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Structural characterization of novel Schiff base compounds: Investigation of their Spectral, Thermal, Structural, Morphological and biological studies

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Abstract**:** A novel Schiff bases have been synthesized by reacting 4, 4'- diaminodiphenyl ether with R-substituted salicylaldehyde (R= H, 5-Br and 3-OCH_3) and 2-hydroxy -1- naphathaldehyde. They were characterized by spectral (UV-VIS., FTIR, NMR and Mass), thermal and XRD analyses and also tested for the evaluation of biological activities. The TG curves of the Schiff bases were critically analyzed to estimate various kinetic parameters (n, E, Z, ΔS and G) using Coats – Redfern (C.R.) method. The values of E and G are sufficiently high and indicate that the Schiff bases are thermally stable. X-ray Diffraction studies suggest monoclinic crystal system to allSchiff bases. The scanning electron microscopic study reveals that the surface ofSchiff base is without crack hole and homogeneous. The biological studies suggest that the all Schiff bases possess excellent antibacterial activity against B. subtilis and
E. coli, antifungal activity against A. Niger and C. Albicans.
Keywords: *Novel Schiff's bases, Thermal analyses, XRD, SEM, Antibacterialactivity and Antifungal activity.*

1. Introduction

Azomethine group (–C=N–) containing compounds typically known as Schiffbases have been synthesized by the condensation of primary amines with activecarbonyls. Schiff bases form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial, [1-6] antifungal [3-6] and antitumor activity [7-8]. They have beenstudied extensively as a class of ligands [9-11] and are known to coordinate with metal ions through the azomethine nitrogen atom. Schiff base complexes play a vital role in designing metal complexes related to synthetic and natural oxygen carriers [12].

A large number of Schiff bases and their complexes have been studied for their important properties e.g. their ability to reversibly bind oxygen, transfer of an amino group and complexing ability towards some toxic metals [13-15]. The high affinity forthe chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. Schiff base metal complexes have been useful to design and develop some models for biological systems. Transition metal complexes which usually contain nitrogen, sulphur/or oxygen as ligand atoms are becoming increasingly important because these Schiff base can bind with different metal centres involving various coordination sites and allow successful synthesis of metallic complexes with interesting stereochemistry [16-22]. Heterocyclic compounds are widely distributed in the nature and essential to many biochemicals, analytical and industrial processes. Compounds containing these heterocycles have important properties in the field of material science and biological systems. Various heterocyclic especially 2-aminothiazoles are a remarkably versatile group of compounds that have found recent applications in the drug development and production of dyes.

The fresh water snails *L. auricularia* family Lymnaeidae are familiar members of the fauna of ponds, lakes, ditches and other kind of standing waters throughout the World. *L. auricularia* is an intermediate host of liver fluke. The *Fasciola* spp. causes great damage to live stock throughout the world. It is responsible for liver rot, uncomplicated Fascioliasis and the notorious 'black disease'. The considerations of the family Lymnaeidae and species of snails, which act as intermediate host [16] for *F. hepatica* and *F. Gigantia*.

In this paper we report here the syntheses and characterization (spectral, thermal and XRD) of bis bidentate Schiff bases which binds the metal ions through N and O donor atoms (SB-1 to SB-4) (Figure 1) and evaluation of their biological activities.

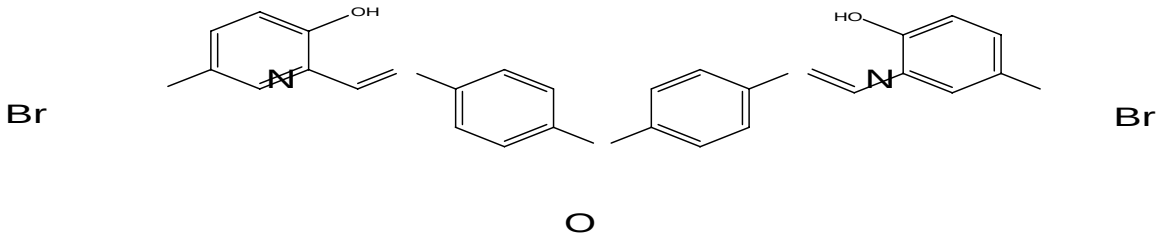


Fig 1: 2-{[4-(4-Amino-phenoxy)-phenylimino]-methyl}-4-bromo-phenol

2. Experimental

All the chemicals used were of AR grad and solvents were purified before use according to standard procedure.

