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Green Synthetic Route for Novel derivatives of Schiff Bases and Their Characterization

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ABSTRACT

The novel and eco-friendly method have been developed for the synthesis of some Schiff bases derived from different aromatic aldehydes with ethylenediamine in presence of ZnO NPs as efficient and green catalyst. The methodology includes the use of ZnO NPs as a new catalyst, mild reaction conditions and good yield of product within limited time duration. The special property of catalyst lies in its reusability, recyclability and severe use without loss of catalytic properties. The confirmation of structures of newly synthesized Schiff bases are confirmed by using physical methods, namely, melting points or boiling point, UV and IR spectra.

Keywords: Schiff's Base, Aromatic Aldehydes, Aromatic Amines, Eco-friendly Method, ZnO Nanoparticle.

I INTRODUCTION

Schiff bases are nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by C=N-R group. These are also known as imine or azomethine, prepared Hugo Schiff, was reported in 1864[1]. Since then a numerous methods for the synthesis of imines have been described. Schiff base polymers with a system of conjugated –C=C- and –C=N- bonds in their main chain are of considerable interest due to their thermal stability and their using as solid stationary phase for gas chromatography[3],have semiconductor properties[4], mechanical strength, electrochemical and nonlinear optical properties[5], and useful catenation ligand, where the coordination polymeric Schiff bases are extensively studies[6]. Schiff base polymers are produced by the polycondensation of diamines with various dicarbonylcompounds[7].Due to various applications of as reagents in organic and inorganic synthesis[8], in photography or electrochemical silver plating[9], and as free radical scavengers in industrial processes[10]. Schiff bases have also been reported as plant growth regulators[11] and antimicrobian[12] or antimycotic[13] activity. Schiff Bases are characterized by the -N=CH- (imine) group which imports in elucidating the mechanism of transamination and rasemination reaction in biological system[14-15].Their metal complexes have been widely studied because they have antifungal activities[16-19] anticancer and herbicidal applications [20-21]. The reaction of imine formation is reversible, usually, it was advisable to remove the water was formed by distillation or by using an azeotrope – forming solvent[22-23]. Till time, large number of methods have been applied were using variable catalyst such as protonic acid[24], BF_3[25]and $POCl_3$[26]. The reported methods have many drawbacks such as use of toxic chemicals, elongated time duration methods, low yields and harsh reactions conditions.

To overcome all problems or earlier reported methods, authors have developed an eco-friendly and efficient method for synthesis of novel Schiff's compounds. Now we report the use of ZnO NPs catalyst for the first time during synthesis of Schiff bases under study. This development in the procedure of synthesis by adding green and efficient catalyst is highly accepted in terms of yield, time saving, economical, ecofriendly nature and reusability of catalyst. A special care is give to the structural elucidation of these new derivatives by using physical methods namely, melting points or boiling point, UV and IR spectra.

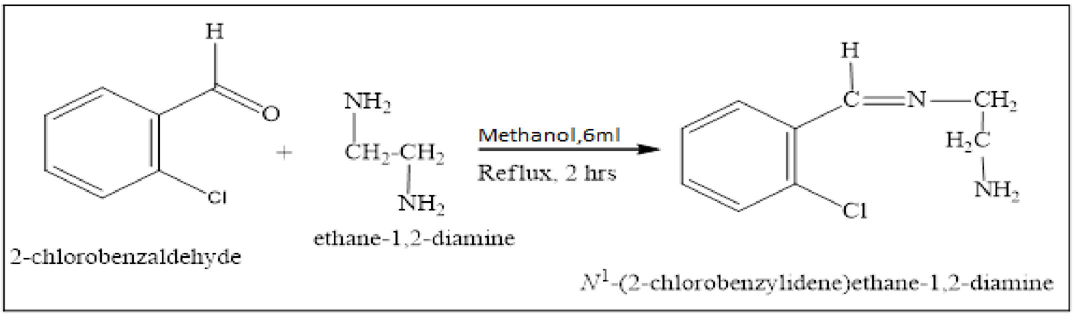
II MATERIALS AND METHODS

MATERIALS

All chemical compounds are used were AR grade. Purification of chemicals has been done by distillation if required. The Melting points were determined in open capillary tubes as well as in digital electrothermal melting point apparatus model and are uncorrected. The IR spectra were taken by a computerized FTIR, Bruker model Tensor 27. The UV for 10^{-3}M ethanolic solutions is measured by a computerized double beam Shimazu type UV-1601.

