Research Paper www.ijcps.com

International Journal of Chemical and Pharmaceutical Sciences
2013, Mar., Vol. 4 (1)

ISSN: 0976-9390
IJCPS

Synthesis and characterization of some new shiff bases

[1]Navneet Kumar*, [2]Pratima Sharma, [2]Aastha Pareek and [3] Prasad AVGS

[1] Department of Applied Science, Raj Kumar Goal Institute of technology Ghaziabad. India.

[2]Department of Applied Science, Research Scholar Banasthali University Rajasthan. India.

[3] Department of Chemistry, K.N Bioscience, Hyderabad, India.

***Corresponding Author:** E-Mail: navneet171080@gmail.com.

ABSTRACT

An innovative protocol to the synthesis of this material emerged on exploring the potential of the 2-Butylbenzimidazole on its reaction with o-phenylenediamine and pentanoic acid. Various Schiff bases are formed, named as 2-methylbenzimidazole, 2-benzylbenzimidazole, Ethylacetate-2-methyl-benzimidazole, 2-substituted benzimidazole derivatives, 5-nitro 2-substituted benzimidazole derivatives. Its treatment with p-hydroxyacetophenone afforded the corresponding p-acetyl substituted derivatives. The structure of the compounds had been established on the basis of IR, ^{1}H NMR and MS spectral data. The explorations of the biological properties of the compounds are in progress.

Keywords: O-phenylenediamine, 2-Butylbenzimidazole, Benzimidazole derivatives, Schiff Bases, Spectral Studies.

1. INTRODUCTION

Schiff bases are the compounds containing azimethine group (-HC=N-). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864. Now a day, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures.

Schiff bases are also condensation products of primary amines with carbonyl compounds and they were first reported by Schiff [1] in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R1, where R and R1 are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. These compounds are also knows as anils, imines or azomethines [2-8]. There are wide applications of Schiff bases and their metal chelates in biological systems [9,10] catalysis [11,12] dying processes [13,14] and analytical applications, the spectral studies of the Schiff bases containing a heterocyclic ring are comparatively minor [15-17]. A Schiff base behaves as a flexidentate ligand and commonly coordinates through the O atom of the deprotonated phenolic group and the N atom of azomethine group. Schiff base ligands have significant importance in chemistry; especially in the development of Schiff base complexes, because Schiff base ligands are potentially capable of forming stable complexes with metal ions [18]. Many Schiff base complexes show excellent catalytic activity in various reactions at high temperature (>100 °C) and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis, hence the need for a review article highlighting the catalytic activity of Schiff base complexes realized [19,20]. Today, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures. A Schiff base behaves as a flexidentate ligand and commonly coordinates through the O atom of the deprotonated phenolic group and the N atom of azomethine group. Schiff bases have been reported in their biological properties, such as, antibacterial, antifungal activities [21-24]. Their metal complexes have been widely studied because they have anticancer and herbicidal applications [25,26]. They serve as modals for biologically important species. O-phenylenediamine Schiff bases show clinical properties [27].

2. MATERIAL AND METHODS

2.1. Materials

All chemicals were used of A.R. grade (NaOH, O-phenylenediamine, Ethanol, Pentanoic acid), Melting points were taken in open capillaries and are uncorrected, all synthesis are carried out in the round bottom flask of Borosil.

Purity of compounds was monitored on silica gel 'G' coated TLC plates. IR spectra were recorded on Schimadzu FTIR-8400S Spectrometer in KBr, ^{1}HNMR spectra were taken in $CDCl_3$+$DMSOd_6$ on BRUKER AVANCE II 400 NMR Spectrometer using TMS as an internal standard and Mass spectra were recorded on a Joel SX-102 (EI/CI/FAB) mass spectrometer.