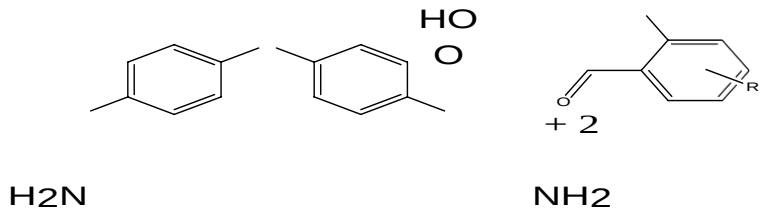
2.1 Instrumentation

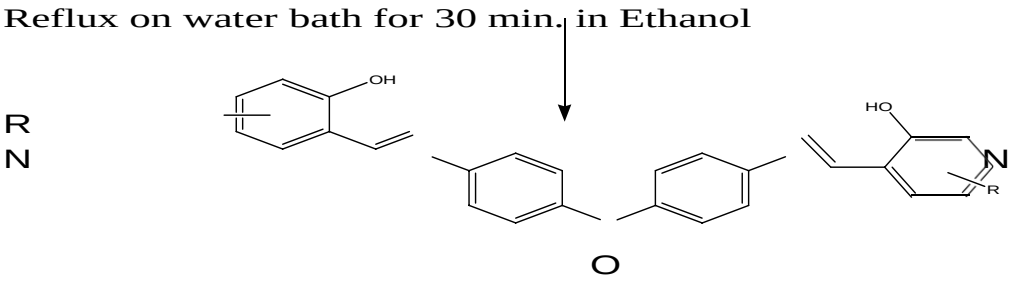
UV-visible spectra were recorded in ethanol on Shimadzu UV-3600 UV-VIS- NIR spectrometer. IR spectra were recorded in KBr pellets on Perkin Elmer FT-IR Spectrum-65 spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ using TMS as the standard on Varian 300MHz spectrometer. GC-MS were recorded on Shimadzu GC-MS QP 5050 mass spectrometer. Thermograms were recorded on V2 4F TA thermal analyzer at the heating rate 20^{o}C per minute in nitrogen atmosphere. X-ray diffractograms were run in the range 10-80^o using a Philips PW-1710 diffractometer attached to a digitized computer along with graphical assembly where Cu Kα radiationsource connected with a tube of Cu-NF 2kV/20mA was used.

2.2 Synthesis of Schiff bases (SB-1 to SB-4):

The 4,4'-diaminodiphenylether (2.00 g, 0.01mol) and salicylaldehyde (1.22g,0.01mol),2-hydroxy-1-naphathaldehyde(1.72g,0.01mol),5-bromo- 2-hydroxy benzaldehyde, (2.00g, 0.01 mol),2-hydroxy-3-methoxybenzaldehyde(1.52g,0.01mol), 2,4-dihydroxybenzaldehyde(1.38g, 0.01 mol) were dissolved in absolute ethanol (30- 40 cm^3) separately in 1:2 molar ratio. The ethanolic solutions were mixed together. After refluxing for 3 hrs, solid crude product was formed after cooling which is recrystallized from ethanol and dried in desiccators over anhydrous $CaCl_2$. The purity of Schiff bases were checked by TLC using silica gel. The reaction is as given below. In the preparation of Benzoin -4-Amino phenol ligand a drop of piperadine is added asa dehydrating agent.