Method for Synthesis of Schiff bases i.e. N'-(substitutedbenzylidene) ethane-1,2-diamine

Equimolar mixture of aromatic aldehyde like 2-chlorobenzaldehyde **(PG_1)**and ethylene diamine (10 mmol each) were taken in a 50 ml round bottom flask, add 6 ml of methanol and 10 % ZnO catalyst to it, the mixture is stirred at room temperature for 2 hrs, the progress of reaction is confirmed by TLC. After due time, the mixture on cooling precipitate out, which is filtered, washed with cold ethanol and dried. Pure products were obtained by recrystallization by the use of 95% ethanol with a yield of 93 %. (Scheme 1)



Scheme 1: General Reaction scheme for the synthesis of Schiff's base

III RESULTS AND DISCUSSION

A new and efficient synthesis method has been formulated for the Schiff's bases with different specific aldehydes in methanol as a solvent an ZnO NP as green catalyst resulted in new series of Schiff's bases with general formula RHC= N-R$_1$. This series is composed of ethylene diamine as amine and five different aryl aldehydes. Such newly synthesized compounds were characterized by different physicochemical techniques like melting point and FTIR spectroscopy. The purity of the compound was checked on silica-gel-coated aluminium plates. IR spectra were recorded in KBr on a Perkin Elmer Spectrum RX-1 FT-IR spectrophotometer. All the physiochemical properties of newly synthesized Schiff's bases are tabulated in table1.

Table 1: Physicochemical propertiesof newly synthesized Schiff bases

Entry	**Schiff's Base**	**M.P (^{0}C)**	**Yield %**	**Colour**	**Solubility**	**UV bands λnm(ε_{max})**
PG$_1$	N'-(2-chlorobenzylidene) ethane-1,2-diamine	180-183	93%	Yellow	DMSO	247(1472), 282(91)
PG$_2$	N'-(4-nitrobenzylidene) ethane-1,2-diamine	195-199	84%	Orange	DMSO	255(1932), 327(680)
PG$_3$	N'-(4-hydroxybenzylidene) ethane-1,2-diamine	184-187	87%	Faint yellow	DMSO	247(2933), 327(1950)
PG$_4$	N'-(3-nitrobenzylidene) ethane-1,2-diamine	160-164	82%	Brown	DMSO	250(2669), 326(1376)
PG$_5$	N'-(2-hydroxybenzylidene) ethane-1,2-diamine	195-197	85%	Milky	DMSO	251(2478), 328(1116)

The structure of the prepared Schiff's bases was confirmed by infrared spectroscopy. The FTIR spectra showed that the band of prepared Schiff's bases corresponds to C=N for imine stretching vibration was found from 1590 to 1,685 cm^{-1}, the band at approximately 3097-3130 cm-^{1} and at 3320-3390 cm^{-1} is due to ν_{sym} and ν_{asym} vibrations of the NH$_2$ group, respectively. There is some variation in appearance of stretching modes assigned to C-H, C=Cand C=C groups in different Schiff's bases were observed at 2825-2900, 1610-1820 and 1255-1328 cm $^{-1}$, respectively. The spectra of complexes demonstrated further shift of NH$_2$ group vibration modes to lower frequencies as a result of bonding. The fundamental frequencies due to C-C have also been observed in the range of 1020- 1150 cm $^{-1}$. An additional band appears in the range 2955-300 cm^{-1} for ν_{C-H} (phenylic ring). Stretching bands occur at 3135-3245cm^{-1}dueto Hydroxyl groups in Schiff bases. Absorption band at 743 and 798 cm^{-1}occurs due to Chloro and Nitro group respectively. All complexes exhibit a broad band relatively in the region of higher frequency between 3400-3200 cm-1 indicating the presence of coordinated water molecules in the complexes. The broadness of the band has been assigned to the combined ν_{H2O} and ν_{N-H} stretching mode of vibrations. The infrared spectral bands of different Schiff's bases are summarized in Table 2.

