were screened for antibacterial activity in vitro against Gram positive and Gram negative bacteria viz. *Eschericchina coli*, *Staphylococcus auereu* , *pseudomonous aeruginosa* and *Klebsiella pneumoniae* using standard agar cup plate or well fiffusion method ^x.

All the ligands are found to show low sensivity against *Eschericchina coli*, *Staphylococcus auereus*, *pseudomonous aeruginosa* and *Klebsiella pneumoniae* using resistant against other bacteria. The inhibition effect of the ligands (BNPSAP, BNBSAP, BIPSAP, and BNESAP) enhancing their biological activity and summarized in table 3. Four ligands have been studied for their antifungal activities ^{xi-xvi}.

Table: 1. Colour, molecular weight, time of refluxes and elemental analysis of bis-bidentate

Sr. No.	Compounds	Colour	Formula Weight of Monomer unit	Time of refluxes (Hour)	Elemental Analysis % found (Calcd.)		
					C	H	N
1	BNPSAP	Brown	490.55	4h	68.23 (71.00)	5.25 (5.34)	17.09 (17.13)
2	BNBSAP	Leaf Brown	520.633	4h	70.30 (71.41)	5.90 (6.20)	15.01 (16.14)
3	BIPSAP	Brown	496.55	4h	70.16 (71.00)	5.04 (5.34)	16.08 (17.13)
4	BNESAP	Brown	476.56	4h	70.20 (70.57)	4.82 (5.08)	17.35 (17.64)

Schiff bases.

Table: 2. Infrared Spectral data of bis-bidentate Schiff bases.

Sr.No.	Compounds	Empirical Formula	$\nu(\text{OH})$ cm^{-1}	$\nu(\text{C}=\text{N})$ cm^{-1}	$\nu(\text{C}-\text{O})$ cm^{-1}	$\nu(\text{N}=\text{N})$ cm^{-1}
1	BNPSAP	$\text{C}_{29}\text{H}_{26}\text{N}_6\text{O}_2$	2952	1625	1290	1585
2	BNBSAP	$\text{C}_{30}\text{H}_{28}\text{N}_6\text{O}_2$	2925	1634	1292	1585
3	BIPSAP	$\text{C}_{29}\text{H}_{26}\text{N}_6\text{O}_2$	2923	1630	1281	1585
4	BNESAP	$\text{C}_{28}\text{H}_{24}\text{N}_6\text{O}_2$	3050	1635	1279	1585

Table: 3. Antibacterial and Antifungal activity of bis–bidentate Schiff bases.

Sr. No.	Compounds	E.coli (mm.)	<i>S. aureus</i> (mm.)	<i>p.aeruginosa</i> (mm.)	<i>K. pneumoniae</i> using
1.	BNPSAP	S(12)	S(11)	S(10)	S(11)
2.	BNBSAP	S(10)	S(10)	S(11)	S(12)
3.	BIPSAP	S(12)	S(11)	S(10)	S(10)
4.	BNESAP	S(11)	S(9)	S(10)	S(12)

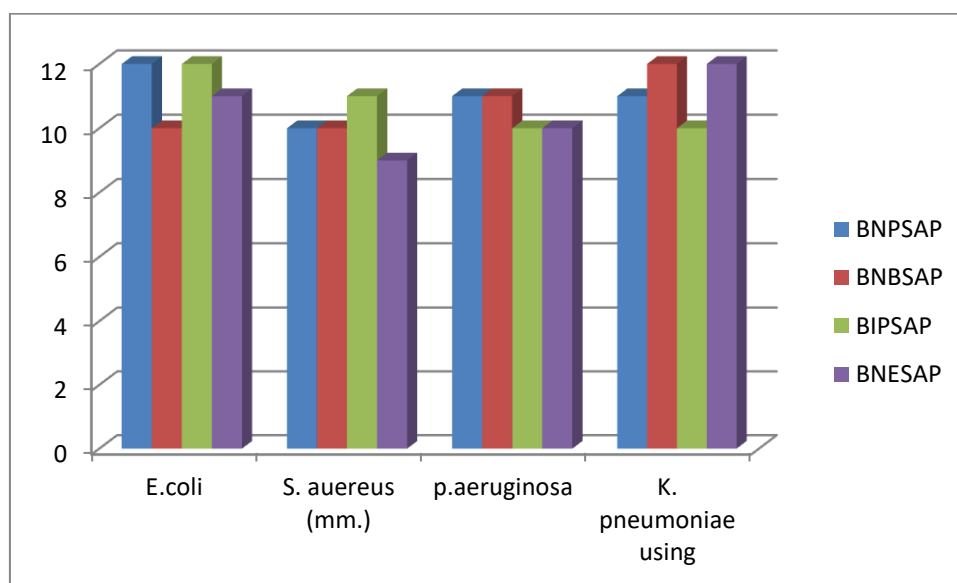


Fig.1 Antibacterial and Antifungal activity of bis–bidentate Schiff bases

CONCLUSION:

In the present study schiff base ligands were synthesized and characterized by elemental analysis, meltingpoint, ¹NMR, IR, UV-Vis-spectra. The insolubility of the ligands in the organic solvents and the high decomposition temperature indicate their polymeric nature. It is suggested that the compounds are coordination chain polymer. The antibacterial activity of all the compounds was tested against bacterial pathogens, *E.coli*, *S.aureus*, *P. aeruginosa* and *K pneumoniae*. In figure 1. It has been found that synthesized schiff base active significant antimicrobial activity.

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