2.2. General method for preparation of Schiff bases

2.2.1. Synthesis of 4-(1H-benzo[d]imidazol-yl)benzamide:

A mixture of o-phenylenediamine (0.1mol) and p-amino benzoic acid (0.1mol) was heated on a water bath for 2 hr. it was cooled and 10% sodium hydroxide solution was added slowly with constant stirring until just alkaline. The crude product was filtered, washed with ice-cold water, decolorized and washed repeatedly and dried. The product was then recrystallized from ethanol. Yield: 70%; m.p. 108^{o}C. (Scheme 1)

IR (KBr, cm-1): 3170(N-H str), 1685(C=N str), 1585(aromatic str); ^{1}H-NMR: 5.0 (s, 1H, NH), 7.5 -7.9 (m, 4H, Ar-H), 7.50 (S, 1H, NH_2) 7.9-8.0 (m, 4H, Ar-H), m/z: 237.09 (100.0%), 238.09 (16.3%), 239.10 (1.1%).

2.2.2. Synthesis of 2-(4-Aminophenyl) benzimidazole:

A mixture of p-Amino benzoic acid (4.5g, 33mM) and o-Phenylenediamine (3.8g, 34mM) were stirred in a syrupy o-Phosphoric acid (45ml) at 200oC for 2 hours. The reaction mixture was cooled and poured on crushed ice. The bulky white precipitate obtained was stirred in cold water (400ml) and sodium hydroxide solution (5M) was added until the PH 7. The resulting solid was filtered and recrystallized from methanol; Yield: 51.43%; m.p. 246-248^{o}C. (Scheme 2)

IR (KBr) cm-1 3437.26 (N-H), 3360.11 (NH_2), 1498.74 (C=C), 1620.26 (C=N), 1180.4; ^{1}H-NMR: 5.0 (s, 1H, NH), 7.5 -7.9 (m, 4H, Ar-H), 6.27 (S, 1H, NH_2) 6.5-7.9 (m, 4H, Ar-H), m/z: 209.10 (100.0%), 210.10 (14.2%), 210.09 (1.1%), 211.10 (1.1%).

2.2.3. Synthesis of 2-Butylbenzimidazole:

O-Phenylenediamine 2.16 g [0.02 mol] and pentanoic acid 3.2 g [0.04 mol] were placed in round bottom flask and refluxed for 7 hours. The reaction mixture was cooled and basified (pH 7-8) with 20% sodium hydroxide solution with continuous stirring. The crude product was dissolved in 95% ethanol and digested with activated charcoal for 45 minutes. Boiling water was then added to the filtrate till slight turbidity appeared. The solution was made clear by addition of few drops of ethanol and kept for recrystallization. The product was obtained as white, needle shaped crystals; Yield: 71.43%; m.p. 244-245^{o}C. (Scheme 3)

IR: 3600-3200 (N-H stretch), 3100, 3050 (Aromatic C-H stretch), 2900, 2800 (Aliphatic C-H stretch), 1400 (C=C and C=N ring), 1240, 1220 (C – N), 880 (N-H). ^{1}H-NMR: 10.3 (s, 1H, NH), 7.5 -7.2 (m, 4H, Ar-H), 2.95 (t, 2H, CH_2, 1.84 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 0.88 (t, 3H, CH_3); m/z: 174.12 (100.0%), 175.12 (12.1%).

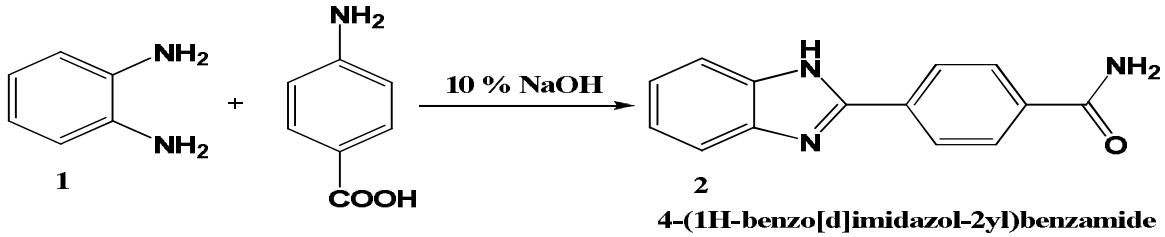
2.2.4. Synthesis of 2-methylbenzimidazole:

