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Synthesis, characterization and biological activity of Some Schiff's Bases from the Reaction of 4,4'-DiaminoBenzanilide with Nitrobenzaldehyde Derivatives

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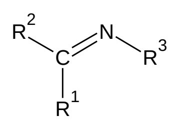
Abstract: *Four double Schiff's bases were prepared from the reaction of 4,4'-diaminobenzanilide with some aldehydes derivatives in ethanol under reflux condition. Schiff bases melting points determined and their structures were identified using various spectroscopic methods. Azomethine (-CH=N-) group band appeared in infrared spectrum around 1620cm^{-1} and secondary amine (-NH-) group band appeared around 3200cm^{-1}. Mass spectra of these compounds showed molecular weight peaks at M-1.*

Keywords: *Schiff bases, 4,4'-DiaminoBenzanilide, Nitrobenzaldehyde, Antibacterial, Antifungal.*

INTRODUCTION

Schiff bases are condensation products of primary amines and carbonyl compounds and they were discovered by a German chemist, Nobel Prize winner, Hugo Schiff in 1864 [1]. Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (C=O) has been replaced by an imine or azomethine group (-CH=N-) (Fig. 1) [1,2].

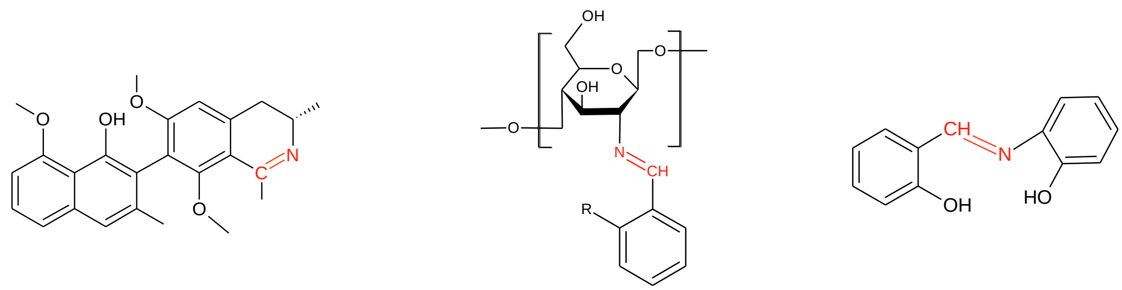


R^1, R^2, and/or R^3 = alkyl or aryl

Figure.1: General structure of a Schiff base.

Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds (see Fig. 2 for some examples). The imine group present in such compounds has been shown to be critical to their biological activities [2]. Schiff base ligands are essential in the field of coordination chemistry, especially in the development of complexes of Schiff bases because these compounds are potentially capable of forming stable complexes with metal ions [1].

Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilisers [2], antibacterial, antitumor, antifungal [3,4], antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties [2,5], anticancer, diuretic and herbicidal activities [4].



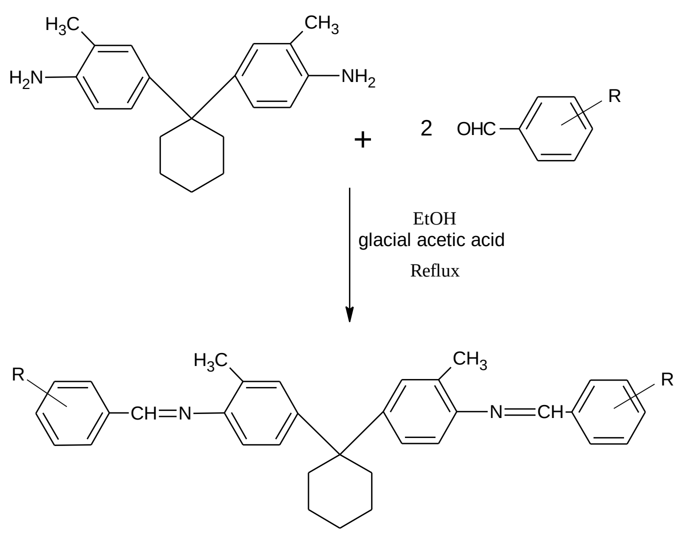
Ancistrocladidine(1)
Natural Product

Chitosan-derived Schiff base
R: H(2) or OH(3)
Natural Product-derived Compound

N-(Salicylidene)-2-hydroxy aniline(4)
Non-natural Compound

Figure.2: Examples of bioactive Schiff bases.

