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Editorial :

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Evaluation of Soil Nutrients under Maize Intercropping System Involving Cowpea *(Vigna unguiculata)*

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ABSTRACT

A field experiment was conducted at the Central Agricultural Station, Kwadaso, Ghana to examine soil fertility under different maize based cropping systems. Fertilizer application of NPK 90 - 60 - 60 kg/ha was compared with intercropping maize with cowpea and sole maize. The results showed no significant effects of intercropping on soil fertility in the short term. Though differences in nitrogen level among the cropping systems were insignificant, the level recorded under each system was high.

Keywords: Intercropping, Nutrient Management, Soil Fertility Maintenance, Monocropping

I. INTRODUCTION

The agriculture of Ghana is predominantly smallholder subsistence farming under rain-fed conditions. Maize has recently come up as the primary food crop mostly grown by small holder farmers in various cropping systems. The maize based cropping systems are mostly sole crop, intercrop between cowpea and cassava. Maize cowpea intercrop is done by farmers to restore soil fertility as well as deriving additional income, cassava is considered by most farmers as a food security crop in case of component crop failure.

Intercropping refers to the growing of two or more crop species simultaneously on the same field during a growing season (Ofori and Stern, 1987). It often results in a more efficient utilization of resources and causes more stable yields. It is also a method to reduce problems with weeds, plant pathogens and nitrogen losses (Dahlmann and Von Fragstein, 2006). In intercropping system, all the environmental resources are utilized to maximize crop production per unit area per unit time (Woolley and Davis, 1991). Vandermeer, (1989) and Zhang *et al.* (2003) claim that competition might be possible in intercropping systems and therefore calls for the need to select compatible crops (Seran and Brintha, 2009) for proper utilization of soil fertility. Ghosh et al. (2007) reported that inclusion of legumes in cereal cropping systems increases soil fertility and consequently the productivity of succeeding cereal crops. Intercropping of cereals with legumes has been popular in the tropics (Hauggaard-Nielsen et al., 2001; Tsubo *et al*., 2005) and rain-fed areas of the world (Agegnehu *et al*., 2006; Dhima *et al*., 2007) due to its advantages for soil conservation (Anil *et al*., 1998), weed control (Poggio, 2005; Banik *et al*., 2006), lodging resistance (Anil *et al*., 1998) and yield increment (Anil *et al*., 1998; Chen *et al*., 2004). Intercropped legumes benefit the associated cereal crop like maize by transferring part of fixed N to the maize because of the less N requirement of the legumes (Singh, 1983; Lupwayi and Kennedy, 2007). Legumes also provide a good canopy cover in the early stages to control soil loss through erosion especially on sloppy lands and also to control weeds (Khola *et al*., 1999).

However, Tulu (2002) indicated that different crops remove different amounts of mineral nutrients from the

soil. In this regard, the practices of intercropping deplete the soil of essential plant nutrients in varying quantities depending on the nutrient demand of crops (Logah, 2009). If the nutrient removal rate is not balanced by soil amendments aimed at nutrient management and soil fertility maintenance, the soil gets poor and productivity is drastically reduced. This is the normal trend in Ghana (Logah, 2009). Greater nutrient uptake by intercropping has been reported by several workers (Adu-Gyamfi *et al*., 1997; Sakala, 1998).

Intercropping of maize and cowpeas (*Vigna unguiculata*) is especially beneficial on nitrogen poor soils (Vesterager *et al*., 2008). As cowpeas obtain the majority of their nitrogen from the atmosphere, they do not compete with maize for soil nitrogen (Mongi et al., 1976). The addition of cowpea to the maize field provides an important protein supply for human and livestock consumption, improves soil fertility and structure, suppresses weeds, and insures against total crop failure (Mongi *et al*., 1976). Maize-cowpea intercropping increases the amount of soil nitrogen, phosphorus and potassium compared to monocrop of maize (Dahmardeh et al., 2010).

The objective of this study was to assess soil organic carbon (C), total nitrogen (N), available phosphorous and exchangeable potassium of soil under maize-cowpea (*Vigna unguiculata*) intercropping systems.

II. METHODS AND MATERIAL

A. Location and Climate

This study was conducted at the Central Agricultural Station of Soil Research Institute Kwadaso, Ghana.

The study site is located within the Semi-Deciduous Rainforest zone of Ghana.

The area enjoys a bimodal rainfall pattern, the minor season (August to September) and the major season (March to July). The major season normally begins in March; reaches a peak in July and drops sharply in August whilst the minor season starts in September with the lowest occurring in late November. Thereafter, there is a long dry period from December to February during which negligible amounts of rain normally (below 10mm) are received (Sadick et al., 2015).

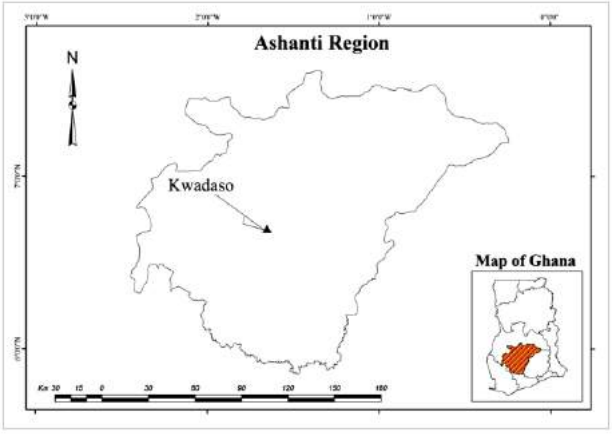

Figure 1. Location of the Study Area (Sadick et al., 2015).

Mean monthly temperatures remain high throughout the year only falling around 24o C in August. February and March are the hottest (nearly 28^{o}C) recorded months. Absolute minimum temperatures of around 20^{o}C are usually recorded in December and January with absolute maximum temperature of about 33^{o}C occurring in February and March(Sadick et al., 2015).

The soil falls within the Kumasi Series and it was a well-drained loamy sand textured soil, easy to cultivate.

B. Treatments / Experimental Design

The treatments used were maize, which was the main crop, and selected leguminous crop which was cowpea. The treatment combinations were maize only (T0) and maize + cowpea (T1). The crops cultivars used were, Dorke SR (maize) and Soronko (cowpea). These were obtained from the Crop Research Institute (CRI) at Fumesua near Kumasi. These varieties are early maturing (90-95 days). The experiment was a randomized complete block design (RCBD) with three replications.

C. Land Preparation

The vegetation on the land was slashed manually and the land later ploughed and harrowed to a fine tilth. The field was then lined and pegged to demarcate it into blocks and plots. The total field area was of dimension 4.5 m x 7 m. The maize was planted intercropped with cowpea. The field consisted of 2 blocks with 2 plots each. The plot area measured 2 m x 3 m. Spacing between blocks was 1 m and 0.5 m between plots as shown in Figure 2

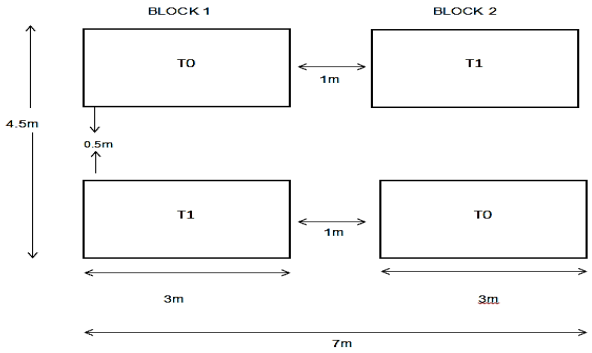

Figure 2. Layout of plot showing treatments allocation (not drawn to scale). T0: maize only and T1: maize + cowpea

D. Initial Soil Sampling

Soils were randomly collected from the field at a 0-15 cm depth. Twelve samples were obtained with an auger from the field and bulked to obtain the final sample. The sample were analysed at the Soil Research Institute Laboratory. Parameters determined were organic carbon, total nitrogen, available phosphorus, exchangeable calcium, magnesium, potassium and sodium, soil pH and soil texture.

E. Planting and Thinning

The test crop was maize sown 2 seeds per hill at a spacing of 90 cm × 40 cm. Cowpea was sown 2 seeds per hill at 20 cm between maize rows.

F. Fertilizer Application

Figure 3. Field experiment showing cowpea intercropped with maize at the study area

Fertilizer application was done in two splits. By side placement, 60-60-60 kg/ha NPK 15-15-15 was applied three weeks after sowing and 30 kg/ha sulphate of ammonia was applied seven weeks after sowing.

G. Weed Control

Weeding was done manually with a hoe and a cutlass just before amendment and two weeks afterwards. And watering was done 40 days after planting (DAP) with a watering can when the natural rains stopped for a while. Pest and disease incidence were not much encountered during the growing stage of the crop. Their incidence was only observed during the tasselling stage. Pests and animal encountered were birds, stem borers, corn ear worms and cotton stainers. Pesticide (25 Emulsifiable Concentrate Lambda) was used to control pests.

H. Final Soil Sampling

Final soil sampling was done two weeks after application of sulphate of ammonia. Soil samples were taken at the depth of 0 - 15 cm from the bases of five plants selected randomly from each plot. These were bulked to get one sample for each plot. For the intercrop plots, samples were taken between the maize and legumes rows. In total, twelve samples were taken. Soil parameters determined were organic carbon, total nitrogen, and available phosphorus, exchangeable cations which are calcium, magnesium, potassium and sodium, soil pH and soil texture.

I. Determination of Physico-chemical Properties of the Soil

The physico-chemical properties of the soil samples were determined using routine methods as described by Allison (1960) and Ibitoye (2006). The physiochemical parameters used for this study were pH, organic carbon, exchangeable cations, total nitrogen, available phosphorus and particle size distribution.

III. RESULTS AND DISCUSSION

A. Initial Soil Properties

Initial soil analysis was carried out to assess the soil fertility status at the study area before the conduct of the experiment. The results of the initial soil analysis are presented in Table 1 below.

Soil organic carbon and total nitrogen contents were 1.42 % and 0.10 % respectively. Available phosphorus recorded was < 5 mg/kg soil whilst soil exchangeable Ca and Mg were < 3 cmol/kg soil. The soil was moderately acidic with a pH value of 5.63. The results for particle size distribution indicated that the soil of the study site was of the textural class - loamy sand.

The initial soil organic carbon content was low. According to Metson (1961), a productive soil should have an organic carbon content of 2.3%. Total nitrogen was low according to the rating by Bruce and Rayment (1982). The low organic carbon and total nitrogen was by virtue of high temperatures resulting in rapid organic carbon decomposition coupled with a generally low input of organic material at the study area. Organic matter is closely associated with the nutrient status of soils because it contributes much to the soil CEC (Magdoff et al., 1985). It has been advocated that soil fertility replenishment in Africa should aim at an integrated nutrient management (Quansah, 1996; Swift, 1997; Sanchez et al., 1997; Quansah et al., 1997).
According to the ratings of Metson (1961), exchangeable bases recorded in this study were generally low. The low exchangeable bases were due to the organic carbon content of the soil. Generally, the fertility status of the soil at the study site before the experiment was low.

B. Soil Properties under the Cropping System

Nitrogen and phosphorus contents were high (Table 2) and showed an increment from the initial values. This was as a result of the NPK fertilizer applied to the respective plots. High P could also be attributed to the very slow diffusion and immobilization of the applied P (Prasad and Power, 1997). Logah (2009) recorded high phosphorus levels under cropping systems following organic and inorganic soil amendments.

Intercropping of legumes and cereals is an old practice in tropical agriculture. Snaydon and Harris (1979) found legume-cereal as the most popular intercropping system in the tropics and Kamanga et al. (2010) reported that maize-legume intercropping resulted in high productivity. Intercropping maize with legume is able to reduce the amount of nutrients taken from the soil as compared to a maize monocrop (Adu-Gyamfi et al., 2007). In the absence of nitrogen fertilizer, intercropped legumes will fix nitrogen from the atmosphere and not compete with maize for nitrogen resources (Adu-Gyamfi et al., 2007). The mixture of nitrogen fixing crop and non-fixing crop gives greater productivity than monocropping (Seran and Brintha, 2009). Banik and Sharma (2009) reported that cereal-legume intercropping systems were superior to monocropping.

TABLE I. INITIAL SOIL PROPERTIES AT THE STUDY SITE

Soil Properties	Value
Organic Carbon (%)	1.42
Total Nitrogen (%)	0.10
Available Phosphorus (mg/kg soil)	4.95
Exchangeable calcium (cmol/kg soil)	2.20
Exchangeable magnesium (cmol/kg soil)	1.40
Exchangeable potassium (cmol/kg soil)	0.13
Exchangeable sodium (cmol/kg soil)	0.17
Soil pH	5.63
Soil texture	Loamy sand

TABLE II. SOIL PROPERTIES OF THE STUDY AREA AFTER INTERCROPPING AND FERTILIZER APPLICATION

Soil nutrient	Maize+Cowpea	Sole Maize
Organic carbon (%)	1.75	1.86
Total Nitrogen (%)	0.32	0.30
Available Phosphorus (mg/kg)	31.00	20.00
Calcium (cmol/kg soil)	5.78	5.52
Magnesium (cmol/kg soil)	2.68	3.16
Potassium (cmol/kg soil)	0.66	0.63
Sodium (cmol/kg soil)	0.14	0.16

IV.CONCLUSION

The main purpose of this study was to evaluate soil properties under various maize based intercropping systems. Generally, the intercropping systems had no significant effects on soil fertility in the short term. Though differences in nitrogen level among the cropping systems were insignificant, the level recorded under each system was high.

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Synthesis and Characterizations of Ethyl (2*z*) - 2 - (aryl) - 5 - (4-methoxyphenyl)- 7 -methyl - 3 - oxo-2, 3, 8, 8a-tetrahydro-5*h*- [1,3] thiozolo [3,2-*a*] pyrimidine-6-carboxylate as Biological Active Agents

J. S. Makwana, Dr. B. B. Baldaniya*

Chemistry Department, M G Science Institute, Navarangpura, Ahmedabad, Gujarat, India

ABSTRACT

Pyrimidine plays a significant role among other heterocycles. Literature survey reveals that partially reduced pyridine and Pyrimidine derivatives are known to have antihypertensive property. Pyrimidine nucleus was synthesized by Biginelli reaction. The purpose of this study was to synthesize several title compounds (2a-2k) evaluate them for their antibacterial activity. The structures of all title compounds have been confirmed on the basis of their analytical, IR spectral data. The title compounds have been tested for antibacterial activities against different strains of bacteria.

Keywords : Thiozolo Pyrimidine, Antibacterial Activity, Biginelli Reaction

I. INTRODUCTION

Medicinal chemistry is introduced as principles of chemistry and biology. It is also give knowledge which leads to the introduction of new therapeutic agents. Pyrimidines are those molecules that make our life possible being the building blocks of DNA and RNA. Also there are some thiouracil derivatives and compounds, which produce adverse reaction in susceptible patients are being widely used[1]. There are many other vital groups of pyrimidines with medicinal uses[11].

In the past decades, the pyrimidines have attracted increasing interest in the realms of natural organic chemistry because of their diverse therapeutic and pharmacological properties. These non-planer heterocyclic compounds have emerged as the integral backbones of calcium channel modulators, antihypertensive agents, α_{1a}- adrenergic receptor antagonists, neuropeptide Y (NPY) antagonist, hepatitis B virus replication inhibitors, several marine derived natural products such as Crambine, Betzelladine β (potent hivgp-120 CD_4 inhibitors)[11]. Ptilomycalin alkaloids have been reported to contain dhpms and thpms moiety[12].