Heated together mixture of o-phenylenediamine dihydrochloride (0.03 mole), 20 mL of water, acetic acid (0.09 mole) under reflux for 45 minutes. Made the cooled reaction mixture distinctly basic by the gradual addition of the concentrated ammonia solution, the precipitated product was collected and recrystallized from 10% ethanol (scheme is shown in Fig. 1). A mixture of 5.43g (0.03 mol) of o-phenylenediamine dihydrochloride, 20 ml of water and 5.4g (0.09 mol) of acetic acid was refluxed for 45 minutes. Then the reaction mixture was poured over crushed ice with stirring.The cooled mixture was made basic by the gradual addition of concentrated ammonia solution. The precipitated product was then filtered and recrystallized from 10% aqueous 0ethanol, Yield: 50%, m.pt: 177-180^{o}C. (Scheme 4)

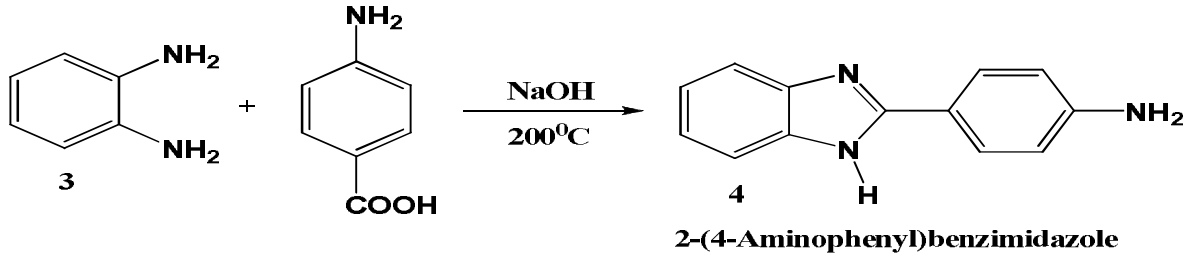
IR (KBr) 1cm: 3295.16(N-H), 1500.15(C=C), 1593.09(C=N), 752.19(CH), 1248.82(C-N), 1156.25(CH). ¹H NMR: 1.92 (t, 3H, J=7.0 Hz, -$COOCH_2CH_3$), 4.19 (q, 1H, J= 8.0 Hz, -CH_2CH_3), 2.64 (S, 1H, -CH_3), 7.35 – 7.69 (m, 4H, ArH), 3.67 (s, 2H, -NCH_2); m/z: 132.07 (100.0%), 133.07 (9.4%).

2.2.5. Synthesis of 2-benzylbenzimidazole:

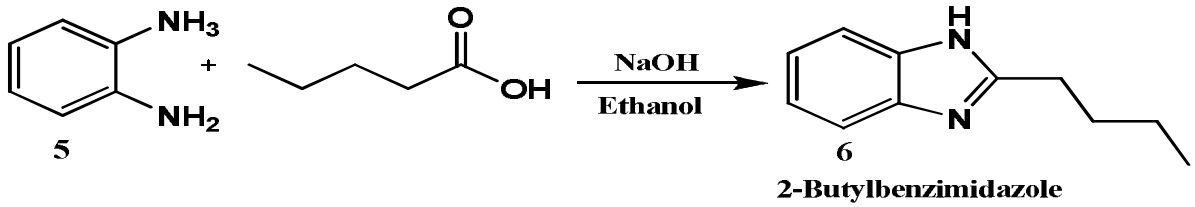
Heated together mixture of o-phenylenediamine dihydrochloride (0.03mole), 20 mL of water, phenylacetic acid (0.09 mole) under reflux for 45 minutes. Made the cooled reaction mixture distinctly basic by the gradual addition of the concentrated ammonia solution, the precipitated product was collected and recrystallised from 40% ethanol. A mixture of 5.43g (0.03 mol) of o-phenylenediamine dihydrochloride, 20 ml of water and 12.3g (0.09 mol) of phenyl acetic acid was refluxed for 45 minutes. Then the reaction mixture was poured over crushed ice with stirring. The cooled mixture was made basic by the gradual addition of concentrated ammonia solution. The precipitated product was then filtered and recrystallised from 40% 0aqueous ethanol, Yield: 48% m.p: 235-236 C. (Scheme 5)