Schiff bases have very flexible and different structures. A wide range of Schiff base compounds and their behavior studied because these compounds have very flexible and diverse structure [6]. The synthesis of a series of Double Schiff bases derived from 1,1′-Bis(4-aminophenyl)cyclohexanec (BAPC) has been reported, Schiff bases were synthesized by condensing BAPC and substituted aldehydes in ethanol by using glacial acetic acid as a catalyst at reflux temperature (Scheme 1) [7].

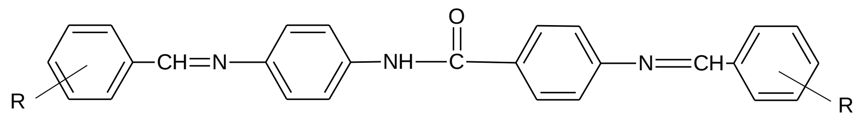


R: 2-NO_2, 4-OCH_3, 2-OH, 2-Cl, 4-NO_2, 3-NO_2, 3-Br, 4-Cl, 3-Cl

Scheme.1: Synthesis of Double Schiff bases derived from 1,1′-Bis(4-aminophenyl)cyclohexanec.

4,4'-DiaminoBenzanilide derived double Schiff bases have also been reported to possess biological activity, The synthesis of Schiff bases derived from the condensation 4,4'-DiaminoBenzanilide and substituted aldehydes (Fig.3) [8,9].

Prepared Schiff base derived from salicylaldehyde showed inhibition against Botrytis cinerea fungus [8], Schiff base derived from 4-chlorobenzaldehyde could act as a potential Anti-Dengue and Anticancer agent [9].



R: 2-OH [8], 4-Cl [9]

Figure.3: Synthesis of Double Schiff bases derived from 4,4'-DiaminoBenzanilide.

MATERIALS AND METHODS

2.1. Materials:

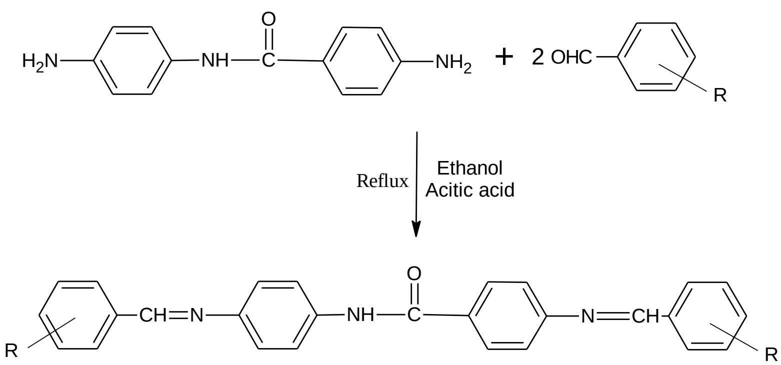
4,4'-DiaminoBenzanilide from Sigma Aldrich. Benzaldehyde from BDH, 2-Nitrobenzaldehyde from TITAN BioTECH LTD., 3-Nitrobenzaldehyde from iT USA and 4-Nitrobenzaldehyde from Dr. THEODOR. Ethanol from Eurolab and Acetic acid from SCP, for biological studies DMSO from Merck. Purity is not less than 98%.

2.2. Techniques:

Melting points were determined on MPM-H 2/D (Germany). UV spectra were scanned on a Jasco UV-Vis (v-630, Japan) spectrophotometer using Ethanol as solvent. IR spectra (KBr pellets) were scanned on a Jasco FTIR-4200 spectrometer (Japan). LC-MS were scanned on a Shimadzu LC-MC (Model-2010) by using methanol as mobile phase.