Several analogs of pyrimidines have been used with the synthesis and functioning of nucleic acids e.g. Fluorouracil, which is used in cancer treatment, cancer antibiotic and cancer drugs[9-10]. One such compound is Monastrol, which has been shown to be a cell-permeable molecule that blocks a normal bipolar spindle assembly in mammalian cells and, therefore, causes cell cycle arrest. Research in this field is in progress for the development of Monastrol as an anti-cancer[15] drug.

II. METHODS AND MATERIAL

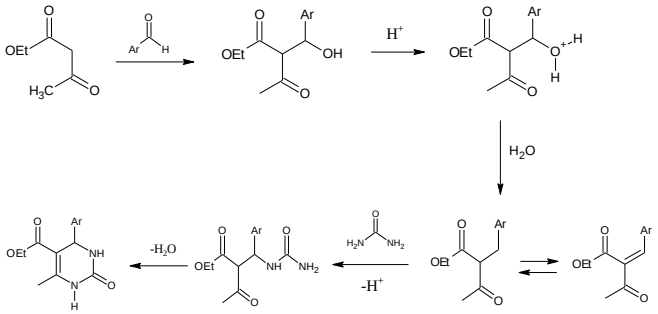
1. Beginelli Reaction

A simple and direct producing compound method, first reported by Biginelli in 1893, involves a three Component, one-pot condensation of an aldehyde, a β–ketoester and urea or thiourea Under strongly acidic condition. This has lead to the development of multi-step Strategies that produce overall higher yield, but lack of the simplicity of the Biginelli synthesis. As a result, many improved procedures for the preparation of given product. The **Biginelli reaction** is a reaction that creates 3,4-dihydropyrimidin-2(1*H*)-ones[2-3-4-5], an aryl aldehyde ,

and urea or thiourea . Its name was coming from Italian chemist Pietro Biginelli.

Reaction Mechanism :

The reaction mechanism of the Biginelli reaction is a series of bimolecular reactions and compounds[6]. The aldol condensation of ethylacetoacetate[13-14] and the aryl aldehyde. The nucleophilic addition of urea. It gives the intermediate, which immediately dehydrates to give the desired product[7-8].

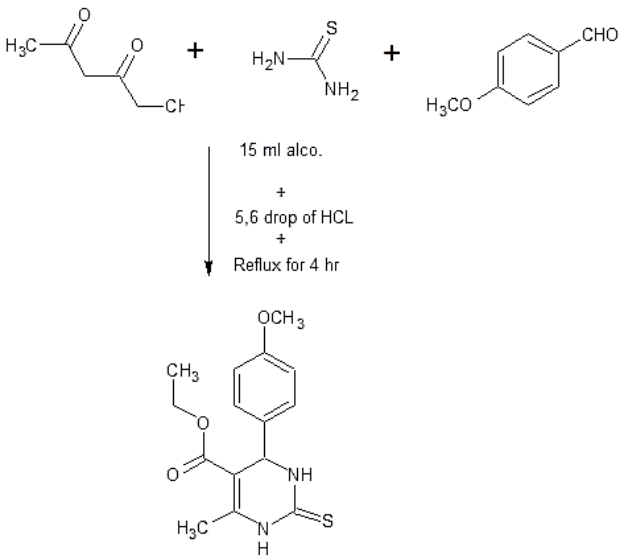


This mechanism is superseded by one by Kappe in 1997

Section – 1:

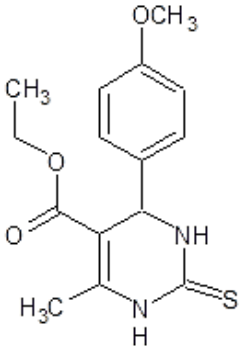
Preparations of ethyl (2*Z*) – 2 - (Aryl) – 5 - (4-methoxyphenyl) – 7 – methyl – 3 – oxo -2, 3, 8, 8a-tetrahydro-5*H* - [1,3] thiazolo [3, 2-*a*]pyrimidine-6-carboxylate.

Reaction 1:

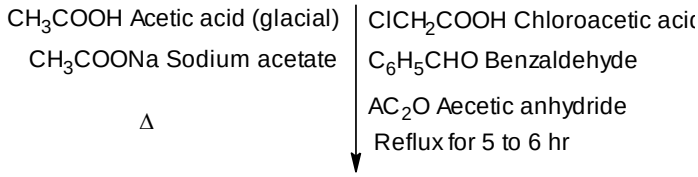


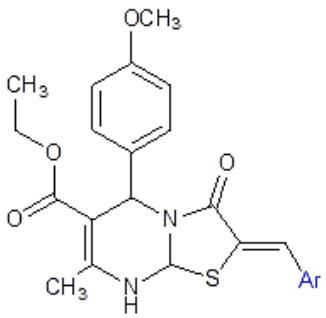
Ethyl 4-(4-methoxyphenyl)-6 methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

Reaction 2:



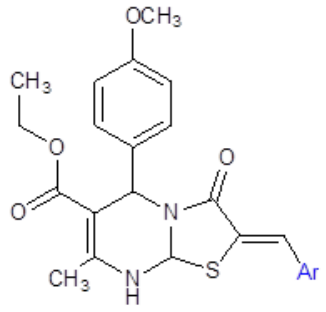
Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate





Ethyl (2*Z*)-2-(Aryl)-5-(4-methoxyphenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]thiozolo[3,2-*a*]pyrimidine-6-carboxylate

Physical constants of ethyl (2*Z*) – 2 - (Aryl) – 5 - (4-methoxyphenyl) -7- methyl – 3 - oxo-2, 3, 8, 8a-tetrahydro-5*H*-[1,3] thiozolo [3,2-*a*]pyrimidine-6-carboxylate.



Sr No.	-Ar	MOLECULAR FORMULA	M. P. ^{O}C	YIELD (%)	% OF CARBON FOUND	REQD.	% OF NITROGEN FOUND	REQD.	MOLECULAR WEIGHT
2a	$-C_6H_5$	$C_{24}H_{24}N_2O_4S$	237^0C	56	66.00	66.03	6.39	6.42	436.52
2b	$-OCH_3-C_6H_4$	$C_{25}H_{26}N_2O_5S$	210^0C	59	64.34	64.36	5.54	6.00	466.54
2c	$-2,4-(CL)_2-C_6H_3$	$C_{24}H_{22}Cl_2N_2O_4S$	217^0C	53	57.00	57.03	5.50	5.54	505.41
2d	$-4-CH_3-C_6H_4$	$C_{25}H_{26}N_2O_4S$	138^0C	68	66.59	66.64	6.15	6.22	450.54
2e	$-4-F-C_6H_4$	$C_{24}H_{23}FN_2O_4S$	192^0C	61	63.38	63.42	6.10	6.16	454.51
2f	$-4-Br-C_6H_4$	$C_{24}h_{23}brn_2o_4s$	225^0C	64	55.90	55.93	5.40	5.44	515.41
2g	$-4-Cl-C_6H_4$	$C_{24}h_{23}cln_2o_4s$	219^0C	70	61.20	61.21	5.90	5.95	470.96
2h	$-3-OH-C_6H_4$	$C_{24}H_{24}N_2O_5S$	267^0C	53	63.68	63.70	6.14	6.19	452.52
2i	$-4-OH-C_6H_4$	$C_{24}H_{24}N_2O_5S$	186^0C	64	63.69	63.70	6.14	6.19	452.52
2j	$-3-OCH_3-4-OH-C_6H_3$	$C_{25}H_{26}N_2O_6S$	249^0C	50	62.20	62.23	5.79	5.81	482.54
2k	$-2-NO_2-C_6H_4$	$C_{24}H_{23}N_3O_6S$	240^0C	52	59.82	59.86	8.70	8.73	481.52

Preparation of ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

A mixture of Ethyl aceto acetate (0.01 mole), benzaldehyde (0.01 mole) and thiourea (0.01 mole) in ethanol (20 ml) was refluxed for 6 h. The reaction mixture was poured in crushed ice and product was isolated and re-crystallized from ethanol: DMF. Yield 68% The progress of the reaction and the purity of compounds was routinely checked on TLC aluminum sheet silica gel 60 F_{245} (E.Merck) using benzene-methanol (4.5:0.5 v/v) or benzene-ccl_4–methanol (2.5:2.0:0.5 v/v) as irrigate and was developed in an iodine chamber.

Preparation of ethyl (2*Z*) – 2 - (Aryl) – 5 - (4-methoxyphenyl) – 7 – methyl – 3 - oxo-2, 3, 8, 8a-tetrahydro - 5*H* - [1,3] thiozolo [3,2-*a*] pyrimidine-6-carboxylate:

A mixture of ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(0.01 mole), benzaldehyde (0.01 mole), chloroaceticacid, sodium acetate (0.01 mole), acetic anhydride (0.01 mole) in acetic acid (20 ml) was refluxed for 5 to 6 hr. The reaction mixture was poured in crushed ice and product was isolated and re-crystallized from ethanol: DMF m.p 170^0C Yield 58%.

Table 2 : Antibacterial and Antifungal Activities

SR NO.	Minimal bactericidal concentration (MBC) in µg/ml				Minimal fungicidal concentration (MFC) in µg/ml		
	E.coli	*P.aeruginosa*	*S.aureus*	*S.pyogenus*	*C.albicans*	*A.nigar*	*A.clavatus*
	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC
	- 443	-1688	-96	- 442	-227	-282	-1323
2a	500	1000	500	500	>1000	>1000	>1000
2b	500	500	1000	1000	1000	1000	1000
2c	200	500	1000	1000	1000	1000	1000
2d	100	500	500	500	500	500	500
2e	250	1000	500	500	500	500	200
2f	100	100	1000	500	1000	1000	1000
2g	500	500	1000	500	>1000	>1000	>1000
2h	100	200	1000	1000	1000	1000	1000
2i	500	500	500	1000	>1000	>1000	>1000
2j	100	100	1000	500	1000	500	500
2k	200	200	1000	1000	500	500	500

Antibacterial Activity

Antibacterial activity is taken by broth dilution method. Concentrations of 1000,500, 200, 100, 50, 25, 12.5 µg/ml respectively in shown table. The standard drug used in the present study is "Gentamycin" for evaluating antibacterial activity which showed 0.25, 0.05, 0.5 and 1 µg/mL MBC against *E. coli, S. aureus, E. pyogenes and P. aeruginosa* respectively.

Antifungal Activity

"K. Nystatin" used as a standard drug for antifungal activity, which showed 100 µg/mL MFC against fungi, that used in antifungal activity. Same coumpounds are tested for antifungal activity against C. albicans A. niger and A. clavatus. Concentrations is 1000, 500, 200, 100, 50, 25, 12.5 µg/ml respectively taken.

III. RESULTS AND DISCUSSION

Experimental:

Melting points of Ethyl (2Z)-2-(Aryl)-5-(4-methoxyphenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]thiozolo[3,2-*a*]pyrimidine-6-carboxylate and other derivatives were determined in open glass capillaries in a paraffin bath.

The 1H-NMR spectrum of compound verified on the basis of their chemical shifts, multiplicities, and coupling constants. A triplet appeared at δ 2.18 ppm and quartet at δ 3.99 ppm indicate the presence of methyl and methylene protons of the ester chain. Benzylidene proton appeared as a singlet at δ 7.48-7.80 ppm. Two singlets observed at δ 2.23 ppm and δ 2.31 ppm indicated the presence of two methyl group present in the structure. Two singlets appeared at δ 5.95 ppm and δ 8.51 ppm was due to the proton present in the pyrimidine and pyrazole ring respectively.

The IR spectrum of Ethyl (2Z)-2-(Aryl)-5-(4-methoxyphenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]thiozolo[3,2-*a*]pyrimidine-6-carboxylate (in KBr pellets) was recorded on a BRUKER FT-IR spectrophotometer.

IR (KBr): νmax (cm−1), 3382 (>NH), 3260 (-CO-NH), 3099 (C-H), 1552 (C=N and aromatic C=C), 1037 (C-Cl), 642-613 (str., tri-substituted aromatic).

1H-NMR (500 MHz, DMSO-d6): δ ppm, 1.09 (t, 3H, *J* = 7 Hz, ester-CH3), 3.99 (q, 2H, *J* = 7.12 Hz ester-CH2), 2.31 (s, 3H, CH3), 2.23 (s, 3H, Ar-CH3), 5.95 (s, 1H, pyrimidine-CH), 7.48 (s, 1H, CH).

13C-NMR (100 MHz, DMSO-*d6*): δ ppm, 13.88 (ester CH3), 20.67 (CH3), 22.47 (CH3), 54.72 (ester CH2), 60.14 (CH), 108.75, 115.56, 122.24, 127.38, 127.69, 128.32, 128.71, 129.21, 131.13, 131.75, 131.79, 131.88, 137.47, 138.00, 138.49, 150.97, 151.01, 155.14, 163.91,164.82 (C=O).

The progress of the reaction and the purity of compounds was routinely checked on TLC aluminum sheet silica gel 60 F_{245} (E.Merck) using benzene-methanol (4.5:0.5 v/v) or benzene-ccl_4–methanol (2.5:2.0:0.5 v/v) as irrigate and was developed in an iodine chamber.

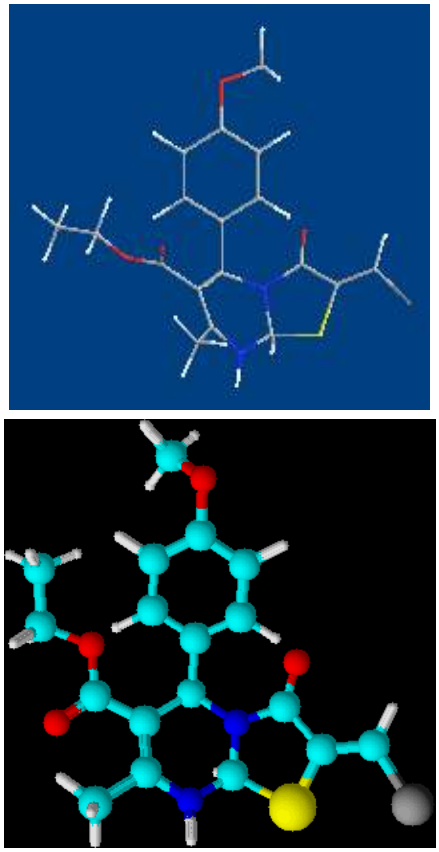


Figure 1. 3d view of compound

IV. ACKNOWLEDGEMENT

We are thankful to the principal of M. G. Science Institute, Ahmadabad to providing research facilities, IR data collection and North America Institute of Pharmaceutical Technology, Toronto for NMR data collection.

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Synthesis and Characterizations of Oxazolo Pyrimidine Derivatives as Biological Active and Antiinfective Agents

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ABSTRACT

Pyrimidines are those molecules that make our life possible being the building blocks of DNA and RNA. Pyrimidine plays a significant role among other heterocycles. Literature survey reveals that partially reduced pyridine and Pyrimidine derivatives are known to have antihypertensive property. Pyrimidine nucleus was synthesized by Biginelli reaction. The aim of this study was to synthesize and introduse many title compound (1a -1m) evaluate them for their antibacterial and antifungal activity. The structures of all title compounds have been confirmed on the basis of their analytical, IR and NMR spectral data. The title compounds have been tested for antibacterial activities against different strains of bacteria.
Keywords: Oxazolo Pyrimidine, Antibacterial Activity, Biginelli Reaction.