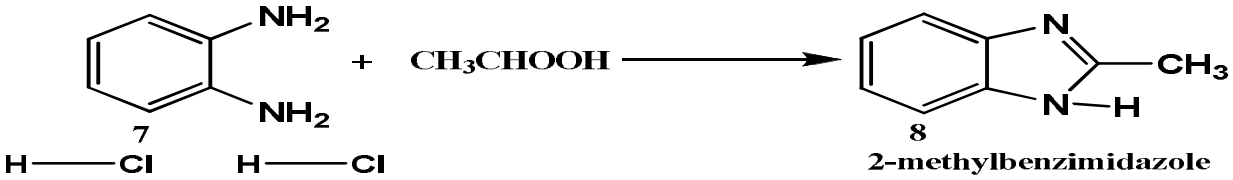
Scheme -1: Synthesis of 4-(1H-benzo[d]imidazol-2yl)benzamide



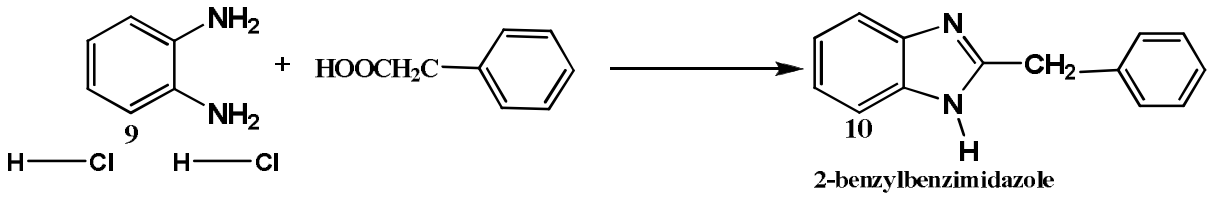
Scheme -2: Synthesis of 2-(4-Aminophenyl) benzimidazole



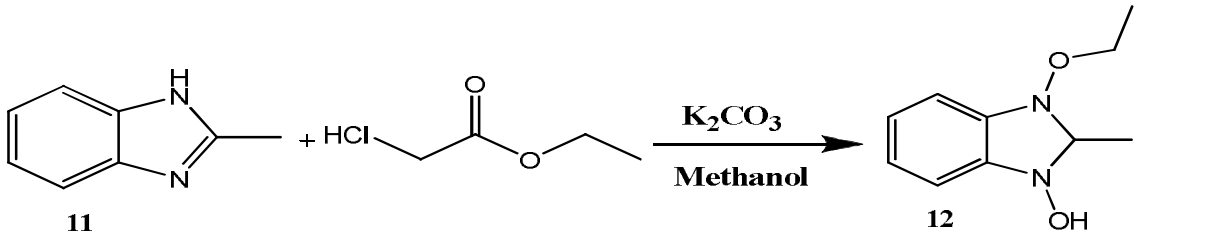
Scheme -3: Synthesis of 2-Butylbenzimidazole



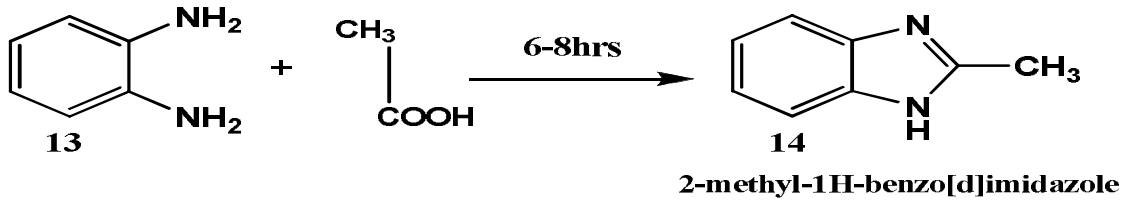
Scheme 4: Synthesis of 2-methylbenzimidazole