2.3. Schiff bases synthesis:

2 mmol of 4,4'-DiaminoBenzanilide is dissolved in 25ml of ethanol and 5 drops of acetic acid added to it. The reaction mixture stirred for 5minutes. 4 mmol of aldehydes derivatives dissolved in 25ml of ethanol and the solution was added to the reaction mixture. The reaction is refluxed for two hours with stirring. The precipitate was filtered and washed by hot ethanol. The products melting point was determined and their structures were identified using various spectroscopic methods.



R: H	Compoud(1)
R: 2-NO_2	Compoud(2)
R: 3-NO_2	Compoud(3)
R: 4-NO_2	Compoud(4)

Scheme.3: Synthesis of Double Schiff bases derived from 4,4'-DiaminoBenzanilide.

2.4. Biological studies:

The synthesized compounds were screened for their antibacterial and antifungal activity by the agar well diffusion method. The compounds were dissolved in DMSO at a concentration of 1 mM. The antibacterial activity were tested against Escherichia coli, Pseudomonas aeruginosa (Gram-negative) and Staphylococcus aureus (Gram-positive). The antifungal were tested against Saccharomyces cerevisiae and Aspergillus niger.

RESULT AND DISCUSSION

3.1. Physicals properties:

The (Table 1) gives prepared Schiff bases color, yield and melting point. Compounds color are deferent. Melting point for all compounds are high.

Table.1: Prepared Schiff bases formula, molecular weight, color, yield and melting point.

No.	Chemical formula	M_w (g/mol)	Color	Yield %	M.P. (°C)
1	$C_{27}H_{21}ON_3$	403	Yellowish white	79.83	256.8
2	$C_{27}H_{19}O_5N_5$	493	Yellow	79.94	230.6
3	$C_{27}H_{19}O_5N_5$	493	Yellow	93.11	273.8
4	$C_{27}H_{19}O_5N_5$	493	Yellow	85.82	242.4

3.2. UV-Vis spectra:

From UV-Vis spectra for prepared compound (Fig. 4) we observe the appearance of two absorption peaks for each compound, due to the electronic transitions ($\pi \rightarrow \pi^*$) in the aromatic systems as well as the transitions ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) in the double bonds with the heterogeneous atoms in the two groups (C=O) and (-CH=N-) [10]. The insertion of a nitro group at a different positions on the aromatic ring leads to a red shift of the absorption peak which is at 339 nm towards the higher wavelengths compared to the non-substituted compound, as the intensity of this displacement increases when two nitro groups are introduced, except that this displacement is less intense in relation to the other peak located at 273 nm.