I. INTRODUCTION

Organic chemistry has its own descent in the study of natural products. This still remains the most important role in our life and whole world. Many organic compounds occur naturally. Their functions are often of fundamental importance to living organisms.

In the past decades, the pyrimidine and their derivatives have attracted increasing interest in the realms of natural and synthetic organic chemistry because of their diverse therapeutic and pharmacological properties. These non-planner heterocyclic compounds have medicinal importance for further modification in the heterocyclic frame work. In medicinal there are not a single paper is published on the anticancer screening of compounds.

"DRUG DESIGN" requires the knowledge of the structure of a drug molecule as well as that of receptor molecule involved in drug receptor interaction. The structure of a molecule is responsible for its biological activities as the small change in the structure.

Pyrimidines are among those molecules that make life possible being the building blocks of DNA and RNA. Several analogs of pyrimidines have been used as compounds that interfere with the synthesis and functioning of nucleic acids e.g. Fluorouracil, which has been used in cancer treatment. Also there are some thiouracil derivatives, which produce adverse reaction in susceptible patients and are found to be more potent and less likely to produce side effects and hence are being widely used[1]. There are several other important groups of pyrimidines with medicinal uses.

II. METHODS AND MATERIAL

Recent Developments in the Area:

The determination of structure of a molecule provides two fold benefits-it helps to modify the drug and also to synthesize a new drug as the changes in the structure are accompanied with change in the biological activity. The crystal structure studies of these series compounds are important.

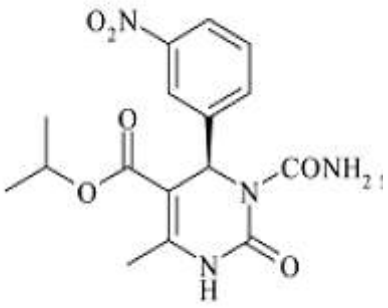
The new synthesis organic molecules and its biologically activity, characterizations include crystal structure determination of various organic.

Molecules by X-ray crystallographic technique are well known. The crystal structures of large variety of organic compounds are determined and large numbers of research papers are published every year in the International Journals such as Acta Crystallographica, journal of Medicinal chemistry, journal of Heterocycle, European journal of medicinal chemistry, journal of American chemical society, analytical science, molecules, Zeitscrift Fur Kristallographie, Journal of Applied Crystallography, Journal of Molecular Structure etc.

A broad range of biological effects and reactivity, including antibacterial activities have been ascribed to Biginelli compounds. One such compound is Monastrol, which has been shown to be a cell-permeable molecule that blocks a normal bipolar spindle assembly in mammalian cells and, therefore, causes cell cycle arrest. Research in this field is in progress for the development of Monastrol as an anti-cancer drug.

Beginelli Reaction:

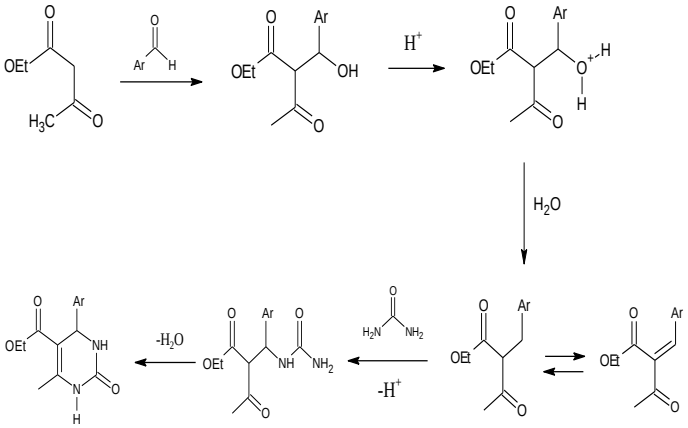
A simple and direct method, first reported by Biginelli in 1893, involves a three Component, one-pot condensation of an aldehyde, a β–ketoester and urea or thiourea Under strongly acidic condition. This has lead to the development of multi-step Strategies that produce overall higher yield, but lack of the simplicity of the Biginelli synthesis. As a result, many improved procedures for the preparation of given product. The **Biginelli reaction**[2-3] is a chemical reaction that makes 3,4-dihydropyrimidin-2(1*H*)-ones from ethyl acetoacetate[4-5] , an aryl aldehyde similar to benzaldehyde , and urea . So that's why it is named for the Italian-chemist Pietro Biginelli. The synthesis of pyrimidines and Thiazolopyrimidine are published large in number in above International Journals every year[6-10]. The result of the three-component reaction was a new product that was correctly characterized as a ethyl 4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(THPM)[11]. They have emerged as integral backbones of several calcium channel blockers[12-14] **Fig 1**.



(*R*)-SQ 32926

Figure1.

Reaction Mechanism:

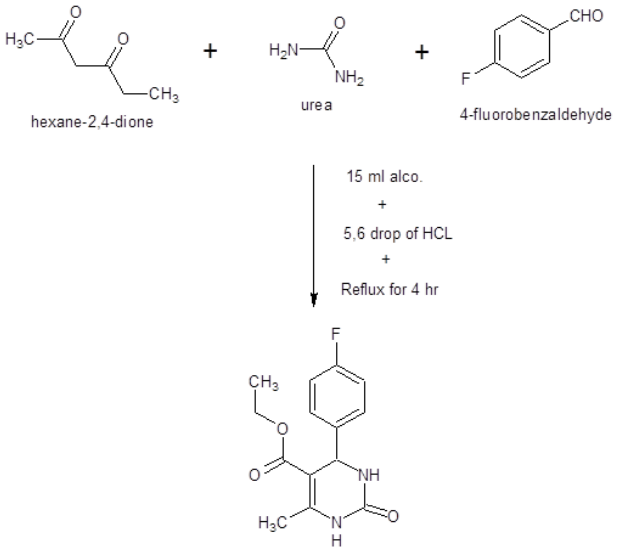


This mechanism is superseded by one by Kappe in 1997

Section -1:

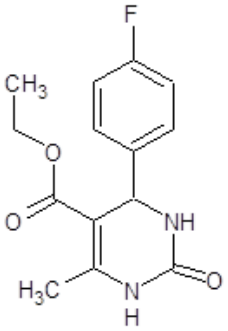
Preparations of ethyl (2*Z*)-2-(Aryl)-5-(4-fluorophenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]oxazolo[3,2-*a*]pyrimidine-6-carboxylate:

Reaction 1:



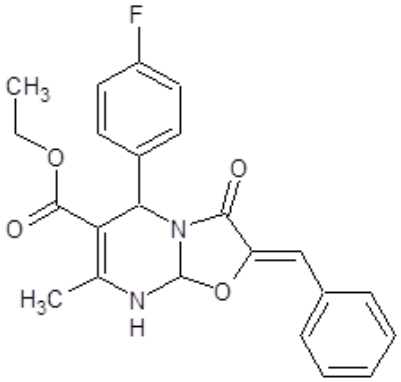
Ethyl4-(4-fluoroyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

Reaction 2:



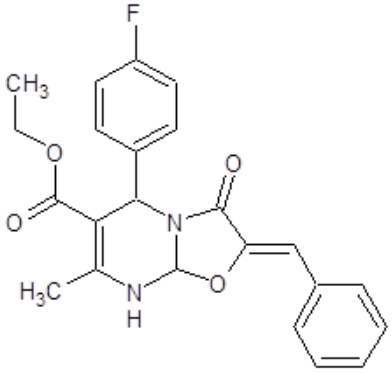
Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

CH_3COOH Acetic acid (glacial) | $ClCH_2COOH$ Chloroacetic acid
CH_3COONa Sodium acetate | C_6H_5CHO Benzaldehyde
Δ | AC_2O Aecetic anhydride
Reflux for 5 to 6 hr



Ethyl (2*Z*)-2-(benzylidene)-5-(4-fluorophenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]oxazolo[3,2-*a*]pyrimidine-6-carboxylate

Physical constants of ethyl (2*Z*)-2-(Aryl)-5-(4-fluorophenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]oxazolo[3,2-*a*]pyrimidine-6-carboxylate:



Sr No.	-Ar	MOLECULAR FORMULA	M. P. ^{O}C	YIELD (%)	% OF CARBON		% OF NITROGEN		Mol. Wt
					FOUND	REQD.	FOUND	REQD.	
1a	$-C_6H_5$	$C_{23}H_{21}FN_2O_3S$	169^0C	56%	65.03	65.08	60.58	6.60	424.48
1b	$-4-OCH_3-C_6H_4$	$C_{24}H_{23}FN_2O_4S$	163^0C	64%	63.40	63.42	6.12	6.16	454.51
1c	$-2,4-(CL)_2-C_6H_3$	$C_{23}H_{19}Cl_2FN_2O_3S$	162^0C	62%	55.94	55.99	5.64	5.68	493.37
1d	$-4-CH_3-C_6H_4$	$C_{24}H_{23}FN_2O_3S$	156^0C	59%	65.71	65.73	6.34	6.39	438.51
1e	$-4-F-C_6H_4$	$C_{23}H_{20}F_2N_2O_3S$	171^0C	61%	62.40	62.43	6.30	6.33	442.47
1f	$-4-Br-C_6H_4$	$C_{23}H_{20}BrFN_2O_3S$	158^0C	53%	54.85	54.88	5.51	5.57	503.38
1g	$-4-Cl-C_6H_4$	$C_{23}H_{20}ClFN_2O_3S$	166^0C	64%	60.18	60.19	6.6	6.10	458.93
1h	$-3-OH-C_6H_4$	$C_{23}H_{21}FN_2O_4S$	170^0C	68%	62.69	62.71	6.32	6.36	440.48

1i	-4-OH-C_6H_4	$C_{23}H_{21}FN_2O_4S$	167^{0}C	70%	62.69	62.71	6.31	6.36	440.48
1j	-3-OCH_3-4-OH-C_6H_3	$C_{24}H_{23}FN_2O_5S$	179^{0}C	64%	61.24	61.26	5.94	5.95	470.51
1k	-2-NO_2-C_6H_4	$C_{23}H_{20}FN_3O_5S$	160^{0}C	53%	58.81	58.84	8.90	8.95	469.48
1l	-3-NO_2-C_6H_4	$C_{23}H_{20}FN_3O_5S$	190^{0}C	71%	58.80	58.84	8.91	8.95	469.48
1m	-4-NO_2-C_6H_4	$C_{23}H_{20}FN_3O_5S$	152^{0}C	66%	58.79	58.84	8.93	8.95	469.48

Preparation of ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

A mixture of Ethyl aceto acetate (0.01 mole), benzaldehyde (0.01 mole) and urea (0.01 mole) in ethanol (20 ml) was refluxed for 6 h. The reaction mixture was poured in crushed ice and product was isolated and re-crystallized from ethanol: DMF .Yield 78% The progress of the reaction and the purity of compounds was routinely checked on TLC aluminum sheet silica gel 60 F_{245} (E.Merck) using benzene-methanol (4.5:0.5 v/v) or benzene-ccl_4–methanol (2.5:2.0:0.5 v/v) as irrigate and was developed in an iodine chamber.

Preparation of ethyl (2*Z*)-2-(Aryl)-5-(4-fluorophenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]oxazolo[3,2-*a*]pyrimidine-6-carboxylate.(1a)

A mixture of ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (0.01 mole), benzaldehyde (0.01 mole),chloroaceticacid,sodium acetate (0.01 mole), acetic anhydride (0.01 mole) in acetic acid (20 ml) was refluxed for 5 to 6 hr. The reaction mixture was poured in crushed ice and product was isolated and re-crystallized from ethanol: DMF m.p 170^{0}C Yield 58%

The progress of the reaction and the purity of compounds was routinely checked on TLC aluminum sheet silica gel 60 F_{245} (E.Merck) using benzene-methanol (4.5:0.5 v/v) or benzene-ccl_4–methanol (2.5:2.0:0.5 v/v) as irrigate and was developed in an iodine chamber.

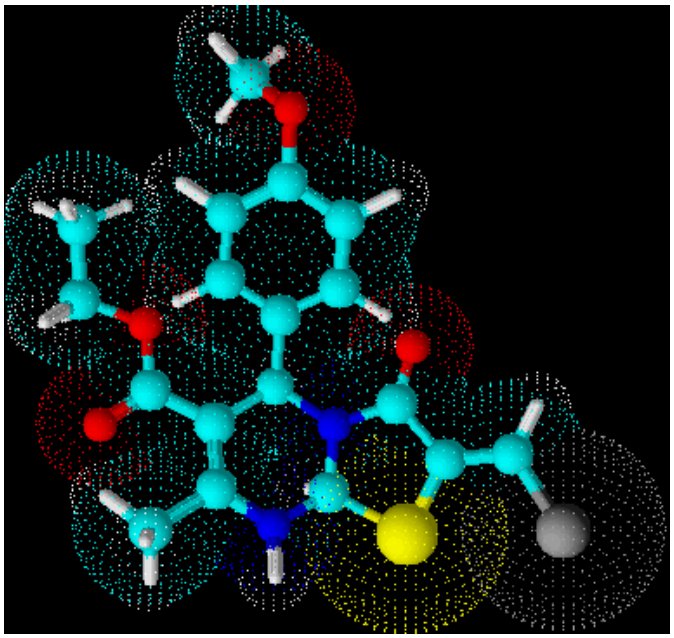


Figure 2. 3d view of compound

Table 2: Antibacterial and Antifungal Activities

SR NO.	Minimal bactericidal concentration (MBC) in µg/ml				Minimal fungicidal concentration (MFC) in µg/ml		
	E.coli	***P.aeruginosa***	***S.aureus***	***S.pyogenus***	***C.albicans***	***A.nigar***	***A.clavatus***
	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC
	- 443	-1688	-96	- 442	-227	-282	-1323
1a	200	500	1000	500	500	500	500
1b	50	100	1000	1000	500	500	500
1c	200	500	1000	1000	1000	1000	1000
1d	100	50	500	250	500	500	500
1e	100	1000	500	500	500	500	200
1f	100	100	1000	500	1000	1000	1000

1g	100	250	500	500	500	500	500
1h	100	200	1000	1000	1000	1000	1000
1i	50	500	500	1000	500	500	500
1j	50	100	1000	500	1000	500	500
1k	200	250	1000	1000	500	500	500
1l	200	100	1000	1000	1000	1000	1000
1m	100	500	500	1000	1000	1000	1000

Antibacterial Activity

Antibacterial activity is taken by broth dilution method. Concentrations of 1000,500, 200, 100, 50, 25, 12.5 µg/ml respectively in shown table. Antibacterial activity showed 0.25, 0.05, 0.5 and 1 µg/mL MBC against *E. coli*, *S. aureus*, *E. pyogenes and P. aeruginosa* respectively.

Antifungal Activity:

"K. Nystatin" used as a standard drug for antifungal activity, which showed 100 µg/mL MFC against fungi, that used in antifungal activity. Same coumpounds are tested for antifungal activity against C. albicans A. niger and A. clavatus. Concentrations is 1000, 500, 200, 100, 50, 25, 12.5 µg/ml respectively taken.