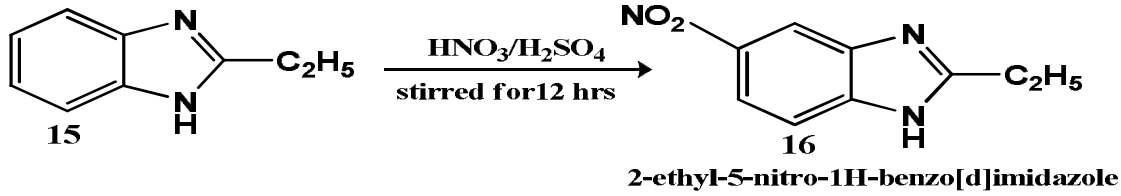
Scheme -5: Synthesis of 2-benzylbenzimidazole



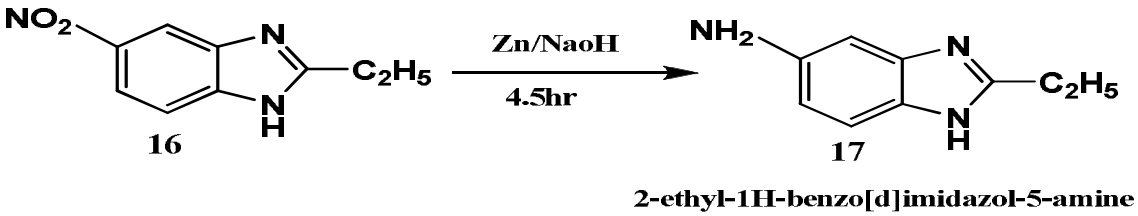
Scheme 6 Synthesis of Ethylacetale-2-methyl-benzimidazole



Scheme -7: Synthesis of 2-methyl-1H-benzo[d]imidazole derivatives



Scheme – 8: Synthesis of 2-ethyl-5-nitro-1H-benzo[d]imidazole derivatives



Scheme – 9: Synthesis of 2-ethyl-1H-benzo[d]imidazol-5-aminederivatives

IR (KBr) Cm: 3416.66 (N-H), 1486.05 (C=C), 1645.17 (C=N), 1185.18 (C-N), 857.30 (Ar-H), 2884.35 (CH). ^{1}H-NMR: 10.5 (s, 1H, NH), 7.9 - 8.2 (m, 4H, Ar-H), 2.83 (t, 2H, CH_2, 1.94 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 0.88 (t, 3H, CH_3); m/z: 208.10 (100.0%), 209.10 (15.9%), 210.11 (1.1%).

2.2.6. Synthesis of Ethylacetale-2-methyl-benzimidazole:

A mixture of 2-methyl-benzimidazole (0.30 mole, 39.60 g) and ethyl-chloroacetate (0.30 mole, 36.74 g) with K_2CO_3 (6.168 g) in methanol (250 ml) was kept overnight at room temperature. The reaction mixture was refluxed on a steam bath for about 3hr. It was cooled filtered and solvent was distilled off under reduced pressure and the solid thus obtained was passed through a column of silica gel using chloroform: methanol (5:5 v/v) mixture as eluant. The eluate (250 ml) was concentrated to give a product which was recrystallized with ethanol to furnish colorless needles of compound Yield: 83%, m.p. 94-96ºC. (Scheme 6)

IR (KBr) Cm: 2866, 1470, 1270 (-NCH_2), 2912, 2875, 1427, 710 (-CH_2 and -CH_3), 1720 (>C=O of ester), 1050 (C-O-C), 3012, 2842, 1598, 1392, 744 (benzimidazole ring), 2816 (-CH_3) ; ^{1}HNMR : 1.90 (t, 3H, J=7.0 Hz, -$COOCH_2CH_3$), 4.19 (q, 2H, J= 7.0 Hz, -CH_2CH_3), 2.64 (s,1H, -CH_3), 7.30 – 7.65 (m, 4H, ArH), 3.63 (s, 2H, -NCH_2); m/z: 194.11 (100.0%), 195.11 (11.1%), 196.11 (1.0%).