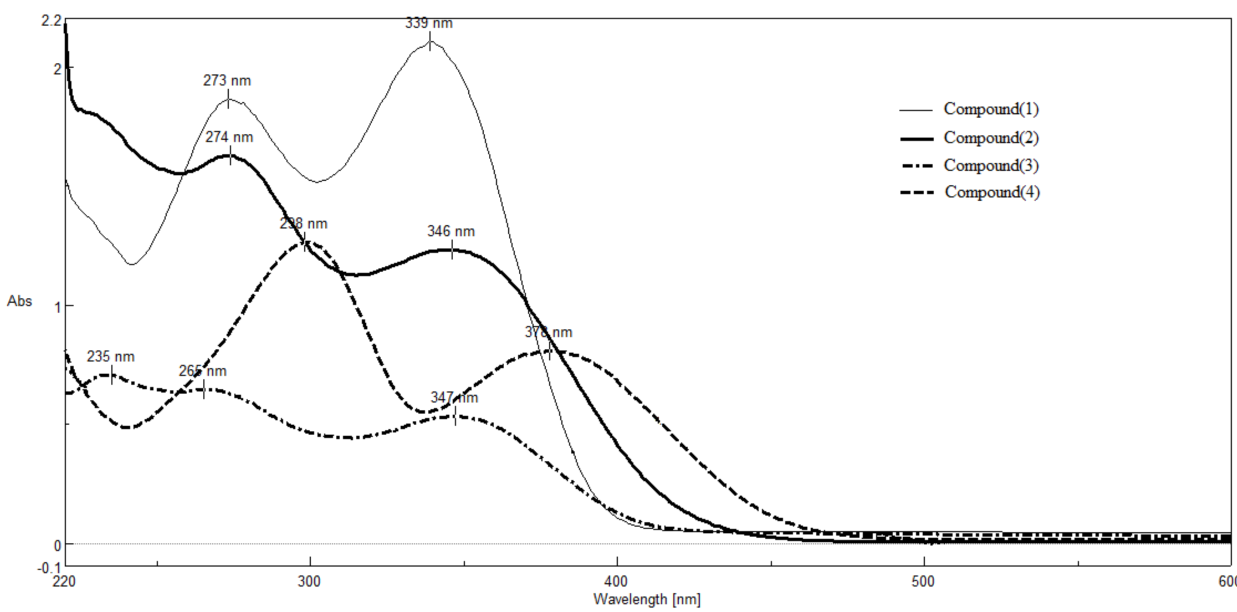
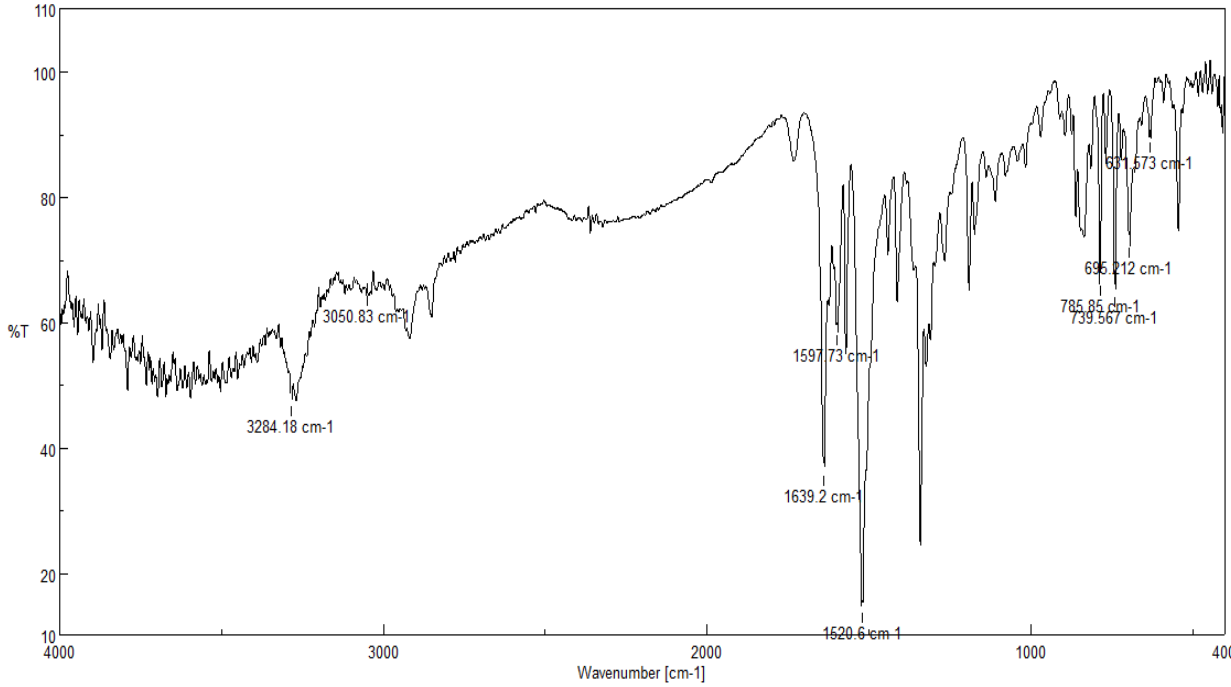


Figure.4: UV-Vis Spectrums for prepared Schiff bases.