III. RESULTS AND DISCUSSION

Melting points of Ethyl (2*Z*)-2-(benzylidene)-5-(4-fluorophenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]oxazolo[3,2-*a*]pyrimidine-6-carboxylate and other derivatives were determined in open glass capillaries in a paraffin bath. The 1H-NMR spectrum of compound verified on the basis of their chemical shifts, multiplicities, and coupling constants. Two singlets appeared at δ 5.95 ppm and δ 8.79 ppm was due to the proton present in the pyrimidine and pyrazole ring respectively. A triplet appeared at δ 1.09 ppm and quartet at δ 3.99 ppm indicate the presence of methyl and methylene protons of the ester chain. Benzylidene proton appeared as a singlet at δ 7.48 ppm. Two singlets observed at δ 2.23 ppm and δ 2.31 ppm indicated the presence of two methyl group present in the structure. In the IR spectrum, the sharp absorption band appeared at 1,653 cm−1 was due to carbonyl group of the ester and other sharp band appeared at 1,614 cm−1 was due to the cyclic carbonyl group. LCMS and 13C-NMR spectrum was in complete agreement with the title compound.

The IR spectrum of Ethyl (2*Z*)-2-(benzylidene)-5-(4-fluorophenyl)-7-methyl-3-oxo-2,3,8,8a-tetrahydro-5*H*-[1,3]oxazolo[3,2-*a*]pyrimidine-6-carboxylate(1a) and other derivatives (in KBr pellets) was recorded on a BRUKER FT-IR spectrophotometer.
IR (KBr): νmax (cm−1), 3402 (>NH), 3111 (C-H), 1714 (C=O ester), 1552 (C=N and aromatic C=C) , 1159 (C-O), 756 (C-Cl), 698,754 (str., tri-substituted aromatic).

1H-NMR (400 MHz, DMSO-d6): δ ppm, 1.09 (t, 3H, *J* = 7 Hz, ester-CH3), 3.99 (q, 2H, *J* = 7.12 Hz ester-CH2), 2.31 (s, 3H, CH3), 2.23 (s, 3H, Ar-CH3), 5.95 (s, 1H, pyrimidine-CH), 7.48 (s, 1H, CH), 7.11–8.02 (m, 12H, Ar-H), 8.79 (s, 1H, pyrazole CH).
13C-NMR (100 MHz, DMSO-*d6*): δ ppm, 13.88 (ester CH3), 20.67 (CH3), 22.47 (CH3), 54.72 (ester CH2), 60.14 (CH), 108.75, 115.56, 119.35, 119.42, 122.24, 127.38, 127.69, 128.32, 128.71, 129.21, 129.58, 130.08, 131.13, 131.75, 131.79, 131.88, 137.47, 138.00, 138.49, 150.97, 151.01, 155.14, 163.91,164.82 (C=O).

The progress of the reaction and the purity of compounds was routinely checked on TLC aluminum sheet silica gel 60 F_{245} (E.Merck) using benzene-methanol (4.5:0.5 v/v) or benzene-ccl_4–methanol (2.5:2.0:0.5 v/v) as irrigate and was developed in an iodine chamber.

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Synthesis and Characterizations of Triazine Derivative - N^2,N^4-bis(6-bromo-1,3-benzothiazol-2-yl)-N^6-aryl-1,3,5-triazine-2,4,6-triamine, derivative of 2,4,6-trimethyl-1,3,5-triazine as Biological Potent Agents

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ABSTRACT

A series of N^2,N^4-bis(6-bromo-1,3-benzothiazol-2-yl)-N^6-aryl-1,3,5-triazine-2,4,6-triamine 2a-k indole fused triazine derivatives have been synthesized by reaction between cyanuric chloride and benzothiazole. Product characterized by elemental and spectral analysis like IR and NMR.Further the compounds have been screened for antimicrobial activity against ten strains of Gram (+) and Gram (-) bacteria.

Keywords: Triazine, Antibacterial Activity.

I. INTRODUCTION

Antibacterial disease is very common all over the world. Currently used antimicrobial agents are not effective due to the resistance developed by the microbes. And therefore, it is an ongoing effort to synthesize new antimicrobial agents[1]. The quest for a more reliable and suitable drugs is always fascinating and challenging. A number of drugs containing simple heterocyclic or a combination of different moieties have been in use these days[2,31].

1,2,4-Triazines and their derivatives have been widely studied in terms of their synthetic methodologies and reactivity since some of these derivatives were reported to have promising biological activities like A1 Adenosine receptor antagonists[3], Age-related macular degeneration[4], analgesic[5], anti-inflammatory activities[5], Anticancer Activity[6,7], anticonvulsant activity[8], antimicrobial activity[9,10], antinociceptive activity[11], Antiproliferativeactivity[12], anxioselective agent[13], Kinase inhibitor activity[14], Muscle Relaxant activity [15] .

An indole nucleus have arose great attention in recent years due to their wide variety of biological activities and pharmacological studies as cytotoxicity activity[16], Kinase inhibitors[17], anticancer[17], antiangiogenic agents[17], antimicrobial activity[18-21,23], Anti-HIV[22], anti-inflammatory[24], analgesic activity [24], Anticonvulsant activity[25,26] , Sedative-Hypnotic Activities[26] . Desai and co-workers[27] synthesized 2-(4-methoxy/2-methyl phenyl)-4-phenyl acetyl hydrazino-6-isonicotinyl hydrazino-s-triazines and tested them for their anti-HIV activity against susceptible human host cell (CEM cell line) over a wide range of concentrations. Based on the above observations, herein are reported the synthesis of various indole fused Triazine derivatives and evaluation of their antibacterial activity.

II. METHODS AND MATERIAL

Biological Activity

Antibacterial Activity

Antibacterial activity was carried out by TWO dilution method[28]. The strains used for the activity were secured from Institute of Microbial Technology. The compounds 2a-2k were observed for their antibacterial activity against Escherichia coli bacteria, Staphylocous aureus, Pseudomonas aeruginosa and Staphyloccous pyogenes at concentrations of 1000, 500, 200, 100, 50, 25, 12.5 µg/mL respectively (Table 2).

Antifungal Activity

Same compounds are analyze for antifungal activity against *C. albicans A. niger and A. clavatus* at a concentrations of 100, 200, 500, and 1000 µg/mL

respectively Table 2, for 2a-2k.The results are noted in the form of primary and secondary screening. Each synthesized drug was diluted to obtain 1000 µg/mL concentration, as a stock solution.

Experimental Section

Melting points are taken in open capillaries using paraffin. IR spectra were recorded on FTIR- Bruker spectrometer (V_{max} in cm^{-1}); Purity was checked by TLC using TLC aluminum sheets silica gel 60, supplied by E.Merck. The spots were located by keeping the plates in iodine vapor. 6-chloro-1,3-benzothiazol-2-amine was prepared by methods as described in literature[29-30].

For 2a compound: IR (kbr): 3454 (-N-H str., sec.amine), 3083(-C-H str., aromatic), 1527 (> C = N- str., ter. Amine), 1122 (C-S-C str., thiazol), 808 (disubstituted aromatic),1431 (C = N str., sec.amine).

NMR Spectra: 1H NMR spectra, were recorded in CDCl3 solution on a Bruker Avance DPX 200 MHz spectrometer Chemical shifts are reported as d (ppm) relative to TMS as internal standard.10.18δ (s, -NH, 2H), 9.34 δ (s, -NH, 1H), 8.54 δ (s, Ar-H, 8H).

Preparation of 6-chloro-N, N'-bis (6-bromo-1,3-benzothiazol-2-yl)-1,3,5-triazine-2,4-diamine:

In a conical flask, 2,4,6-trichloro-1,3,5-triazine (1) (0.01 mol) was taken acetone (20 ml) and 6-bromo-1,3-benzothiazol-2-amine (2) (0.02 mol) was added to it. To this mixture, 4% NaOH was added drop wise at room temperature. The solution was stirred for 4 h. The reaction mixture was poured onto crushed ice with constant stirring. The solution was neutralized with dil. HCl. The solid was filtered and washed with water. The product was recrystallized from acetone.; yield 76.00%.

Preparation of N^2,N^4-bis(6-bromo-1,3-benzothiazol-2-yl)-N^6-aryl-1,3,5-triazine-2,4,6-triamine :

In a round bottom flask, 6-chloro-N, N'-bis (6-bromo-1, 3-benzothiazol-2-yl)-1, 3, 5-triazine-2, 4-diamine. (3) (0.01 mol) and 1,4-dioxane (20 ml) was taken. To this mixture, aniline (0.01 mol) was added. The $p^H$was adjusted to neutral by adding 8% NaOH. The reaction mixture was refluxed for 2.5 h. And was poured onto crushed ice with constant stirring. The mixture was then neutralized with dil. HCl. The product was filtered and washed with cold water. The product was dried and recrystallized from methanol; Yield 65%

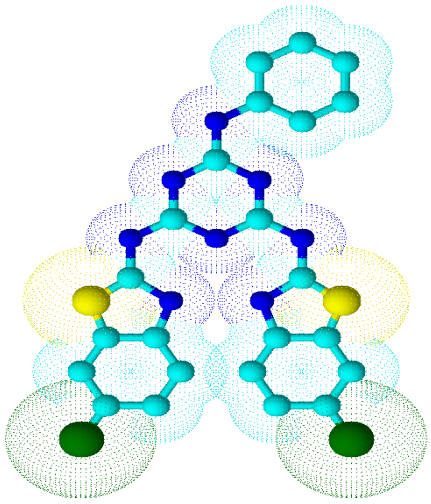

Figure 1. Structure of 2a

Scheme 1:

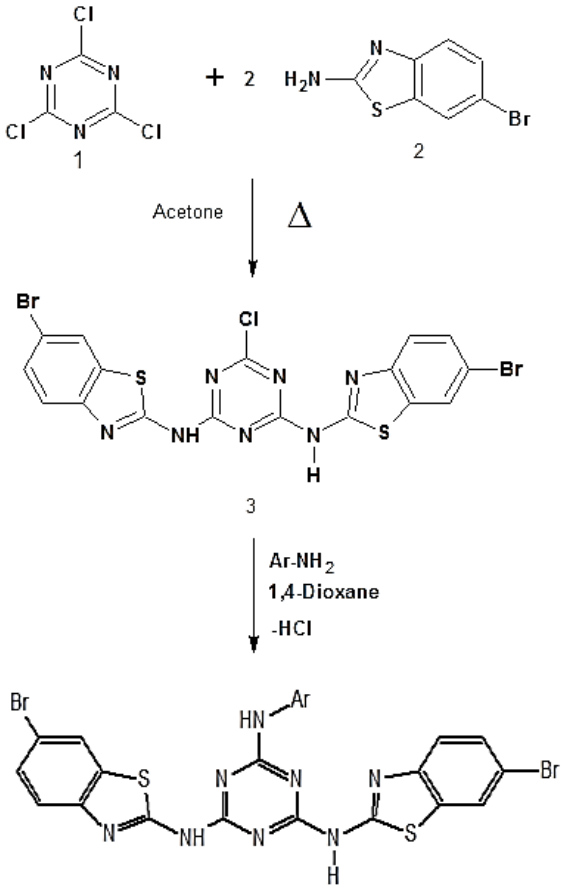

Figure 2. 2a-2k

Table I : Physical constant of the compounds (2a-2k)

Compd.	-Ar	Molecular Formula	m.p. (ºC)	Yield (%)	C (%) Found	C (%) Reqd.	N (%) Found	N (%) Reqd.
2a	-C_6H_5	$C_{23}H_{14}Br_2N_8S_2$	230	68	44.05	44.10	17.85	17.89
2b	-3-Cl-C_6H_4	$C_{23}H_{13}Br_2ClN_8S_2$	220	56	41.60	41.81	16.95	16.96
2c	-4-Cl-C_6H_4	$C_{23}H_{13}Br_2ClN_8S_2$	195	64	41.71	41.81	16.92	16.96
2d	-3-NO_2-C_6H_4	$C_{23}H_{13}Br_2N_9O_2S_2$	134	62	41.10	41.15	18.75	18.78
2e	-4-NO_2-C_6H_4	$C_{23}H_{13}Br_2N_9O_2S_2$	129	67	41.11	41.15	18.76	18.78
2f	-4-Br-C_6H_4	$C_{23}H_{13}Br_3N_8S_2$	220	58	39.15	39.17	15.84	15.89
2g	-4-F-C_6H_4	$C_{23}H_{13}Br_2FN_8S_2$	205	63	42.80	42.87	17.35	17.39
2h	-2-$C_5H_4N_2$	$C_{22}H_{13}Br_2N_9S_2$	215	64	42.10	42.12	20.04	20.09
2i	-4-$C_5H_4N_2$	$C_{22}H_{13}Br_2N_9S_2$	230	69	42.09	42.12	20.06	20.09
2j	-N-CH_3-C_6H_4	$C_{24}H_{16}Br_2N_8S_2$	215	58	45.00	45.01	17.49	17.50
2k	-4-CH_3-C_6H_4	$C_{24}H_{16}Br_2N_8S_2$	247	57	44.96	45.01	17.46	17.50

Table 2: Antibacterial and Antifungal Activities

SR NO.	Minimal Bactericidal Concentration (MBC) in µg/ml				Minimal Fungicidal Concentration (MFC) in µg/ml		
	E.coli	***P.aeruginosa***	***S.aureus***	***S.pyogenus***	***C.albicans***	***A.nigar***	***A.clavatus***
	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC
	- 443	-1688	-96	- 442	-227	-282	-1323
2a	100	200	100	500	500	500	500
2b	100	100	500	500	200	200	200
2c	100	500	100	250	100	100	100
2d	100	100	500	500	100	100	100
2e	100	500	100	500	500	500	500
2f	250	500	100	250	100	100	100
2g	250	500	500	250	500	1000	1000
2h	500	100	100	500	500	500	500
2i	1000	1000	500	500	500	500	500
2j	100	100	500	500	200	200	200
2k	100	250	500	500	500	500	500

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Evaluation of Seasonal Variations of Physico-chemical and Bacteriological Quality of Groundwater from a Chemical Industry in Port Harcourt Area, Port Harcourt, Rivers State, Nigeria

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ABSTRACT

Groundwater samples were collected from a chemical industry in Port Harcourt Area of Rivers State, Nigeria in two sampling seasons (Wet and Dry seasons) and were evaluated for Physico-chemical and Bacteriological Quality. Physico-chemical and Bacteriological results of the dry season groundwater samples showed slightly higher concentrations when compared to the wet season ground water samples except for acidity which had higher value of 43.67 ± 1.20 obtained for the wet season samples. Physico-chemical groundwater parameters such as electrical conductivity, acidity, pH, chloride, sodium chloride and silica showed significant seasonal variations ($p<0.05$). Results of the average physico-chemical concentrations of the seasonal groundwater samples were all in compliance with the Nigerian Standard for Drinking Water Quality (NSDWQ) except for pH which had an average seasonal concentration of 4.90 ± 0.17. Average seasonal bacteriological results of the potable groundwater samples indicated the presence of total bacterial concentration of 5.34 ± 0.17/100mg/l which was above the NSDWQ stipulated value of Nil/100mg/l. Based on these findings, it is therefore necessary to properly disinfect the groundwater before human use so as to avoid the risk of contracting water-borne diseases.

Keywords: Groundwater, Pollution, Chemical Industry, Physico-chemical, Bacteriological.