Entry	Schiff's base name	Type of IR Fundamental Bands					
		$\nu_{C=C}$ Bending	$\nu_{N\text{-}H}$ Stretching	$\nu_{C\text{-}C}$ Bending	$\nu_{C\text{-}N}$ Stretching	$\nu_{C=N}$ Stretching	$\nu_{C\text{-}H}$ Stretching
PG$_1$	N'-(2-chlorobenzylidene) ethane-1,2-diamine	1272	3100	1020	1630	1590	2855
PG$_2$	N'-(4-nitrobenzylidene) ethane-1,2-diamine	1310	3116	1077	1610	1676	2895
PG$_3$	N'-(4-hydroxybenzylidene) ethane-1,2-diamine	1290	3120	1032	1820	1685	2848
PG$_4$	N'-(3-nitrobenzylidene) ethane-1,2-diamine	1328	3097	1058	1613	1660	2900
PG$_5$	N'-(2-hydroxybenzylidene) ethane-1,2-diamine	1255	3130	1150	1753	1685	2825

Table 2: FTIR spectra of all newly prepared Schiff's bases.

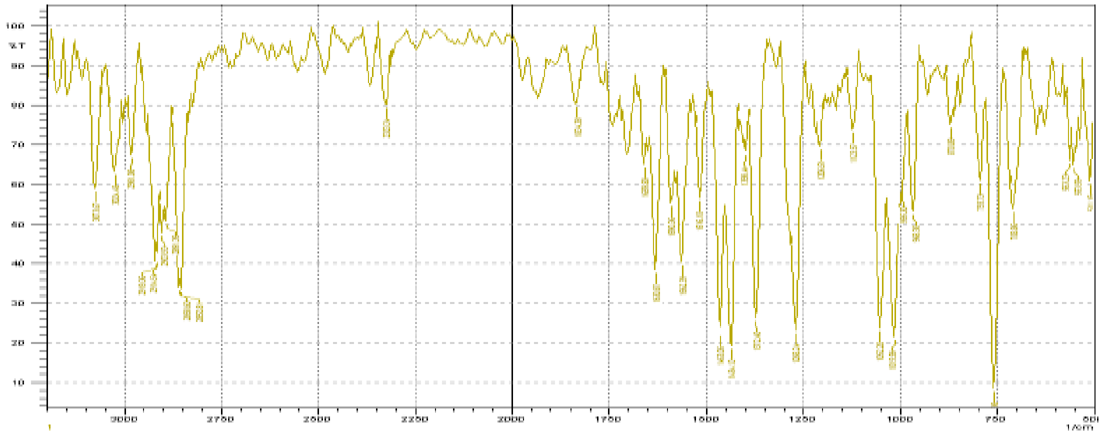


Figure 2: FTIR spectra of N'-(2-chlorobenzylidene)ethane-1,2-diamine (PG$_1$)