3.3. FTIR spectra:

Imine group band -CH=N- appears around 1620cm^{-1}, and the distinctive band of the secondary amine group -NH- appears around 3200cm^{-1}, while the band around 1650cm^{-1} is for the carbonyl group elongation amid[11].



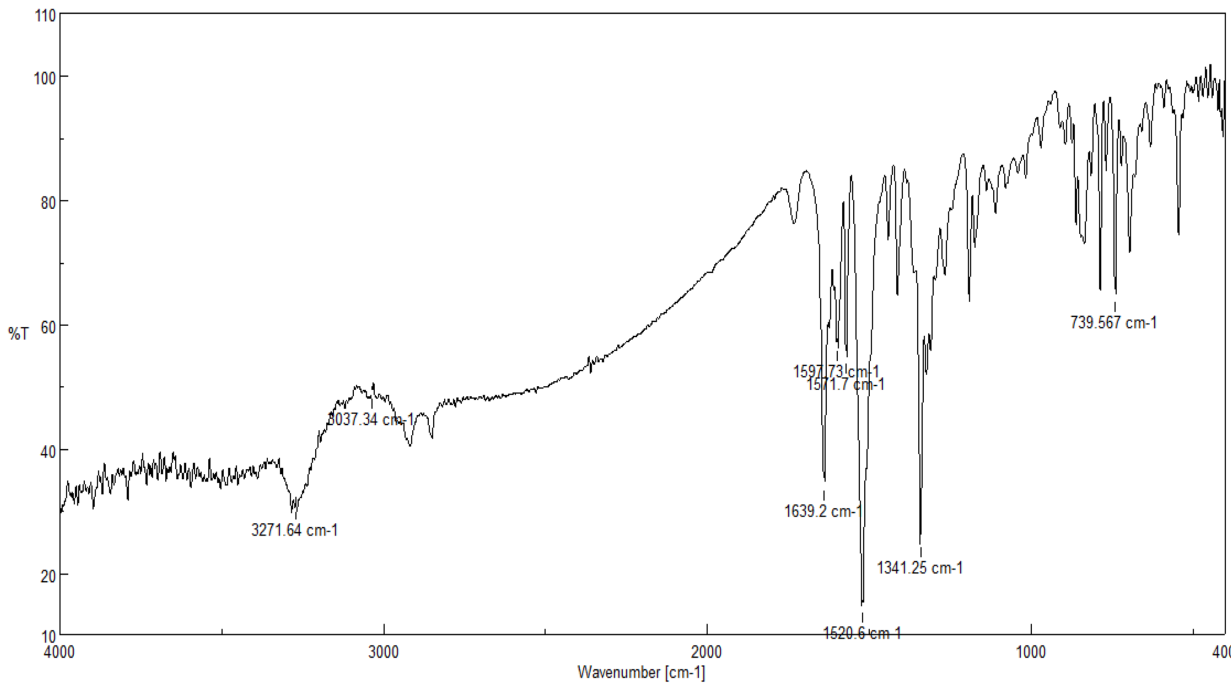
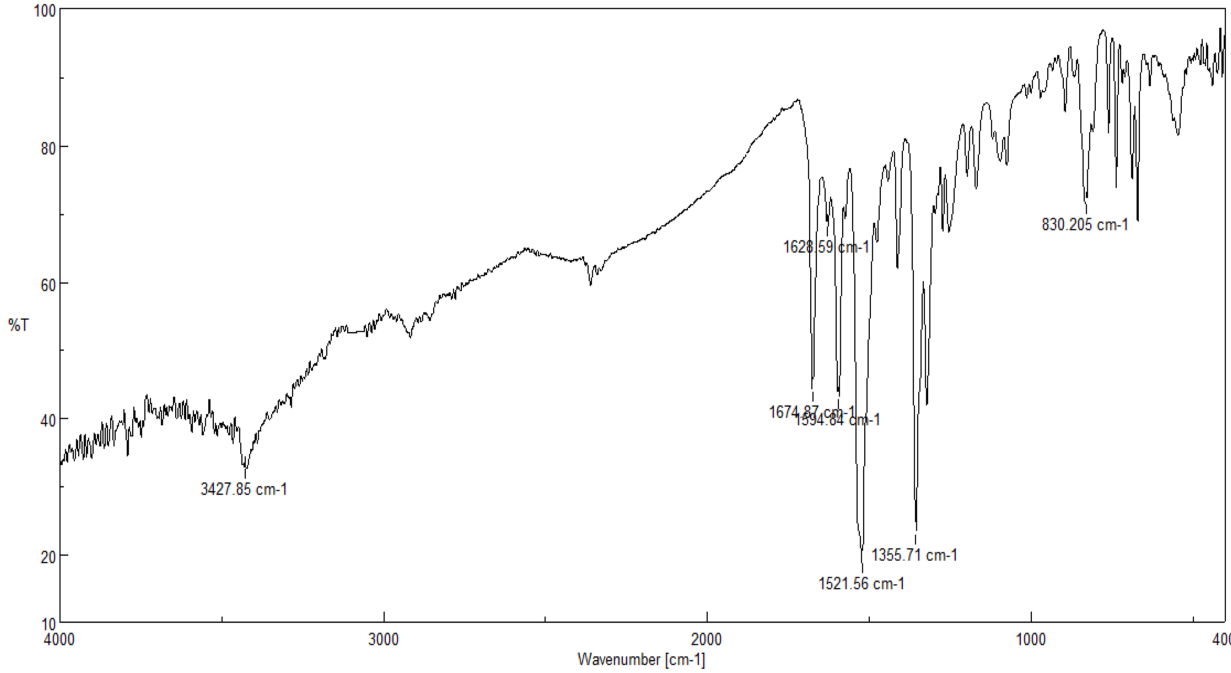