Table -1: Physical data of schiff bases

Schiff Bases	Molecular Formula	Melting Point °C	Yield %	Elemental Analysis			
				C%	H%	N%	O%
4-(1H-benzo[d]imidazol-2yl)benzamide	$C_{14}H_{11}N_3O$	108-109	70	70.87	4.67	17.71	6.74
2-(4-Aminophenyl) benzimidazole	$C_{13}H_{11}N_3$	246-248	51	74.62	5.3	20.08	-
2-Butylbenzimidazole	$C_{11}H_{14}N_2$	177-180	50	75.82	8.1	16.08	-
2-methylbenzimidazole	$C_8H_8N_2$	235-236	48	72.7	6.1	21.2	-
2-benzylbenzimidazole	$C_{14}H_{12}N_2$	94-96	83	80.74	5.81	13.45	-
Ethylacetate-2-methyl-benzimidazole	$C_{10}H_{14}N_2O_2$	210-212	78	61.84	7.27	14.42	16.47
2-methyl-1H-benzo[d]imidazole	$C_8H_8N_2$	200-201	86	72.7	6.1	21.2	-
2-ethyl-5-nitro-1H-benzo[d]imidazole	$C_9H_9N_3O_2$	150-152	75	56.54	4.74	21.98	16.74
2-ethyl-1H-benzo[d]imidazol-5-amine	$C_9H_{11}N_3$	167-169	84	67.06	6.88	26.07	-

2.2.7. Synthesis of 2-methyl-1H-benzo[d]imidazole derivatives:

O-phenylenediamine (0.25 mol) and appropriate carboxylic acid (0.34 mol) was heated on a water bath at 100^0C for 6-8 h. The completion of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled and basified to a pH of 7-8 by using 10% sodium hydroxide solution. The crude benzimidazole was filtered at the pump, washed with ice cold water. The crude product was dissolved in 400 ml of boiling water and 2 g of decolorizing carbon was added and digested for 15 min. The solution was filtered while hot, cooled the filtrate to about 10°C. The pure product was filtered, washed with 25 ml of cold water and dried at 100°C, Yield: 78%, m.p 210-212°C. (Scheme 7).

IR (KBr) Cm: 2546.67 (N-H), 1476.02 (C=C), 1445.27 (C=N), 1175.28 (C-N), 847.20 (Ar-H), 2984.32 (CH). ^{1}H-NMR: 10.4 (s, 1H, NH), 7.6 - 8.1 (m, 4H, Ar-H), 2.84 (t, 2H, CH_2, 1.96 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 0.89 (t, 3H, CH_3); m/z: 132.07 (100.0%), 133.07 (9.4%).

2.2.8. Synthesis of 2-ethyl-5-nitro-1H-benzo[d]imidazole derivatives:

Concentrated HNO3 (7.5 ml) was placed in three necked round bottom flask fitted with a mechanical stirrer. The flask was immersed in ice cold water and added slowly conc. H_2SO_4 (7.5 ml) down the condenser with slow stirring. After the addition, 2-substituted benzimidazoles (0.028 mol) were added in a portion over a period of 1 h at such a rate that the temperature did not exceed 35ºC. After continuous stirring for 12 h, the reaction mixture was poured very slowly over crushed ice with vigorous stirring. The formed product was filtered, washed with cold water and recrystallized from ethanol, Yield: 75%, m.p 200-20. (Scheme 8)

IR (KBr) Cm: 2546.67 (N-H), 1476.02 (C=C), 1445.27 (C=N), 1175.28 (C-N), 847.20 (Ar-H), 2984.32 (CH). ^{1}H-NMR: 10.4 (s, 1H, NH), 7.6 - 8.1 (m, 4H, Ar-H), 5.04 (S, 2H, NH_2) 1.96 (m, 2H, CH_2), 1°C; m/z: 191.07 (100.0%), 192.07 (10.9%).