Reaction -1: Scheme of synthesis of Schiff bases (SB-1 to SB-4)





R = H, 3-OCH_3, 5-Br, Benzo,

2.3 Biological Evaluation

2.3.1 Antibacterial and antifungal activities

Antibacterial and antifungal activities of Schiff bases were tested by serial dilution technique [19]. Eight test tubes containing 5 ml of sterile nutrient / sabouraud broth were inoculated with 0.02ml of 24 h old culture of bacteria *B. subtilis* and *E. coli* and fungi *A. niger* and C. *albicans* respectively. Different amounts of Schiff basesin ethanol were aseptically added with the help of sterile pipettes from the stock solution 200 µg/ml to 5 ml quantities of respective media so as to reach the concentration from 1µg/ml to 50µg/ml. All test tubes were inoculated at 37^0C and at room temperature for bacteria and fungi respectively. Test tubes inoculated with organism were observed for presence of turbidity after 24h and 48h respectively. The lowest concentration of Schiff bases inhibiting the growth of organism was determined as MIC value.

3. Results And Discussion

3.1 Chemistry

All Schiff bases (SB-1 to SB-4) are crystalline solids having sharp melting point. They are soluble in common organic solvents. Synthesised Schiff base was completed in good yield of desired product (Table 1).

Table 1: Analytical and Physical data of the compounds studied.

Sr. No	Compound	Molecularformula	Colour	MeltingPoint (Temp. ^{0}C)	Yield %
1	SB-1	$C_{26}H_{20}N_2O_3$ (408)	Faint Yellow (Shining Crystals)	214 - 216	92
2	SB-2	$C_{34}H_{24}N_2O_3$ (508)	Dark Yellow	185 - 187	91
3	SB-3	$C_{26}H_{18}N_2O_3Br_2$(565)	Yellow	240 - 242	85
4	SB-4	$C_{28}H_{24}N_2O_5$(468)	Orange	134 - 136	90

3.2 Spectral analyses

Uv-visible spectra of the Schiff bases in chloroform exhibit an intense band at~400nm. UV-visible spectrum of 4, 4'-diaminodiphenyl ether in chloroform exhibits an intense band at ~350 nm. The shifting of λmax (~400 nm) of the reported Schiff bases towards longer wavelength may be due to extended conjugation in the molecule [23]. Infrared spectra of the Schiff bases in KBr pellets exhibit ν (O-H), ν(C=N) and ν(C-O) modes at ~ 3330 to 3400, ~1620 and ~ 1260 cm^{-1} respectively. These values are in accordance with the earlier reported values. The ν (O-H) mode is broad and weak. This may be due to hydrogen bonding between phenolic –OH and nitrogen of the azomethine group [24]. The assignments of ^{1}H NMR signals show close resemblance with the earlier results [25-26]. The mass spectra of Schiff bases exhibit M^+ peak corresponding to the molecular weight and confirms their molecular formulae.

SB-1: 2-{[4-(4-Amino-phenoxy)-phenylimino]-methyl}-phenol

Uv-Vis.: λmax 352 nm; **IR:** ν (O-H) 3300-3400 cm^{-1}, ν (C=N) 1620.12 cm^{-1}, ν (C-O)1262.75, 1299 cm^{-1}, ν (C=C) 1573 ; **^{1}H NMR** signals (δppm): 13.110 (1H, s, Ar-OH), 8.803 (1H, s, benzene), 6.879-7.492 (4H, m, Ar-H); **GC-MS:** m/z (relativeintensity %): M^+ peak 408 (Molecular Formula: $C_{26}H_{20}N_2O_3$, Mol. Weight: 408)