Figure.5: FTIR Spectrums for compounds (1,2).



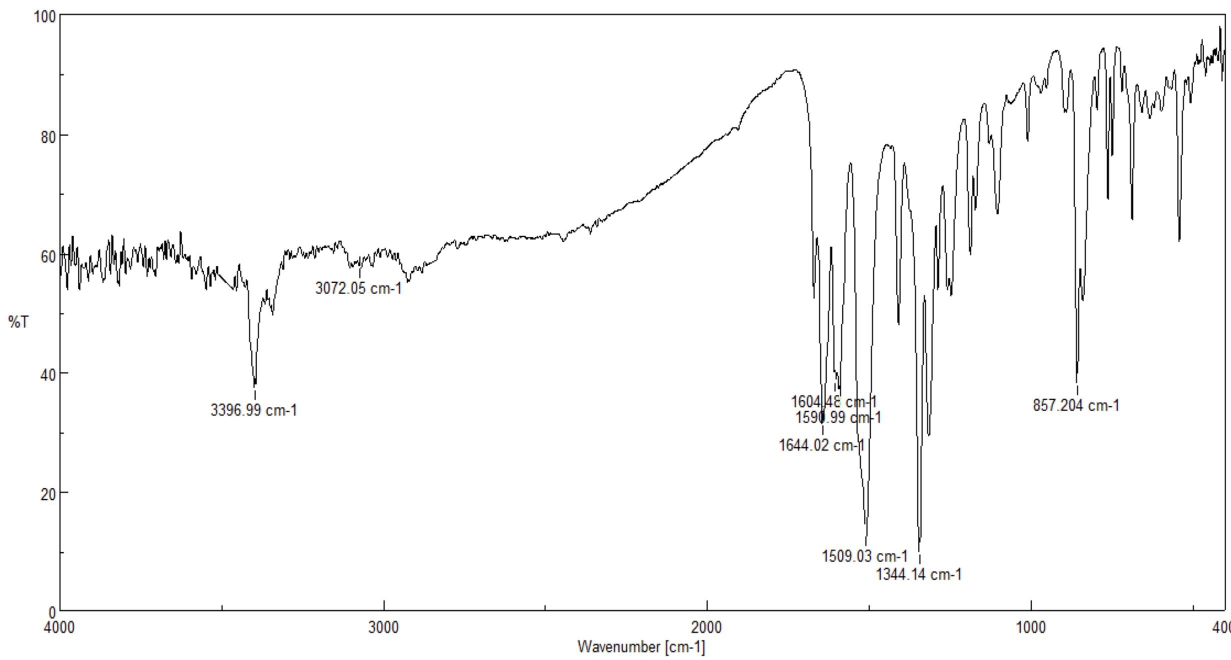


Figure.6: FTIR Spectrums for compounds (3,4).