I. INTRODUCTION

The importance of water in a society cannot be overemphasized as water is a limited commodity that is of great significant importance for agricultural purposes, industrial purposes as well as human existence, etc. thus in the absence of quality and adequate water supply the development and sustenance of a country is greatly deterred. Most developing countries are often faced with issues of adequate and quality water supply due to their economy or shortage/absent of advance technology for the treatment of obtainable water which is meant to serve the growing population of these countries thus, the populace have no choice but to resort to the obtainable water whose quality is uncertain (Calamari and Naeve, 1994; Aina and Adedipe, 1996). Insufficiency of Quality water and contamination of clean water has thus brought about situations in which one-fifth of those living in the metropolis in developing countries and three-quarters of those living in rural areas lack access to potable water sources (Lloyd and Helmer, 1992). However, people around the world have used groundwater as a source of drinking water, and even today more than half the world's population depends on groundwater for survival (UNESCO, 1992). The value of groundwater lies not only in its wide spread occurrence and availability but also in its consistent good quality, which makes it an ideal supply of drinking water (UNESCO, 2000).

Intensive use of natural resources and the large production of wastes in modern society often pose a threat to groundwater quality and have already resulted in many incidents of groundwater contaminations. As said by Adeyeye, (2002); "industrial growth is identified as a major tool for economic development in Nigeria". Man in its pursuits to boost his food bank, get uncontaminated water for consumption and reduce damage and injury to his healthiness; the industrial

materials, waste and chemicals supposedly meant for his benefits had become a quiet vanquisher and danger to his life (NEST, 1991).

Contamination of ground water and surface water often repeatedly happens due to escapes, spills and constant release of contaminants from dispensational activities from industries, municipalities, etc (NORAD, 1996). This has consequently resulted to reported cases of water bone diseases which cause health damage to those affected (Ratna and Deepti, 2012). Hence, this research seeks to assess the wet and dry season's physicochemical status of ground water from a chemical industry in Port Harcourt Area, Rivers State of Nigeria, if it meets the minimum requirements set by the Nigerian Standard for Drinking Water Quality (NSDWQ) standard limits and also if the groundwater from the said chemical industry poses any risk to the health of consumers of the groundwater.

II. METHODS AND MATERIAL

2.1 Study Area

This study was conducted in a chemical industry located along East West road, Rumuodara in Port Harcourt Area, Rivers State. The chemical industry produces organic and inorganic chemicals and industrial gases. They are also into the production of chemical products such as pesticides, inks, detergents and cosmetics. The climate of the area is a humid torrential rain type of weather with prolonged and profound rainy seasons and very short dry season. December and January are the only months are eligible for dry season months in the area. Normally, December is often the least rainy month of the year, with average rainfall of 20mm. The heaviest precipitation occurs during September with an average of 367mm of rain. Temperatures all through the year are frequently stable, presenting slight deviation all through the year. On the average, the temperature range is normally between 25^{o}C and 28^{o}C.

2.2 Collection of water samples

Groundwater samples were collected from different locations within the chemical industry in two sampling seasons (July, 2015 in wet/rainy season and December, 2015 in dry season), in pre cleaned plastic bottles from bore hole well head, tank supply, and public pump supply points respectively. Another potable groundwater sample serving as control was also collected from a non-industrial area (Diobu, Port Harcourt, Rivers State).

Before collection of the samples from the public pump supply, the pump was allowed to flow out for about two minutes to avoid any water resident in the pipe being taken as a sample. The piping material can contaminate the water resident in the piping system with the result such water is not a true representative of the potable water source.

The sample from the bore hole well head was not collected from the surface but from inside of the water body so as to avoid possible particles on the surface.

The sample from the tank supply was collected directly from the pipe connected to the overhead reservoir tank after allowing the water to flow out of the pipe for about two minutes. After collection, the groundwater samples were immediately taken to the laboratory for analyses.

2.3 Analysis of water samples

Physicochemical and bacteriological water quality parameters analyzed in accordance to standard methods (APHA (1995), Bartran and balance (1996) were; Appearance, Temperature, Colour, Turbidity, Odour, Taste, Conductivity, Acidity, pH, Chlorides as Cl, Chlorides as NaCl, Total Alkalinity, Total Hardness, Calcium Hardness, Magnesium Hardness, Sulphate, Bicarbonates, Saline & Free Ammonia, Nitrate, Silica, TDS, TSS, Dissolved Free CO_2, Total Iron, Total Bacteria and E. Coli (Coliform). The quality of groundwater has been assessed by comparing the wet season parameters to the dry season parameter, using student t-test, employing the Statistical Package for Social Sciences (SPSS) and comparing each parameter with the standard desirable limit of that parameter in drinking water as prescribed by NSDWQ and WHO.

III. CONCLUSION

Comparative Physical and Bacteriological Results of the Seasonal variations of the Groundwater Samples from the Chemical Industry are summarized and presented on Table 1a. Results of the average concentrations of the Seasonal Physical and Bacteriological Parameters of the Groundwater Samples from the Chemical Industry are summarized and presented on Table 1b. Comparative

Chemical Results of the Seasonal variations of the Groundwater Samples from the Chemical Industry are summarized and presented on Table 2a. Results of the average concentrations of the Seasonal Chemical Parameters of the Groundwater Samples from the Chemical Industry summarized and presented on Table 2b.

3.1 Appearance

The groundwater samples were clear in appearance both in the wet and dry season samples. These appearance results of the groundwater samples were in conformity with the control groundwater sample as well as with the NSDWQ limit value for appearance in drinking water samples.

3.2 Temperature

The temperature values of the groundwater samples for both wet (24.00 ± 0.00 (^{0}C)) and dry (25.00 ± 0.00 (^{0}C) seasons were in agreement with the (25.00 (^{0}C)) value obtained for the control groundwater sample. These results were therefore in compliance with the 25^{0}C value set by NSDWQ. Though, temperature value obtained for the dry season groundwater samples was slightly higher than the value obtained for the wet season samples, this increase was however not significant difference ($p<0.05$).

3.3 Colour

The colour of the groundwater samples were found the same as 5.00 ± 0.00 (HU) for both the wet and dry season samples as well as in the control groundwater Sd sample. These values were all in compliance with the 15 (HU) colour limited set by NSDWQ and are similar to those reported by Ukpong and Okon, (2013).

3.4 Turbidity

Turbidity in most waters is due to the presence of suspended matter such as silts, finely divided organic and inorganic matter, and microscopic organisms which cause light to be scattered and absorbed rather than be transmitted through the samples (APHA, 1995). Turbidity value of the groundwater sample was 0.57 ± 0.00 (NTU) for dry season samples which was slightly higher than the turbidity value of the 0.18 ± 0.00 (NTU) obtained for the wet season groundwater samples. The slight increase was however not significant ($p<0.05$). Though these values obtained for both seasons were higher than the 0.00 (NTU) value obtained for the control groundwater sample, they were however all in compliance with the 5 (NTU) turbidity value set by the NSDWQ.

3.5 Odour

Odour in groundwater samples is indicative of organic or non-organic contaminants that originate from municipal or industrial discharges or from natural sources in the ground water samples (Patherson *el al.,* 1984). Odour of the groundwater samples were nil for both seasons, which was in conformity with the control ground water sample and also in compliance with the nil value set by NSDWQ.

Table 4.1a: Comparative Physical and Bacteriological Results of the Seasonal Variations of the Groundwater Samples from the Chemical Industry.

PARAMETERS	**Season**		**CONTROL**	**NSDWQ**
	Wet	**Dry**		
Appearance	Clear[a]	Clear[b]	Clear	Clear
Temperature (^{o}C)	24.00 ± 0.00[a]	25.00 ± 0.00[b]	25.00 ± 0.00	25^{o}C
Colour in Hazen Unit	5.00 ± 0.00[a]	5.00 ± 0.00[b]	5.00 ± 0.00	15 Hazen Units
Turbidity in NTU	0.18 ± 0.04[a]	0.57 ± 0.09[b]	0.00 ± 0.00	5 NTU
Odour	Nil[a]	Nil[b]	Nil	Nil

Taste	Unobjectionable[a]	Unobjectionable[b]	unobjectionable	Unobjectionable
TDS Dried at 180°C (mg/l)	10.33 ± 0.67[a]	10.93 ± 0.01[b]	10.28 ± 0.34	500 mg/l
TSS (mg/l)	0.03 ± 0.01[a]	0.06 ± 0.02[b]	0.03 ± 0.00	25 mg/l
Total Bacteria (mg/l)	5.00 ± 0.00[a]	5.67 ± 0.33[b]	2.48 ± 0.20	Nil/100mg/l
E. Coli [Coliform] (mg/l)	0.00 ± 0.00[a]	0.00 ± 0.00[b]	0.00 ± 0.00	Nil/100mg/l

Results presented are Means ± SEM for n = 3. Values in the same row with the same superscript (a) are significantly different at $p<0.05$ level.

Legend:
NSDWQ = Nigerian Standard for Drinking Water Quality

Table 4.1b: Results of the average concentrations of the Seasonal Physical and Bacteriological Parameters of the Groundwater Samples of the Chemical Industry.

PARAMETERS	AVERAGE CONCENTRATION	CONTROL	NSDWQ
Appearance	Clear	Clear	Clear
Temperature (^{0}C)	24.50 ± 0.00	25.00 ± 0.00	25(^{0}C)
Colour in Hazen Unit	5.00 ± 0.00	5.00 ± 0.00	15 Hazen Units
Turbidity in NTU	0.75 ± 0.07	0.00 ± 0.00	5 NTU
Odour	Nil	Nil	Nil
Taste	Unobjectionable	unobjectionable	Unobjectionable
TDS Dried at 180 ^{0}C (mg/l)	10.63 ± 0.34	10.28 ± 0.34	500 mg/l
TSS (mg/l)	0.05 ± 0.02	0.03 ± 0.00	25 mg/l
Total Bacteria (mg/l)	5.34 ± 0.17	2.48 ± 0.20	Nil/100mg/l
E. Coli [Coliform] (mg/l)	0.00 ± 0.00	0.00 ± 0.00	Nil/100mg/l

Legend:
NSDWQ = Nigerian Standard for Drinking Water Quality

Table 4.2a: Comparative Chemical Results of the Seasonal Variations of the Groundwater Samples of the Chemical Industry.

PARAMETERS	Season		CONTROL	NSDWQ
	Wet	Dry		
Conductivity (µS/cm)	69.40 ± 0.34[a]	130.73 ± 0.98[a]	60.97 ± 0.22	1000 µS/cm
Acidity	43.67 ± 1.20[a]	37.67 ± 1.45[a]	35.86 ± 0.09	NS
pH	4.40 ± 0.10[a]	5.40 ± 0.23[a]	7.09 ± 0.14	6.5 – 8.5
Chlorides as Cl (mg/l)	3.57 ± 0.24[a]	6.80 ± 0.00[a]	5.00 ± 0.44	250 mg/l

Chlorides as NaCl (mg/l)	5.20 ± 0.11^{a}	8.63 ± 0.03^{a}	4.98 ± 0.35	250 mg/l
Total Alkalinity (mg/l)	9.67 ± 0.33^{a}	9.83 ± 0.17^{b}	10.05 ± 0.53	NS
Total Hardness (mg/l)	11.67 ± 0.33^{a}	12.50 ± 0.29^{b}	10.20 ± 0.05	150 mg/l
Calcium Hardness (mg/l)	8.00 ± 0.58^{a}	8.67 ± 0.33^{b}	5.95 ± 0.19	NS
Magnesium Hardness (mg/l)	3.67 ± 0.67^{a}	3.88 ± 0.60^{b}	3.00 ± 0.21	20 mg/l
Sulphates as SO_4^{2-} (mg/l)	0.07 ± 0.00^{a}	0.08 ± 0.00^{b}	0.00 ± 0.00	100 mg/l
Bicarbonates as HCO_3 (mg/l)	9.67 ± 0.33^{a}	9.83 ± 0.17^{b}	10.02 ± 0.72	NS
Saline & Free Ammonia (mg/l)	0.00 ± 0.00^{a}	0.00 ± 0.00^{b}	0.00 ± 0.00	0.05 mg/l
Nitrate (mg/l)	0.17 ± 0.11^{a}	0.02 ± 0.00^{b}	0.01 ± 0.00	50 mg/l
Silica as SiO_2 (mg/l)	0.02 ± 0.00^{a}	0.04 ± 0.00^{b}	0.00 ± 0.00	NS
Dissolved Free CO_2 (mg/l)	30.33 ± 0.88^{a}	31.33 ± 0.87^{b}	32.50 ± 0.038	NS
Total Iron as Fe (mg/l)	0.00 ± 0.00^{a}	0.00 ± 0.00^{b}	0.00 ± 0.00	0.3 mg/l

Results presented are Means ± SEM for n = 3. Values in the same row with the same superscript (a) are significantly different at $p<0.05$ level.

Legend:

NS = Not Stated.
NSDWQ = Nigerian Standard for Drinking Water Quality

Table 4.2b: Results of the average concentrations of the Seasonal Chemical Parameters of the Groundwater Samples of the Chemical Industry.

PARAMETERS	**AVERAGE CONCENTRATION**	**CONTROL**	**NSDWQ**
Conductivity (µS/cm)	100.07 ± 0.66	60.97±0.22	1000 µS/cm
Acidity	60.67 ± 1.33	35.86±0.09	NS
pH	4.90 ± 0.17	7.09±0.14	6.5 – 8.5
Chlorides as Cl (mg/l)	5.19 ± 0.24	5.00±0.44	250 mg/l
Chlorides as NaCl (mg/l)	6.92 ± 0.07	4.98±0.35	250 mg/l
Total Alkalinity (mg/l)	9.75 ± 0.25	10.05±0.53	NS
Total Hardness (mg/l)	12.09 ± 0.31	10.20±0.05	150 mg/l
Calcium Hardness (mg/l)	8.34 ± 0.46	5.95±0.19	NS
Magnesium Hardness (mg/l)	3.78 ± 0.64	3.00±0.21	20 mg/l
Sulphates as SO_4^{2-} (mg/l)	0.08 ± 0.00	0.00±0.00	100 mg/l
Bicarbonates as HCO_3 (mg/l)	9.75 ± 0.25	10.02±0.72	NS
Saline & Free Ammonia (mg/l)	0.00 ± 0.00	0.00±0.00	0.05 mg/l

Nitrate (mg/l)	0.10 ± 0.06	0.01±0.00	50 mg/l
Silica as SiO_2 (mg/l)	0.03 ± 0.00	0.00±0.00	NS
Dissolved Free CO_2 (mg/l)	30.83 ± 0.87	32.50±0.038	NS
Total Iron as Fe (mg/l)	0.00 ± 0.00	0.00±0.00	0.3 mg/l

Legend:

NSDWQ = Nigerian Standard for Drinking Water Quality
NS = Not Stated.

3.6 Taste

There was no seasonal variation in taste parameter of the groundwater samples. The tastes of the groundwater samples for both seasons were unobjectionable which was in agreement with the unobjectionable taste vale of the control groundwater sample as well as with the unobjectionable taste value set by NSDWQ. Yadav *et al.*, (2012) also reported similar result.

3.7 Total Dissolved Solids (TDS)

Total dissolve solid (TDS) values of the groundwater samples were all in compliance with the 500mg/l TDS limit value set by NSDWQ. The TDS value 10.93± 0.01 (mg/l) obtained for the dry season groundwater samples was slightly higher but not significantly higher than the 10.33 ± 0.67 (mg/l) TDS value obtained for the wet season groundwater samples.