SB-2: 1-{[4-(4-Amino-phenoxy)-phenylimino]-methyl}-naphthalen-2-ol

Uv-Vis.: λmax 394 nm; **IR:** ν (O-H) 3300-3400 cm^{-1}, ν (C=N) 1622.05 cm^{-1}, ν (C-O)1326, 1249.14 cm^{-1} , ν (C=C) 1577 cm^{-1} ; **^{1}H NMR** signals (δppm): 15.536 (1H, s,
Ar-OH), 9.396 (1H, s, benzene), 7.131-8.166 (4H, m, Ar-H); **GC-MS:** m/z (relativeintensity %): M^+ peak 508 (Molecular Formula: $C_{34}H_{24}N_2O_3$, Mol. Weight: 508)

SB-3: 2-{[4-(4-Amino-phenoxy)-phenylimino]-methyl}-4-bromo-phenol

Uv-Vis.: λmax 360 nm; **IR:** ν (O-H) 3300-3400 cm^{-1}, ν (C=N) 1617.73 cm^{-1}, ν (C-O)1300, 1275.26 cm^{-1}, ν (C=C) 1561 cm^{-1}, ν (C=C) 1561 cm^{-1}; **^{1}H NMR** signals (δppm): 10.536 (1H, s, Ar-OH), 8.396 (1H, s, benzene), 6.131-7.166 (4H, m, Ar-H);
GC-MS: m/z (relative intensity %): M^+ peak 566 (Molecular Formula:$C_{26}H_{18}N_2O_3Br_2$, Mol. Weight: 566)

SB-4: 2-{[4-(4-Amino-phenoxy)-phenylimino]-methyl}-6-methoxy-phenol.

Uv-Vis.: λmax 334 nm; **IR:** ν (O-H) 3300-3400 cm^{-1}, ν (C=N) 1614.78 cm^{-1}, ν (C-O)1338, 1276.88 cm^{-1}, ν (C=C) 1579 cm^{-1}; **^{1}H NMR** signals (δppm): 13.536 (1H, s,
Ar-OH), 8.390 (1H, s, benzene), 7.531-8.121 (4H, m, Ar -H); **GC-MS:** m/z (relativeintensity %): M^+ peak 468 (Molecular Formula: $C_{28}H_{24}N_2O_5$, Mol. Weight: 468)

3.3 Thermal analyses

A representative TG curve of SB-3 is shown in Figure 2. The Schiff bases (SB- 1 to SB-8) undergo decomposition in two stages. In the first stage they decompose in the range 210^{0}C to 420^{0}C (60-70% weight loss) and in the second stage in the range 550^{0}C to 800^{0}C (40-30% weight loss). The major weight loss occurs in first stage. From the first stage of TG curves, the values of kinetic parameters E- energy of activation, Z- pre-exponential factor, ΔS- entropy change and G- free energy change were calculated using Coats – Redfern (C.R.) (Equation 1) [27], (Table 2). The values of E (lying in the range 20– 40 kcal mol^{-1}) and G (lying in the range 30 - 49 kcal mol^{-1}) are sufficiently high indicating that all the Schiff bases are thermally stable. The ΔS values are negative indicate exothermic reaction.

Table 2: Kinetic parameters of Schiff bases estimated by Coats – Redfern (C.R.)method

Method.	Kinetic Parameters	SB-1	SB-2	SB-3	SB-4
C.R.	n	0.62	0.92	1.37	1.43
	E	28.82	19.91	28.77	38.29
	Z	$3.4x10^{8}$	$1.2x10^{5}$	$1.6x10^{8}$	$2.6x10^{10}$
	ΔS	-8.62	-22.59	-17.57	-8.38
	G	33.83	31.57	34.95	39.91
Units: E-kcal mol^{-1}, Z-S^{-1}, ΔS- $JK^{-1}mol^{-1}$, G- kcal mol^{-1}					

Coats-Redfern method

$$\log \frac{1-(1-\alpha)^{1-n}}{(1-n)T^2} = \log \left[\frac{ZR}{Eq\,2.303R} - \frac{E}{T}\times\frac{1}{T}\right] \quad \text{..... 1}$$

In all three equations: α is fraction of weight loss at particular temperature, T_s is temperature at half weight loss, q is rate of heating, θ is difference of particular temperature and temperature at half weight loss ($T-T_s$). From the calculated values ofE and Z, the values of ΔS and G were determined by using the equations 2 and 3.