2.2.9. Synthesis of 2-ethyl-1H-benzo[d]imidazol-5-aminederivatives:

A solution of 0.5 g of 5-nitro, 2-substituted benzimidazole in 15 ml of rectified sprit was taken in round bottom flask. To this, 5 ml of 20 % sodium hydroxide and 2.5 g of zinc dust powder was added. The reaction mixture was refluxed until color of the solution changed from deep red to colorless (about 4.5 h), the hot mixture was filtered. The zinc residue was returned to the flask and extracted with 10 ml of hot rectified sprit for two times. The extracts were combined and the solvent was removed under vacuum, yielded the brown solid and recrystallized from methanol, Yield: 84%, m.p 167-169°C. (Scheme 9).

IR (KBr) Cm: 2546.67 (N-H), 1476.02 (C=C), 1445.27 (C=N), 1175.28 (C-N), 847.20 (Ar-H), 2984.32(CH). ^{1}H-NMR: 10.4 (s, 1H, NH), 7.6 - 8.1 (m, 4H, Ar-H), 5.04 (S, 2H, NH_2) 1.96 (m, 2H, CH_2), m/z: 161.10 (100.0%), 162.10 (9.9%), 162.09 (1.1%).

3. RESULTS AND DISCUSSION

The newly synthesized shiff base stable at room temperature. The shiff bases are soluble in common Organic solvents, such as ethanol, methanol, and chloroform but partially soluble in hexane. The shiff base compounds were relatively well soluble in DMF and DMSO. The synthesized compounds were characterized by elemental analysis, spectra data. The biological properties of the compounds are in progress.

4. CONCLUSION

In conclusion, various Schiff bases was synthesized which show failure synthesis from salicylaldehyde or benzaldehyde with some amino acids, by the usual classical synthetic method [28], this is because Schiff base have reversible nature of synthesized Schiff bases reaction. Some workers had previously used a several catalysts [28-30] to overcome on such problem, but now there is way to use sodium hydroxide catalyst for the first time during synthesis of Schiff bases, which is highly accepted as a catalyst and kinetic [31] point of view. All the synthesized compounds **(2-17)** were purified by successive recrystallization using ethanol. The purity of the synthesized compounds was checked by performing TLC. The structures of the synthesized compounds were determined on the basis of their FTIR and 1HNMR data.

Acknowledgement

The authors are thankful to SAIF, Punjab University Chandigarh for providing spectral and analytical data of the compounds. We are also thankful to Department of Biotechnology of Banasthali University for providing help in carrying out the antimicrobial screening.

5. REFERENCES

1. Cimerman Z. Miljanic Z and Galic N. Microwave assisted synthesis of some Schiff bases on NaY zeolite: A green chemical approach. **Croatica Chemica Acta**. 2000; 73: 81- 95.

2. Singh P. Goel RL and Singh BP. Synthesis, Characterization and Biological Activity of Schiff Bases. **J. Indian Chem. Soc**. 1975; 52: 958-959.

3. Perry BF. Beezer AE. Miles RJ. Smith BW. Miller J and Nascimento M G. Microbois, Synthesis, Characterisation and Antimicrobial Studies of Zn(II), Ni(II) and Cu(II) Complexes of a Schiff base derived from o-Vanillin and N-Allyl Thiourea. **International Journal of Chem Tech Research**. 1988; 45: 181.

4. Elmali A. Kabak M and Elerman Y. Synthesis and Antimicrobial activities of Schiff Bases. **J. Mol. Struct**. 2000; 477: 151.

5. Patel PR. Thaker BT and Zele S. Synthesis and characterisation of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff base complexes derived from o-phenylenediamine and acetoacetanilide. **Indian Acad. Sci. (Chem. Sci.)**. 2001; 113: 183–189.

6. Valcarcel M and Laque de Castro MD. Flow-Throgh Biochemical Sensors. **Elsevier**. 1994; Amsterdam.

7. Spichiger-Keller U. Chemical Sesors and Biosensors for Medical and Biological Applications. **Wiley-VCH**. 1998; Weinheim.

8. Lawrence JF and Frei RW. Chemical Derivatization in Chromatography. **Elsevier**. 1976; Amsterdam.

9. Raafat Issa M. Abdalla Khedr M and Rizk H. 1H NMR, IR and UV/VIS Spectroscopic Studies of Some Schiff Bases Derived From 2-Aminobenzothiazole and 2-Amino-3-hydroxypyridine. **Journal of the Chinese Chemical Society**. 2008; 55: 875-884.