3.8 Total Suspended Solids (TSS)

Total suspended solids (TSS) value of 0.06±0.02 (mg/l) obtained for the dry season groundwater samples was slightly higher, though not significantly higher than the TSS value of 0.03 ± 0.01 (mg/l) obtained for the wet season groundwater samples. These values were in conformity with the TSS value of 0.03 (mg/l) obtained for the control groundwater sample and also in compliance with the 25(mg/L) TSS value set by NSDWQ. TSS are a significant factor in observing water clearity, the more solids presence in the water the less clear the water will be (Langland and Crown, 2003).

3.9 Total Bacteria

Total bacteria value of 5.67 ± 0.33/(100mg/l) obtained for the dry season groundwater samples was slightly higher, though not significantly higher than the total bacteria value of 5.00 ± 0.00/(100mg/l) obtained for the wet season groundwater samples. These value were higher than the total bacteria value of 2.48/(100mg/L) obtained for the control groundwater sample. The NSDWQ limit value for total bacteria in drinking water is nil/100mg/L, thus, the total bacteria results of the groundwater were not in compliance with NSDWQ limit.

3.10 E.coli

E.coli (Coliform) was absent in all the groundwater samples, which therefore indicates compliance with the Nil/100mg/l *E.coli* value set by NSDWQ. The presence of *E.coli* in water samples is of great concern, as it implies faecal contamination which may pose a health problem (Pipes and Christian, 1984).

3.11 Electrical Conductivity (EC)

The electrical conductivity (EC) result of the dry season groundwater samples was 130.73± 0.98 (µS/cm), which was significantly higher than the EC value of 69.40± 0.34 (µS/cm) obtained for the wet season groundwater samples. Though these values were higher than the EC value of 60.97 (µS/cm) obtained for the control groundwater sample, they were all in agreement with the EC value of 1000 (µS/cm) set by NSDWQ. Ukpong and Okon, (2013) obtained EC range of 89.18 - 103 (µS/cm) for public bore hole water, in their studies of comparatives analysis of public and private bore hole water supply sources in Uruan, Akwa Ibom State of Nigeria.

3.12 Acidity

Acidity value obtained for the wet season groundwater samples was 43.67 ± 1.20, which was significantly higher than the 37.67± 1.45 acidity value obtained for the dry season groundwater samples. These values were higher than the 35.86 acidity value obtained for the

control groundwater sample. Acidity limit value was not stated by NSDWQ.

3.13 pH

The pH value obtained for the wet season groundwater samples was 4.40 ± 0.10 which was significantly more acidic than the 5.40 ± 0.23 pH value obtained for the dry season groundwater samples. These results did not comply with the 7.00 pH value obtained for the control groundwater sample as well as with the 6.5-8.5 pH limit range set by NSDWQ. Agbalagba *et al.,* (2011) and Nwala *et al.,* (2007) also reported similar values in the Niger Delta region of Nigeria.

3.14 Chloride (Cl^-)

The chloride value of 6.80 ± 0.00 (mg/l) obtained for the dry season groundwater was significantly higher than the 5.20 ± 0.11 (mg/l) value obtained for the set season samples. These values though higher than the control groundwater sample, were all in compliance with the 250 (mg/l) limit value set by NSDWQ for chloride in drinking water. These values were also within the range values reported by Nwala, (2007) and Agbalagba *et al.,* (2011).

Chloride usually occurs as NaCl, $CaCl_2$ and MgCl in widely varying concentration, in all natural waters. They may enter water from polluting materials like sewage and trade wastes (Shaikh and Mandre, 2009). NaCl result of the dry season groundwater samples of 8.63 ± 0.03 (mg/l) was significantly higher than the 5.20 ± 0.11 (mg/l) obtained for the wet season groundwater samples. Though, these values were higher than the 4.98 (mg/l) NaCl value obtained for the control groundwater, they were however in conformity with the 250 (mg/l) NaCl value limit set by NSDWQ.

3.15 Alkalinity

Alkalinity of water is its capacity to neutralize a strong acid and it is normally due to the presence of bicarbonate, carbonate and hydroxide compounds of calcium, sodium and potassium (Pandey *et al.,* 2012). Total alkalinity values of the ground water samples were 9.67± 0.33 (mg/l) for wet season samples and 9.83 ± 0.17 (mg/l) for dry season samples. There was no significant difference ($p<0.05$) between the wet and dry season total alkalinity values. Though, NSDWQ alkalinity value was not stated, these values were however in compliance with the 10.05 (mg/l) total alkalinity value obtained for the control groundwater sample.

3.16 Total Hardness

The total hardness value of 12.50 ± 0.29 (mg/l) obtained for the dry season groundwater samples was slightly higher, though not significantly higher than the 11.67 ± 0.33 (mg/l) total hardness value obtained for the wet season groundwater samples. Though, these values were slightly higher than the 6.62 (mg/l) value obtained for the control groundwater sample, they were however in compliance with the 150 (mg/l) total hardness value set by NSDWQ. Ukpong and Okon (2013) reported total hardness range of 12-26 (mg/l).

3.17 Calcium Hardness

Calcium hardness values of 8.00 ± 0.67 (mg/l) and 8.67 ± 0.33 (mg/l) obtained respectively for wet and dry season water sample were not significantly difference ($p<0.05$). Though the NSDWQ for calcium hardness was not stated, these values were higher than the 5.95 (mg/l) calcium hardness value obtained for the control groundwater samples.

3.18 Magnesium Hardness

Results of magnesium hardness of the groundwater samples were 3.67 ± 0.67 (mg/l) for wet season samples and 3.88 ± 0.60 (mg/l) for dry season samples. These results did not indicate significant difference at ($p<0.05$). These results though higher than the 3.00 (mg/l) value obtained for the control groundwater sample, were all in compliance with the 20 (mg/l) magnesium hardness value set by NSDWQ.

3.19 Sulphate (SO_4)

Sulphate value of the groundwater samples was 0.08 ± 0.00 (mg/l) for the dry season samples, which was slightly higher but not significantly higher than the 0.07 ± 0.00 (mg/l) value obtained for the wet season samples. Sulphate was not detected in the control groundwater sample. These values were in conformity with the 100 (mg/l) sulphate limit value set by NSDWQ. Ukpong and

Okon, (2013) reported sulphate value range of 0.38-2.64 (mg/l).

3.20 Bicarbonate (HCO_3^-)

The presence of bicarbonate in water contributes to water total alkalinity concentration (Pandey *et al.*, 2012). Bicarbonate value of the groundwater samples were 9.83 ± 0.17 (mg/l) for the dry season samples which was slightly higher, though not significantly higher than the 9.67 ± 0.33 (mg/l) value obtained for the wet season samples. Bicarbonate value for NSDWQ was not stated, however, these values were in conformity with the 10.02 (mg/l) bicarbonate value obtained for the control groundwater sample.

3.21 Saline and Free ammonia

Saline and free ammonia occurs in water supply as a result of microbiological reduction and can also indicate sewage pollution (Dieter and Moller, 1991). Saline and free ammonia were not detected in all the ground samples. These results were therefore in compliance with the 0.05 (mg/l) Limit value set by NSDWQ for saline and free ammonia in potable water samples.

3.22 Nitrate (NO_3)

The nitrate value of 0.17 ± 0.11 (mg/l) obtained for the wet season groundwater samples was slightly higher but, not significantly higher than the 0.02 ± 0.00 (mg/l) nitrate value obtained for the dry season groundwater samples. These values, though, higher than the 0.01 (mg/l) nitrate value obtained for the control groundwater sample, were all in agreement with the 50 (mg/L) limit value set by NSDWQ for nitrate in drinking waters. Ukpong and Okon, (2013) also reported similar nitrate values.

3.23 Silica

Silica results revealed 0.04 ± 0.00 (mg/l) for the dry season groundwater samples and 0.02 ± 0.00 (mg/l) for the wet season groundwater samples. These values did not show significant difference ($p<0.05$). Silica Limit value was not stated by the NSDWQ. However, these values were slightly higher than the 0.00 (mg/l) silica value obtained for the control groundwater samples.

3.24 Dissolved Free Carbon Dioxide (CO_2)

The dissolved free CO_2 values of the groundwater samples were 30.33 ± 0.88 (mg/l) for wet season and 31.33 ± 0.87 (mg/l) for dry season. These values were not significantly different ($p<0.05$). Though the dissolved free CO_2 limit value was not stated by NSDWQ, these values were slightly higher than the 32.50 (mg/l) dissolved free CO_2 value obtained for the control ground water sample. Decomposition of organic matter by microbes leads to formation of CO_2 in water, which increases the concentration of carbonate and bicarbonate, increasing the level of alkalinity in groundwater (Vyas *et al.*, 2008).

3.25 Total Iron (Fe)

The concentration of total iron in all the groundwater samples were at a not detectable level which were in compliance with the 0.3 (mg/l) limit value set by NSDQ for total iron in drinking waters.

IV.CONCLUSION

The results from this study are supportive with the conclusion that, the physicochemical parameters had higher values during the dry season which could be attributed to increased industrial activities carried out by the chemical industry during the dry season and also by the fact that during the wet season, run off by rain water washes off most of the pollutants from the chemical industry. Average physicochemical concentrations of the seasonal ground water samples of the chemical industry were all in compliance with the standards set by NSDWQ except for pH which had an average seasonal concentration of 4.90 ± 0.17 which was not in compliance with the 6.5 - 8.5 pH limit value set by NSDWQ. pH however does not have any direct adverse effect on human health. On the other hand, bacteriological results of the groundwater samples indicated the presence of total bacterial concentration of 5.34 ± 0.17/(100mg/l) which was above the NSDWQ stipulated value of Nil/(100mg/l). Based on this result, the groundwater poses human health risk to the consumers. It is therefore necessary to disinfect the groundwater before human use so as to avoid the risk of contracting water-borne diseases.

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Microwave Assisted Synthesis, Characterization and Antibacterial Activity of 2-Chloromethyl Benz imidazole Derivatives

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ABSTRACT

Objective-the objective of present research work to synthesize and screen novel 2-chloromethyl-1-h-benzimidazole derivative for antibacterial activity. Method-2-chloromethyl-1-H-benzimidazole was prepared by condensing 2-chloromethyl-1-h-benzimidazole with different aromatic amines and heterocyclic. The synthesized compounds were screened for their antibacterial activity against stap. aurious by well plate method. 2-chioromethyl benzimidazole can be synthesized by the reaction of o-phenylenediamine with chloroaceticacid. This on reaction with substituted anilines in presence of ethanolic KOH gives corresponding benzimidazolederivatives.The synthesized compounds were characterized by TLC & IR data.

Keywords: 2-chloromethyl benzimidazole, o-Phenylenediamine, chloroacetic acid aniline.

I. INTRODUCTION

In the field of science of technology, medicinal chemistry has been a fascinating subject. The rapid development in the last 7 decades has been truly a challenging and very exciting. Medical chemistry according to Burger, tries to be based on the ever inceasing hope that biochemical rationals for drug discovery may be found.

Medicinal chemistry is the branch of science, which has remarkable value for synthesis of novel drugs with intense therapeutic activity. It concern with discovery, development, identification and interpretation of mode of action of biologically active compounds at molecular level.

These developments have provided new challenges and opportunities for drug research in general and drug desing in particular. Pure organic compounds, natural or synthetic products are the chief source of agents for the cure, the mitigation or the prevention of disease today. The major objectives of the medicinal chemists are transformation of path biochemical and physiological data into a 'chemical language' with the aim of designing molecules interacting specifically with the derailed or degenerating processes in the diseased organisms.

The development of chemotherapy during past 60 years constitute one of most important therapeutic advances in history of medicine and antibacterial drugs are the greatest contribution of present century to therapeutics. Potential therapeutic targets are being disclosed with increasing frequency and the exponential growth will continue during the next decates.

The benzimidazole contain a phenyl ring fused to an imidazole ring, was shown in structure (1).

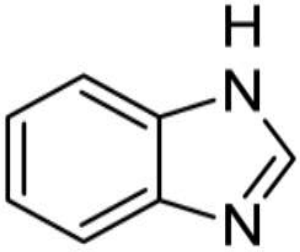

Figure 1. Benzimidazole

Compounds bearing Benz imidazole nucleus have been of great interest to synthetic and medicinal chemists for a long time due to their unique chemical and biological properties. Historically the first Benz imidazole was prepared in 1872 by Hoebrecker who obtained 2, 5 or 2, 6-dimethyl Benz imidazole by the reduction of 2-nitro-4-methylacetanilide. Several years later Ladenburg obtained the same compound by refluxing 3, 4-diaminotoluene with acetic acid. The Benz imidazole is known also as Benz imidazole or benzoglyoxalines. Thus, Benz imidazole according to this nomenclature would be called methyl-o-phenylenediamine and 2-methyl Benz imidazole.

This tautomerism is analogous to that found in the imidazole and amidines. In fact, the Benz imidazole may be considered as cyclic analogs of the amidines.

Benz imidazole is a aromatic heterocyclic compound having imidazole ring fused to benzene. The most prominentBenz imidazole compound in nature is N-ribosyl –dimethyl Benz imidazole, which serves as an axial ligand for cobalt in vitamin B12. The nucleus is present in some drugs such as proton pump inhibitors and anthelmintic agents.

Mebendazolethiabendazole which have anthelmintic and antifungal properties are Benz imidazole class of compounds. Benz imidazole and its derivatives are widely used as intermediate in synthesis of organic target compound ncluding pharmaceuticals, agrochemicals, dyes, photographic chemicals, corrosion inhibitors , epoxy curing agents , adhesives and plastic modifiers Benz imidazole is a white to slightly being solid; melting at 145-150 c, boils at 360°c, slightly soluble in water , soluble in ethanol. Benz imidazole and its derivatives are used in organic synthesis and vermicides and fungicides.

Melting points of the synthesized compounds were determined by open capillary method and were uncorrected.IR spectral analysis was carried out using FTIR-410, Jasco at Rajarambapu college of pharmacy, Kasegaon.

Physical properties of Benzimidazole:

1) Benzimidazoleshaving high melting points.The introduction of substituents at 1-position lowers the melting point.
2) Benzimidazoles are usually soluble in polar solvents and sparingly soluble in non-polar solvents.
3) Benzimidazoles are weakly basic, being somewhat less basic than imidazole.
4) Benzimidazoles are also sufficiently acedic to be generally soluble in aq. alkali and form N-metaliccompounds.The acidic properties of benzimidazole, like those of imidazole, seem to be due to stabillisation of the ion by resonance.
5) The pKa value of BenzimidazolespKa=5.30 for 2-methyl Benzimidazoles and pKa=12.33 for 2-amino Benzimidazoles.

Role of Pharmaceutical Chemistry in Drug Discover:

Pharmaceutical chemistry plays important role in identification of lead compound it is also known as Hit. So 1) Identification of lead, 2) Optimization of lead, 3) Lead Development these are most important steps in discovery.

Further chemistry and analysis is necessary, first to identify and “triage” compounds that do not provide series displaying suitable SAR and chemical characteristics associated with long-term potential for development, then to improve remaining hit series with regard to the desired primary activity, as well as secondary activities and physicochemical properties such that agents will be useful when administered in real patients.

The next through final synthetic chemical stages involve production of lead compound in suitable quantity and quality to allow large scale animal and eventual, extensive human clinical trials. This involves the optimization of the synthetic route for bulk industrial production, and discovery of the most suitable drug formulation.

Review of Literature:

1) Z. Kazimirerczuk, M. Anderzejewska ET; al. Are evaluated the synthesized compound for their activity agaist 4 mycobacterium strains.
2) A.IdhayaDhullaet. Al.(2011) reported synthesis of Benz imidazole derivative and their antimicrobial activity.
3) R.K.Bansal (2005) Heterocyclic chemistry reported I.R and NMR interpretation.