ΔS = 2.303 x Log [(Z x h) / (Ts x k)] 2

G = E-(ΔS x Ts).....3

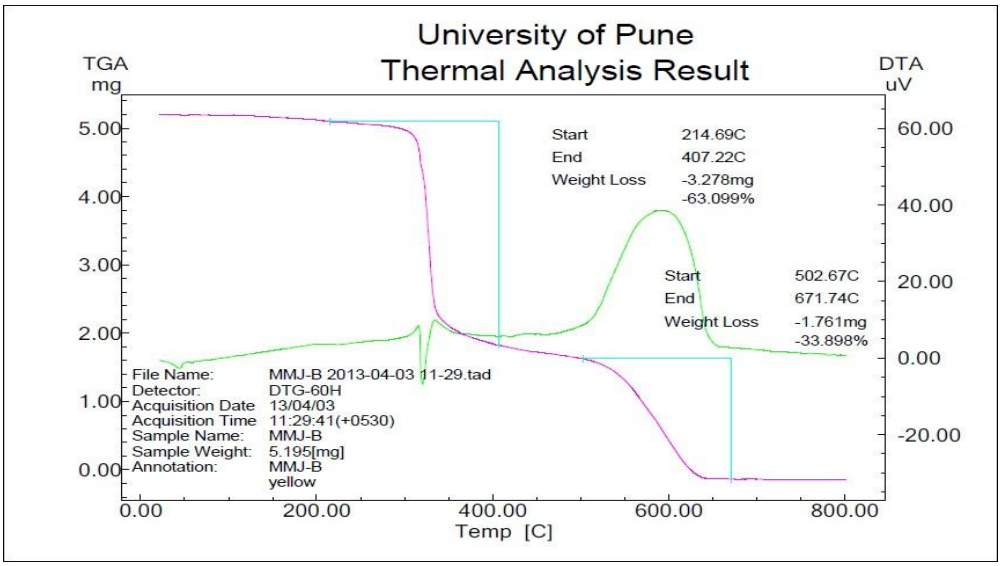


Fig 2: TG curve of SB-3

3.4 Structural and Morphological analyses

The novel Schiff bases have been characterized by powder x-ray diffraction studies to predict the crystal system. The diffractograms is depicted in Fig. 4, which shows 13 reflections (2θ) between 20.00^0 to 80.00^0. The cell parameter calculated are mentioned in parenthesis (a=06.0234A^o, b=46.234A^o c=9.437A^o β= 129.634^o) and these values are found to be in agreement with those required for a monoclinic crystal system where a = b ≠ c and α = γ ≠β. Therefore, it may be concluded that the crystal system of the all Schiff bases is monoclinic [34]. The volume of unit cell is 2043.06A^o. The scanning electron microscopic study reveals that the surface of Schiffbase is without crack hole and homogeneous shows in Fig. 5.