Table.2: Groups band frequency from FTIR spectrums for prepared compounds.

No.	-NH-	C=O Secondary Amide		-CH=N-	$-NO_2$	Substitution Aromatic Rings	
		Amide I	Amide II				
1	3284 cm^{-1}	1639 cm^{-1}	1520 cm^{-1}	1597 cm^{-1}	-	Five adjacent H	785 cm^{-1} 739 cm^{-1} 695 cm^{-1} 631 cm^{-1}
2	3271 cm^{-1}	1639 cm^{-1}	1571 cm^{-1}	1597 cm^{-1}	1520 cm^{-1} 1341 cm^{-1}	1,2-Substitution	739 cm^{-1}
3	3427 cm^{-1}	1674 cm^{-1}	1594 cm^{-1}	1628 cm^{-1}	1521 cm^{-1} 1355 cm^{-1}	1,3-Substitution	830 cm^{-1}
4	3397 cm^{-1}	1644 cm^{-1}	1591 cm^{-1}	1604 cm^{-1}	1509 cm^{-1} 1344 cm^{-1}	1,4-Substitution	857 cm^{-1}

3.4. LC-MS spectra:

Schiff bases were analyzed using a high performance liquid chromatography (HPLC) technique equipped with a mass spectrometer detector to ensure the purity of the resulting compound and determine its molecular weight. The analysis were performed on column (C18, l=10cm), mobile phase: methanol, flow rate: (2ml/min), injection volume: (5µl), reagent: Mass, displacement pattern: SESI (-). Mass spectra of these compounds showed molecular weight peaks at M-1.

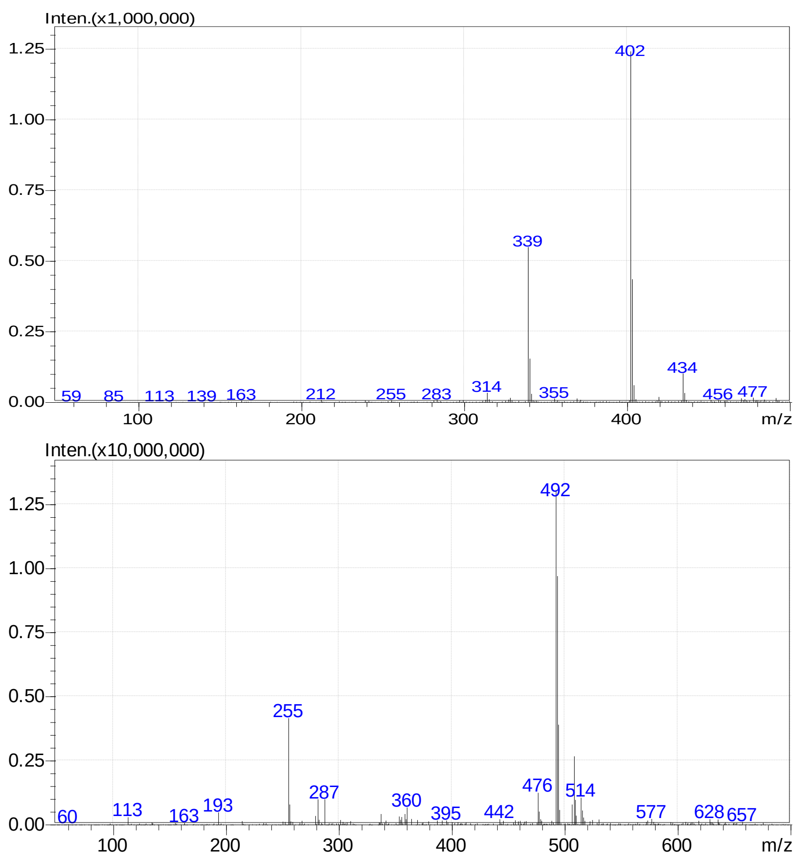


Figure.7: LC-MS Spectrums for compounds (1,2).