Need of Investigation:

Many important biochemical compounds and drugs of natural origin contain heterocyclic ring structure .Among thisee. gcarbohydrate, essential amino acid, vitamins, alkaloids, glycosides, etc the presence of heterocyclic structures in diverse type of compounds is strongly indicative type of the pharmacological activity and recognition of this is reflected in efforts to find useful synthetic drugs.

The development of resistant to current antibacterial therapy continuous to stimulate search for more agents, the increasing clinical importance of drug resistant and bacterial pathogens has lent additional urgency to microbiological research and development of novel biologically active compounds. Hence the aim of this work is to synthesize some novel 2-chloromethyl 1-H-Benzimidazole derivative and carry out antibacterial potentials with good activity and less toxic effects .the biological activity of the compounds containing basic moiety have been well documented.

(1) The present work describes the 2-chloromethyl 1-H-Benzimidazole and their derivatives in search of bioactive molecules.
(2) Work also emphasized on the structural elucidation and pharmacological screening for antibacterial activity of synthesized compounds.

Objectives:-

The discovery and development of pharmacologically active molecules has been guided not only by classical medicinal chemistry but also by the use of sophisticated mechanistic approaches and biochemical assay.

The reviews clearly emohasizes the importance of heterocyclic in naturally occurring as well as synthetic agents and does an important class itself possess diversified pharmacological actions such as antimicrobial, antiprotozoal, antimalarial and ant allergic etc. This point encouragement further investigation in the field. The logic supporting the work presented in this dissertation was formulated, bearing in mind that the biological activities of known moieties and attempting certain structural modification or adaptation in light of the recent trends in drug research incorporating newly emerged pharmacophores on existing moiety.

The development of resistance to current anti-bacterial therapy continues to stimulate the search for more effective agents. The increasing clinical importance of drug resistant and bacterial pathogens has lent additional urgency to microbiologicl research and development of novel biologically active compounds. Hence in the present study we plan synthesized some novel benzimidazoles with good activity and less toxic effect.

II. METHODS AND MATERIAL

Microwave Technique

Some derivatives were synthesized by using Microwave technique. This technique also refers as Green chemistry.By this technique required time was less and yield was higher as compare to conventional technique.

Melting points were taken by using Thiele's tube apparatus and were uncorrected. Thin layer chromatography was used to assess the course of reaction and the purity of intermediate and final compounds, giving single spot on TLC plate (silica gel) , using various solvent systems. Visualization of spot on plate was done by exposure to iodine vapours.

Infrared(IR) spectra were recorded in KBR disc on aJasco FT-IR-410 spectrometer.

Chemicals

All chemicals and solvents werw produced from commercial sources and purified and dried using standard procedures from literature whenever required. Chemicals used for the synthesis were enlisted below with their manufacturer mentioned in parentheses.

O-phenylenediamine - Research laboratory, Islampur

Hydrochloric acid - Research laboratory, Islampur

Chloroacetic acid - Research laboratory, Islampur

Ethanol - Research laboratory, Islampur

Potassium hydroxide - Research laboratory, Islampur.

Ammonium hydroxide - Research laboratory, Islampur

Dimethyl sulfoxide (DMSO).- Research laboratory, Islampur

Preparation of TLC reagent:

For the identification of benzimidazoles using thin layer chromatographic technique the reagent used is a mixture of Chloroform and methanol was taken in a ratio of 9:1as shown in fig no. 2

Figure 2. TLC plate of intermediate

Mobile phase: Chloroform:Methanol-9:1
Rf value = Distance travelled by solute/ Distance travelled by solvent
= 6/9
= 0.66

Methodology

Scheme of the Experiment:

O-Phenylenediamine was condensed in microwave by using chloroacetic acid in the presence of 5N NaCl to give 2-chloromethyl-1-h-benzimidazoles using different aniline derivatives.

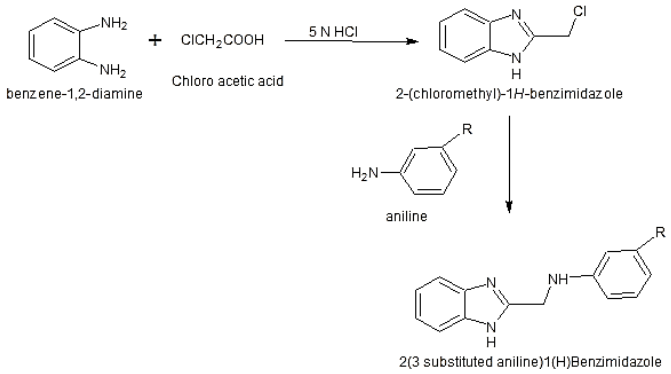

Figure 3. Scheme of the Experiment

1st step-Procedure-

In a 250ml three necked flask a solution containing 3gm of chloroacetic acid and 3gm of O-phenylenediamine dissolved in a 30ml of 5N HCL. The mixture was heated for 35 min. on 7th power with constant stirring in microwave. The reaction mixture is cooled to about 5˚c. It was neutralized with aq. Ammonium hydroxide or dil. NaOH. The product was filtered and washed with water to remove traces of chloromethyl-1 H-benzimidazole derivatives by using different aromatic amines and heterocyclic and to evaluate them for antibacterial activity.

Scheme-1

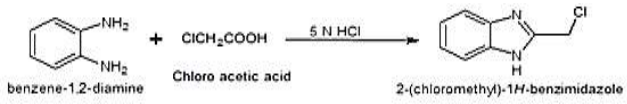

Figure 4. *1st step*

Scheme-2

2nd step- procedure

General procedure for synthesis of 1-H-benzimidazole 2-yl-methyl-amine derivatives.

In the ethanolic KOH solution 2-chloromethyl benzimidazole and substituted anilines were added and it was heated for 35 min. on 7th power in microwave.Hot mixture was poured in crushed ice with constant stirring. Seperated solid was filtered, dried and recrystallized from ethanol .The yields ranged from 30-45%.

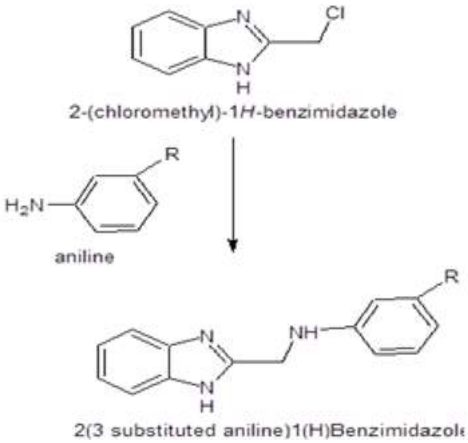

Figure 5. 2nd step- procedure

Physiochemical data of intermediate and derivatives (1A, 1B, 1C):

Sr. no.	Comp. code/name	R	Theroti cal yield	Practi cal yield	% yield	Melting point	RF	Mol. wt
1	Intermed iate	R	3.54gm	2.2gm	62.14%			
2	1A)	-N=N-C_6H_5	3.93gm	2.80g m	71.24%			
3	1B)	-Br	1.81gm	1.42g m	77.34%	154°C	0.61	122
4	1C)	-O-CH_3	1.46gm	1.10g m	75.34%	150-154°C	0.61	122

Table 1. Physiochemical data of intermediate and derivatives

I.R of compound 1A N(1-H-benzimidazole-2ylmethyl)3-phenyldiazonyl aniline:

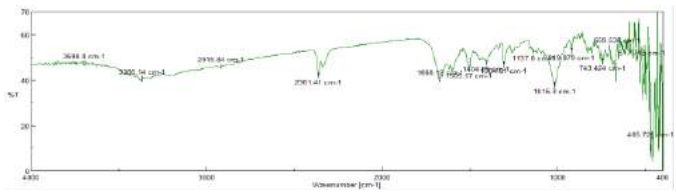

Figure 6. I.R. spectrum of comp. 1A

Sr.no.	Functional Group	Peak
1	N=N	1505
2	C=C	1668
3	NH	3366
4	C=N	1668
5	Phenol	1404

Table 2. I.R spectral data of comp. 1A:

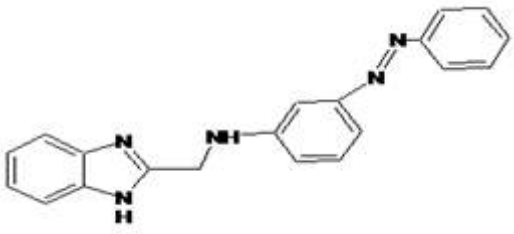

Figure 7. Structure of comp. 1A

I.R of comp. N(1-H-benzimidazole 2ylmethyl) 3-bromo aniline

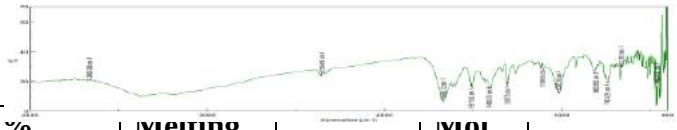

Figure 8. I. R. spectrum data of compound 1B

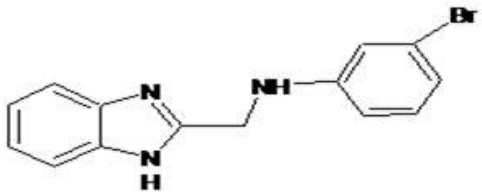

Figure 9. Structure of compound 1B

Sr.no.	Functional Group	Peak
1	C-Br	600-500
2	CH2	1408
3	C=C	1511
4	C=N	1408
5	C-N	1109

Table 3. I.R. spectral data of compound 1B

I.R.of comp. N(1-H-benzimidazole-2ylmethyl) 3-methoxy aniline:

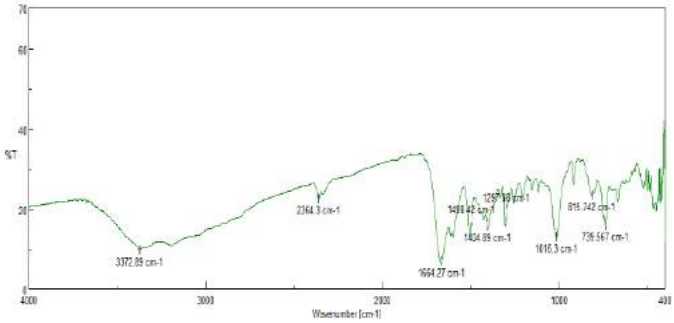

Figure 10. I.R. spectrum data of comp. 1C

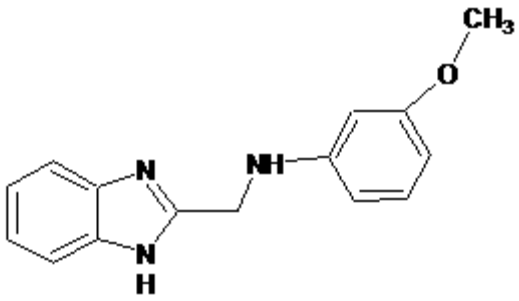

Figure 11. Structure of compound 1C

Sr.no.	Functional Group	Ranges
1	C=C	1498
2	N-H	3372
3	CH2 str.	1498
4	C=N	1664

Table 4. I.R. spectral data of compound 1C

Antibacterial Activity

Antibacterial screening:

Many explanations have been afforded for origin of life on the earth. One of the more acceptable of these proposals suggests that life originated in the sea following millions of years of chemical evolutionary process. According to this hypothesis, the inorganic compounds of atmosphere, under the influence of ultra violet light, electric discharges and/ or high temperature, interacted to form organic compounds which precipitated into the sea, were they accumulated. These organic compounds, subjected to addition physical effects of the environment, combine to form amino acids. The amino acids interact to form peptides, polypeptides and other more complex organic substances which served as the precursor's of the first form of life.

Microorganisms are closely associated with the health and welfare of human beings, some microorganisms are beneficial and others are detrimental. For example, microorganisms are involved in the making of yogurt, cheese and wine, in the production of penicillin, interferon, and alcohol and the processing of domestic and industrial waste. Microorganisms are classified a eukaryotic viz algae, protozoa, fungi and slime molds(sometimes included in fungi) and prokaryotes viz eubacteria, archaebacterial and cyanobacteria. Viruses are classified as microorganisms but they are sharply differentiatedfrom all cellular forms of life. A viral particle consists of a nucleic acid molecule, either DNA, or RNA, enclosed in a protein and capsid.

The large number of bacteria on the skin and in digestive tract. The majority of these bacteria are rendered harmful and beneficial by the protective effects of the immune system, a few are pathogenic bacteria and cause infectious diseases including cholera, syphilis, anthrax, plagueand leprosy. The most common fatal bacterial disease are respiratory infection with
Tuberculosis.

Antibacterial Screening - Materials and Method

Chemicals

All chemicals and solvents were procured from commercial sources, purified andsterilized using standard procedures from literature whenever required. Nutrient agar medium (Research lab, Mumbai)

Dilution of the compounds

All the synthesized compounds were dissolved in dimethyl sulfoxide (DMSO) so as to get concentration of 200µg/ml and standard drugs Ciprofloxacin in DMSO as aconcentration of 10mg/ml.

Preparation of nutrient agar medium slant:

Nutrient agar medium 112 mg and agar powder 100 mg was dissolved in 4 ml distilled water, boiled and then poured in the test tube then plugged with cotton and sterilized in autoclave at 15lbs pressure (121^0C) for 15 min. after sterilization thetubes containing the nutrient agar medium were kept in inclined position for 30min.then on the surface of slants pure culture of bacillus Substiles, Escherichia coliwere streaked in aseptic condition and incubated at 37^0C for 24 hrs.

Antimicrobial Drug sensitivity Tests : Antimicrobial sensitivity test have been carried out by using disc-diffusion method, performed in nutrient agar for bacterial and saboraud's agar for fungi. Inoculation of suspension of bacteria and fungi on culture media: Sterile, non-toxic cotton swab were dipped in to the standardized inoculums (turbidity as adjusted as to obtained confluent growth on the Petri plate) and then the entire agar surface of the plate was streaked with the swab three times, turning the plate at 60°angle between streaking. Then the streaked inoculums were allowed to dry for 5-15mins with lid in place.

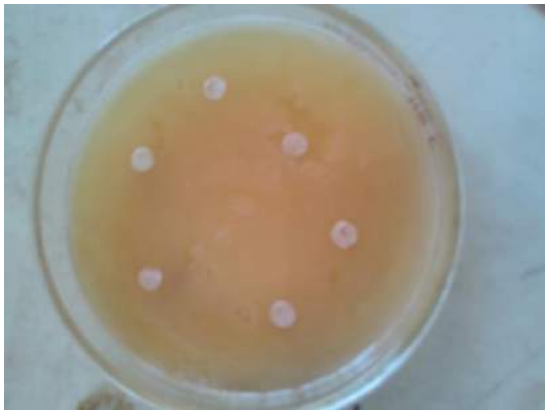

Figure 12. Inoculation of suspension of bacteria and fungi on culture media

Sterile paper disc made by punching whatman (No.41) paper were dipped separately in to the solutions containing synthesized drug (300µg/ml of DMSO) and standard drug ciprofloxacin (10 mg/ml of DMSO.) & Flucanazole (10 mg/ml of DMSO) in aseptic condition with help of sterile forceps and were then placed on the surface of inoculated culture media after which the plates were kept in refrigeration for 30 mins. For the diffusion of the drug from the paper disc in to the culture media. After 30 mins the plates were incubated at 37^0C.