10. Maurer RI. Blover PI. Dilworth JR. Reynoh C A. FT-IR & UV/Vis Spectroscopic Study of Some Schiff bases Derived from amino Benzoic acid and Bromo benzaldehyde. **J. Med. Chem**. 2002; 45: 1420.

11. Selbin J. Oxovanadium (IV) complexes. **Coord. Chem. Rev**. 1966; 1: 293-314.

12. Vasin SV. Cetralla J. Genogel RA. FT-IR & UV/Vis Spectroscopic Study of Some Schiff bases Derived from amino Benzoic acid and Bromo benzaldehyde. **J. Inorg. Chem**.1990; 29: 885.

13. Maki M. Hashimato H. **Bull. Chem. Soc**. 1952; 25: 411.

14. Papie S. Kaprivanae N. Grabarie Z. Paracosterman D. Dyes Pigments: Synthesis Spectral Characterization and Antimicrobial activitiy of some Schiff Bases of 4-Cholro-2-Aminophenol. **Bull. Chem. Soc**. 1994; 25: 229.

15. Khedr AM. Gaber M. Issa RM. Erten H. Dyes Pigments 2005; 67: 117.

16. Cimerman Z. Miljanić S. Antolić J. Fluorescence Characteristics of Schiff. Bases Derived from Amino- and Amino alkyl pyridines. **Spectrosc. Lett.** 1999; 32: 181-196.

17. Issa R M. Khedr A M. and Rizk H F. UV-vis, IR and 1H NMR Spectroscopic Studies of Some Schiff Bases Derivatives of 4-aminoantipyrine. **Spectrochimica Acta Part A.** 2005; 62: 621-629.

18. Souza P. Garcia-Vazquez JA and Masaguer JR. polydentate Schiff bases in coordination

chemistry. **Transition Met. Chem**. 1985; 10: 410.

19. Naeimi H. Safari J. and Heidarnezhad A. Dyes Pigments. 2007; 73: 251.

20. Lippard SJ and Berg JM. Principles of bioinorganic chemistry. University Science Books Mill Valley. California, 1994.

21. Williams DR. Metals, ligands, and cancer. **Chem. Rev**. 1972; 72: 1972.

22. Campos A. Anacona JR and Campos-Vallette M M. **Mian group Metal chem**. 1999; 22: 283.

23. Nair R. Shah A. Baluja S. and Chanda S. Synthesis and antibacterial activity of some Schiff bases Complexes. **J. Serb. Chem. Soc**. 2006; 71: 733–744.

24. Sari N. Arslan S. Logoglu E and Sakiyan I. Antibacterial activities of some Amino acid Schiff bases. **G. U. J. Sci**. 2003; 16: 283.

25. Muhammad AA. Abdul W. Mahmood K. Mohd. J M and Ismail Y. Spectral Investigation of the Activities of Amino Substituted Bases. **Oriental Journal of Chemistry**. 2011; 27: 363-372.

26. Cozzi PG. Metal–salen Schiff base complexes in catalysis: Practical aspects. **Chem. Soc. Rev**. 2004; 33: 410.

27. Chandra S and Sangeetika J. EPR electronic spectral studies on copper (II) complexes of some N-O donor ligands. **J. Indian Chem. Soc**. 2004; 81: 203-206.

28. Mahindra AM and Fisher JM. Rabinovitz. Textbook of Practical Organic Chemistry. **Nature** 1983; 303: 64.

29. Patai Ed S. The chemistry of carbon-nitrogen double bond. **John Wiley and Sons**. New York. 1970; 61-146.

30. Billman J H and Tai K M. Synthesis of Schiff Bases Derived From Benzaldehyde and Salicylaldehyde With Some Amino Acids by a New Develop Method. **J. Org. Chem**. 1958; 23: 535.

31. Curtin D Y and Hausser J W. Acid-catalysed isomerisation of imines. **J. Amer. Chem. Soc**. 1961; 83: 3474.