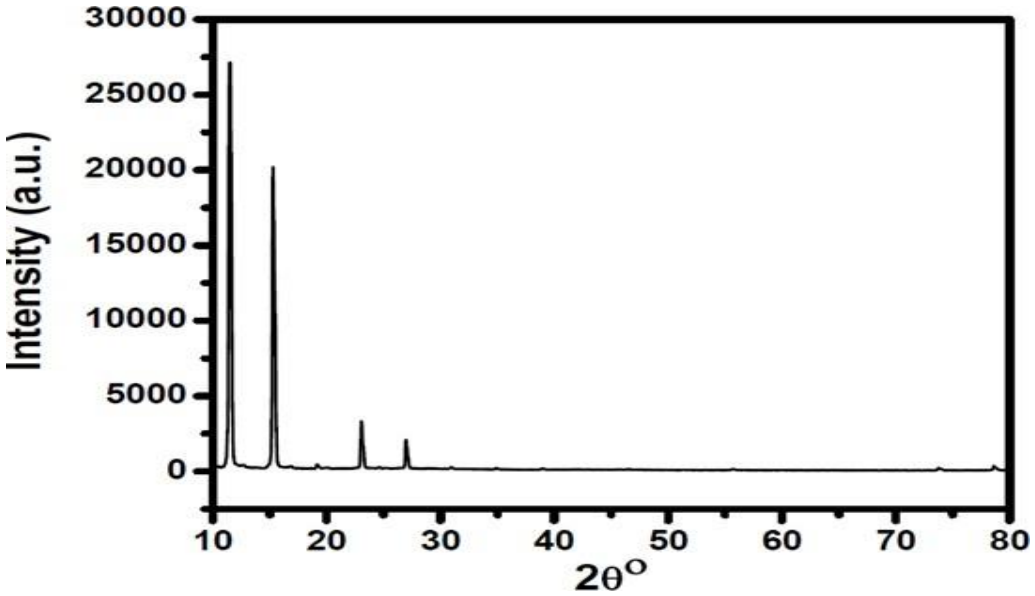


Fig 4: XRD of SB-3

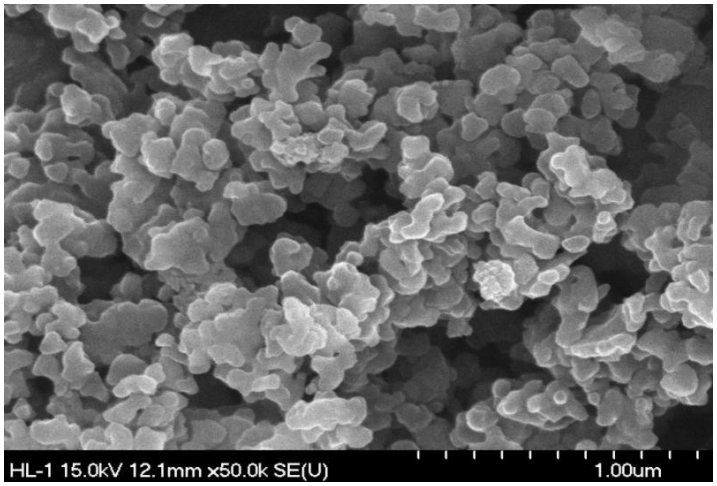


Fig 5: SEM Image for SB-3

3.5 Biological studies

Literature survey reveals that Schiff bases exhibit antibacterial, antifungal, anticancer and antitubercular activities [31] and their nematocidal and molluscicidal activity was less studied. In the present study we have tested Schiff bases (SB-1 to SB-4) for the evaluation of antibacterial and antifungal activities. The MIC valueshave been reported (Table 3).

Table 3: The MIC values of Schiff bases for antibacterial and antifungalactivities

Bio-activity	**Test Organism**	**SB-1**	**SB-2**	**SB-3**	**SB-4**
Antibacterial (µg/ml)	*B. subtilis*	14	11	12	10
	E. coli	14	13	12	10
Antifungal (µg/ml)	*A. niger*	10	9	8	6
	C. Albicans	10	9	8	6

3.6 Antibacterial and antifungal activities

The Schiff bases have been tested for the evaluation of antibacterial activity against *B. subtilis and E. coli* and antifungal activity against *A. Niger* and *C. Albicans*.The MIC values for the Schiff bases lie in the range 10-16 µg /ml for antibacterial activity and 6-10 µg/ml for antifungal activity. They show prominent antifungal activity as compared to antibacterial activity.

4. Conclusion

1. The novel Schiff bases were confirmed by spectral data.
2. Thermal analysis shows that all the Schiff bases are thermally stable.
3. XRD analysis shows monoclinic crystal system to all Schiff bases.
4. All the Schiff bases posses' good antibacterial and antifungal activities in lowconcentration.
5. They are better antifungal agents than antibacterial agents.

5. Acknowledgments

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