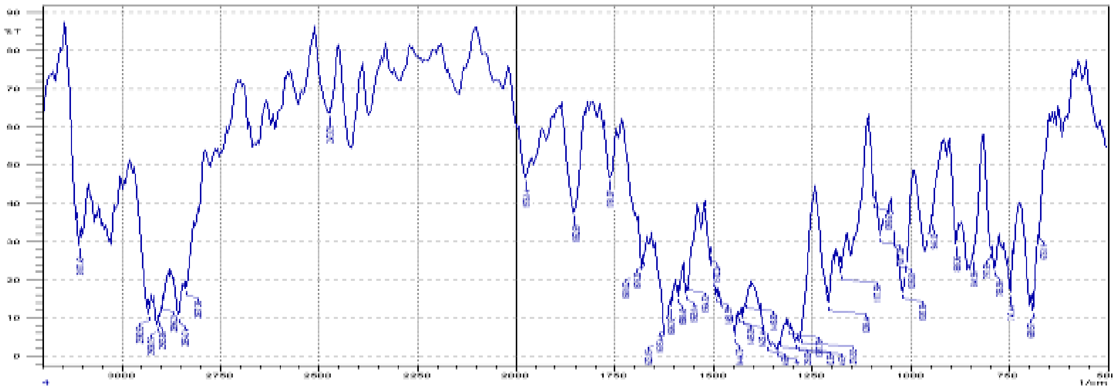


Figure 3: FTIR spectra of N'-(4-hydroxybenzylidene)ethane-1,2-diamine (PG$_3$)

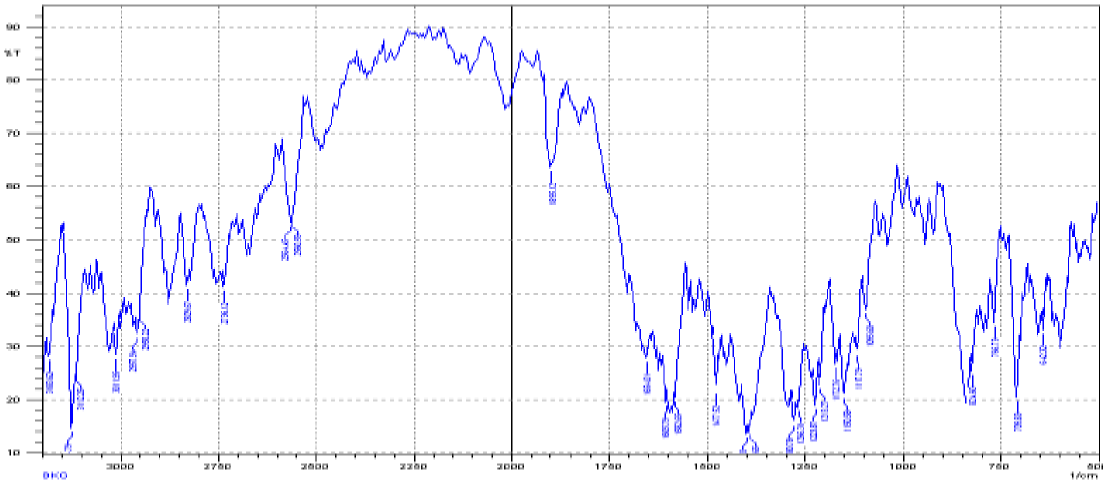


Figure 4: FTIR spectra of N'-(2-hydroxybenzylidene)ethane-1,2-diamine (PG$_5$)

The formation of a Schiff's base from substituted aryl aldehydes and amine in presence of ZnO nanoparticles involves a simple mechanism which consists of a fast reversible step accompanied by the formation of intermediate as carbinolamine in presence of ZnO nanoparticle catalysis (Scheme 1). Once the intermediate is formed, a fast dehydration step, led to the formation of Schiff bases and water. Many Schiff's bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base.Our suggested mechanism is similar to the oximation of aldehyde by amine at mild reaction conditions led to the formation of C=N in oxime or in Schiff bases under study.

IV CONCLUSION

Formulation of new eco-friendly, precise and efficient method for the biologically active derivatives of Schiff base by different substituted aryl aldehydes and ethylene diamine has been developed by this green synthetic protocol avoiding all toxic chemicals with promising results in mild reaction conditions by the use of green and efficient catalyst ZnO nanoparticle. Some of the major advantages of this eco-friendly synthetic protocol are the mild conditions, short reaction times, simple & easy work-up procedure, and use of green and effect catalyst ZnO nanoparticles. All these advantages make this methodology an alternative route to the conventional method and also a step towards green and clean environment. The synthesized compounds were characterized by different spectroscopic methods.

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