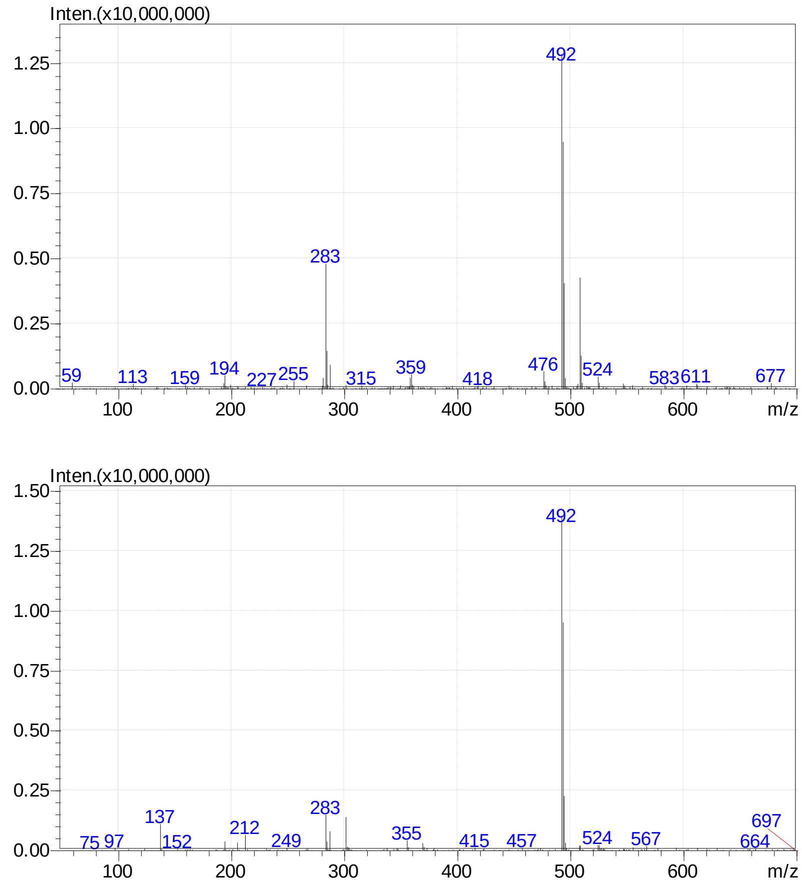


Figure.8: LC-MS Spectrum for compound (3,4).

3.5. Antibacterial activity:

The synthesized compounds were screened for their bactericidal potential against three bacterial strains. The results are summarized in Table 3. All compounds showed moderately growth inhibition against E. coli. 3-Nitro and 4-nitro compounds were more active against P. aeruginosa than compouds (1-2). All compounds showed growth inhibition against S. aureus and the compounds (2-3) were the most active.

Table.3: Antibacterial activity of prepared Schiff bases.

Compound	E. coli	P. aeruginosa	S. aureus
1	++	+	++
2	++	+	+++
3	++	++	+++
4	++	++	++

3.6. Antifungal activity:

Only compound (3) showed weak growth inhibition against S. cerevisiae. All nitro compounds showed growth inhibition against A. niger.

Table.4: Antifungal activity of prepared Schiff bases.

Compound	S. cerevisiae	A. niger
1	-	-
2	-	+
3	+	++
4	-	++

CONCLUSION

The present study describes of new Schiff bases derived from 4,4'-Diaminobenzanilide. Prepared compounds have high melting point. The presence of nitro group changes the color of the compound compared to the non-replaceable compound. Nitro group leads to red shift in the UV spectrum. FTIR and LC-MS spectra correspond to the formula suggested of the compounds. All prepared compounds showed Antibacterial activity.

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