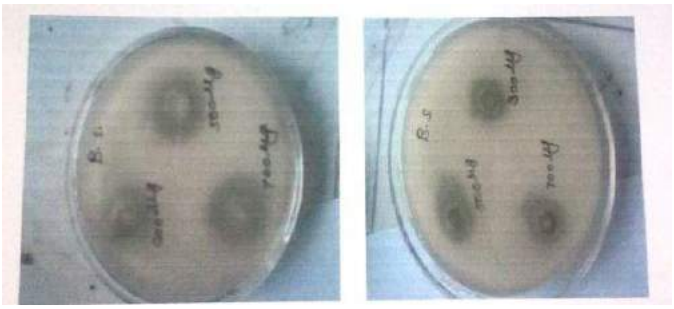

Figure 13. Standard (ciprofloxacin) derivative (1A)

SR. NO.	COMP. NO	NAME OF ORGANISM	
		E. Coli	B.Subtilis
1	1A	++	++
2	Ciprofloxacin	+++	+++

Table 5. Zone of inhibition

Below 6 mm it shows negative activity (-)
Between 6 mm -9 mm (and) sign. (Slight activity)
In between 9 mm – 12 mm (++) sign. (Moderate activity)

In between 12 mm-16mm (+++) sign. (Higher activity)

III. RESULTS AND DISCUSSION

Result

The antibacterial activities of synthesized (1A) was carried out by using disc diffusion method and screened against Bacillus subtilis, E. Coli microorganism using standard ciprofloxacin (300µg/ml) and derivative compound 300,500,700 per ml.

Discussion

Novel compounds 1A, 1B and 1C were found to show antibacterial activity when checked with Ciprofloxacin as standard .Compound 1A showed moderate antibacterial activity against Gram positive, Bacillus subtilis, while higher activity against Gram negative (Escherichia-coli).

IV. CONCLUSION

Evaluation of the novel compounds established that some of the synthesized comp. N(1-H-benzimidazole-2ylmethyl)3-phenyldiazonyl aniline, N (1-H-benzimidazole-2ylmethyl) 3-bromoaniline, N (1-H-benzimidazol-2ylmethyl) 3-methoxy aniline. showed antibacterial activity which was not found to be less than that of ciprofloxacin in case of Gram positive (Bacillus subtilis) while moderate activity against Gram negative (E.coli).

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The Effect of Temperature on the Migration of Phthalate Plasticizers from Plastic Sachet into Water

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ABSTRACT

Phthalates are compounds used principally as plasticizers, to impact flexibility, workability and durability to polymers used to contain consumer products such as water etc. These phthalates are not chemically bound to polymers; hence they are easily released and migrate into the containing consumer product. The leaching may take place in harsh conditions such as under the sun among others. Hence the "PA" sachet water was used as a case study. PA sachet water was subjected to different room temperatures; 25 ^{o}C, 45 ^{o}C, and 65 ^{o}C for 8 hours each day for 5 days. Liquid-liquid extraction of the phthalates from the different samples of water was carried out using dichloromethane. These samples were analyzed for benzyl butyl phthalate (BBP), di-butyl phthalate (DBP), di-2-ethylbutyl phthalate (DEHP), di (n-octyl) phthalates, DNOP, diisononyl phthalates (DINP using UV-VIS spectroscopy and GC-MS. The results showed that there was no leaching of phthalates into the water when the water was subjected to room temperature up to 65^{o}C.

Keywords: Liquid-Liquid Extraction; Water; BBP, DEHP, DINP

I. INTRODUCTION

Phthalates are used as plasticizers in PVC plastics. As the phthalate plasticizers are not chemically bound to PVC, they can leach, migrate or evaporate into indoor air and atmosphere, foodstuff, other materials, etc. (Heudorf et al., 2007). Despite the improved qualities conferred by the addition of plasticizers, plastic materials exposed to sun, rain, snow, etc undergo degradation and plasticizers (primarily phthalates) are released from the plastic (Přemysl et al., 2005). There are multiple human exposure routes for phthalates including oral, inhalation, ingestion, dermal, and intravenous—through transfusions and other medical devices and procedures (Schettler et al., 2006). Some phthalates are reproductive, respiratory and developmental toxicants in animals and suspected endocrine disruptors in humans (Lyche et al., 2009; Jasna et al., 2007; Bornehag, et al., 2004; Hoppin et al., 2004; Rishikesh et al., 2013; Fromme et al., 2012; Kwak et al., 2009; Crinnion et al., 2010; Lorz et al., 2006; Wormuth et al., 2006; Jaakkola and Knight, 2008).

The aim of the present study was to assess influence of temperature on the rate of phthalate (benzyl butyl phthalate (BBP), di-butyl phthalate (DBP), di-2-ethylbutyl phthalate (DEHP), di (n-octyl) phthalates, DNOP, diisononyl phthalates (DINP) migration from plastic sachet containers into the water. The analytees of interest are shown in Figure 1.

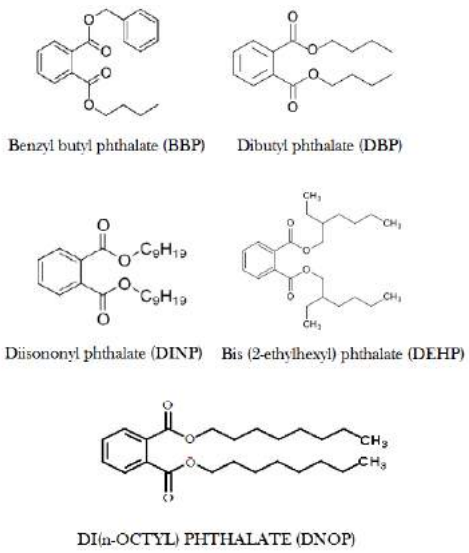

Figure 1. Structures of Analyses

II. METHODS AND MATERIAL

2.1 Reagents and materials

Phthalates were supplied from Supelco (UK). Dichloromethane was supplied from Labscan and anhydrous sodium sulfate was purchased from Merck. The instruments used were gas chromatograph (Shimadzu GC-2010) coupled with a mass spectrometer (Shimadzu QP 2010) and an autosampler (AOC 20i, Shimadzu Corporation), and Spectra UV-VIS Autoscanning spectrophotometer, UV-2602 (Labomed Inc.)

2.2 Sample preparation

Commercial sachet water with a brand name "PA" was purchased from local markets (Bayelsa State, Nigeria) and used as the case study. The sachet water was divided into three groups and the groups were respectively subjected to room temperatures of 25 ^{o}C, 45 ^{o}C, and 65 ^{o}C. In order to maintain these temperatures, samples were kept in a room with appropriate number of electric bulbs in each case. Samples were left in the room for 8 hours (10 am – 6 pm) for 5 days. Analytes (phthalates) were extracted from the aqueous phases into the organic phases (dichloromethane) by using a separatory funnel. In order to increase the efficiency of extraction, 20 mL of water was extracted with 60 mL (20 mL x 3) of dichloromethane. The organic phase was then pre-concentrated by using a stream of nitrogen gas to a volume of 5 mL. Standard dichloromethane and the three samples were ready for UV scan and GC-MS analysis.

2.3 Analytical determination

The pre-concentrated samples were scanned with UV Spectrophotometer. GC-MS determination of benzyl butyl phthalate (BBP), di-butyl phthalate (DBP), di-2-ethylbutyl phthalate (DEHP), di (n-octyl) phthalates, DNOP, diisononyl phthalates (DINP) was performed. Separation of target compounds was effected on a TraceGold TG–5MS 5% diphenyl–95% dimethyl polysiloxane capillary column (30m length, 0.25mm i.d., 0.25mm film thickness) from Thermo Scientific. Instrumental conditions include the following oven program: the column temperature was initially set at 80 ^{o}C for 2 min, and then increased at a rate of 17 ^{o}C/min up to 320 ^{o}C. The column temperature was maintained at 320 ^{o}C for 5 min. The mobile phase (high purity helium gas) flow was maintained at a constant rate of 1.2 mL/min. The ion source and transfer line temperature was set at 280 ^{o}C and at 320 ^{o}C respectively. The injector temperature was maintained at 150 ^{o}C. Mass spectra were obtained using electron impact ionization at 70 eV. The identification of target compounds was based on the relative retention time.

III. CONCLUSION

Considering the ever growing use of plastic sachets for commercial water and the poor storage conditions, especially, under the sun, there is a possibility of these phthalates leaching into the water when they are heated up in the sun. PA sachet water was subjected to room temperatures of 25^{o}C 45^{o}C, 65^{o}C and their UV and GC-MS spectra show that no leaching of phthalates take place even up to 65^{o}C of room temperature; suggesting that storing sachet water under the sun poses no health risk in respect of phthalates plasticizers.

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Removal of Ammonium Nitrate from Aquaculture by Sorption Using Zeolite

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ABSTRACT

Zeolite 4A was found to be useful and feasible method for removal of Ammonium nitrate from aquaculture waste water. These zeolites showed excellent sorption by ion-exchange. They can be successfully regenerated by using 0.1 M NaCl. The regenerated zeolites showed similar sorption capacity as virgin upto 3-4 cycles. During the following cycles their surface gets saturated with permanent sorption of nitrogen which reduces their sorption capacity. Modification of zeolite surface with strong acids leads to an increase (0.2602 gm of ammonium nitrate / gm of zeolite) in sorption capacity for ammonium nitrate. This shows that zeolites are excellent materials for removal of nitrogenous material from aquaculture waste water.

Keywords : Ammonium nitrate, Aquaculture waste, Modification, Regeneration, Sorption, Zeolite 4A.

I. INTRODUCTION

Concentration of nitrogenous material in aquaculture is highly important for proper growth and survival of aquatic animals [1]. The nitrogenous material is released by excretion of aquatic animals (viz., urine, faecal material), food residue, decaying of dead, etc [2]. Accumulation of ammonium, nitrate and nitrite materials leads to depletion of dissolved oxygen in water which results in growth of harmful algae in aquaculture [3]. The presence of unionized ammonia at concentration level of 0.06 ppm and oxygen level below 5.0 ppm could damage gill tissues (hyperplasia), lead to gills diseases, other tissue lesions and reduced growth rate in aquatic animals [4]. This would lead to death of fishes and shrimps in aquaculture. As the concentration of nitrogen increases, growth of aquatic animals slows down [5]. The aquatic nitrogen is commonly present in the forms of ammonia/ammonium (NH^{3+}/NH^{4+}), nitrate (NO_3), nitrite (NO_2), and organic nitrogen [6].

Efficient recycle of aquaculture water requires removal of ammonia and nitrogenous compounds [7]. The range of nitrogen in aquaculture varies from 20 to 70 mg N/L [8]. This is composed of 60-70 % ammonium nitrogen and 30-40% of organic nitrogen [9]. This concentration is very high and would have harmful effect on aquatic life. This makes removal of these nitrogenous material and purification of water highly important for aquatic life. Various technologies have been developed for TAN removal like biological nitrification, chemical de-nitrification, catalytic liquid phase oxidation, air stripping, membrane separation, selective ion exchange [10]. Biological nitrification has been preferred for aquaculture treatment uptill now due to its low cost as compared to physical/chemical process [11] . Other most common procedures for removal of nitrogenous waste and water purification are water aeration treatment, sorption using zeolites and other components, use of formalin and bacterial products for the removal of aquatic nitrogen [12]. Aeration showed lower removal rates for total ammonium nitrogen (TAN) [13]. The nitrogen compounds from water can be removed by adsorption using artificially prepared zeolites which acts as ion exchange media [14].

Treatment of nitrogen containing water by adsorption with zeolites is an important due to ease of treatment and low cost processing. Though natural zeolites are available, but their low sorption capacity makes them unacceptable for real life application [15]. Artificially prepared zeolites can be economical as ion exchange resin in aquaculture

waste water treatment [16]. Zeolites are three dimensional micro porous crystalline solids. Their ion exchange property and thermal stability make them highly useful in waste water treatment [17]. Treatment of aquaculture waste water using zeolites is a standard practice in south east Asia [18]. Modification of these zeolites will make them more attractive by increasing their ion exchange property and ability of selective removal of ammonium, nitrate and nitrite ions [19]. The ion exchange capacity in Zeolite is due to deficiency of positive charge generated by presence of aluminum (Al^{3+}) and substitution for silicon (Si^{4+}) [20]. Negative charge on the zeolites is balanced by NH^{4+}, Na^{+}, K^{+}, Ca^{2+} or Mg^{2+}. Depending upon the interaction capacity; cations in the Zeolite can be exchanged with those present in liquid solutions.

Current study is focused on removal of nitrogenous compound (ammonium nitrate) by using zeolites. The parameters (natural Zeolite and modified Zeolite such as initial ammonium nitrate concentration, pH, NaCl dose) and operating conditions affecting removal of ammonium nitrate by selected zeolites and modifications (Modification of Zeolites with strong acid) will be optimized.

II. METHODS AND MATERIAL

Experimental Setup

Materials

Zeolite (chemical formula: $Na_{16}(Al_{16}Si_{32}O_{96}).16H_2O$, purity: 84% , Surface charge is negative, particle dimension : $4A^0$) grade was obtained from Chemicals India Ahmednagar Maharashtra India . H_2SO_4 98 % pure synthesis grade was obtained from Fisher Scientific. NaCl (extra pure AR grade) was obtained from Sisco Research Laboratories Pvt. Ltd. Ammonium nitrate was obtained from Lobo Chemie Pvt. Ltd. Mumbai (M.W 80.04 purity 98.5 %).

Sorption Studies

An experimental setup was consisting of cylindrical column (1 cm in diameter, 20 cm in height) was prepared, as shown in Figure (1)

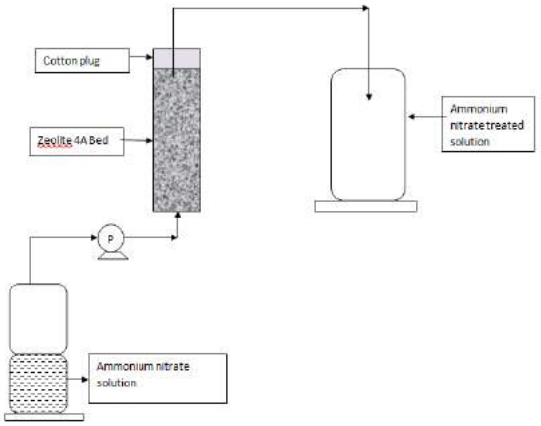

Figure 1. Schematic diagram for Experimental set up

Zeolite regeneration

Zeolite column fed with 0.1 M NaCl solution for three hours. The performance of Zeolite 4A was analyzed for repetitive use, and the sorption capacity is measured.

Zeolite modification

25 gm of Zeolite was kept in H_2SO_4 solution of predetermined concentrations for 16 hr. Treated Zeolites filtered and washed thoroughly with distilled water so as to obtain water with neutral pH. Obtained Zeolites were dried in vacuum oven for 6 hr at 80°C and used in sorption studies.

III. RESULTS AND DISCUSSION

Selection of material

Zeolite 4A is like a clinoptilolite, which has a high cations exchange capacity [21]. It possesses crystalline structure, high porosity, and three dimensional structures. It contains aluminosilicates from the alkali (mainly Na and K) and alkaline- earth (mainly Ca) metals [22]. Their crystal structure is based on a three dimensional framework of $(SiAl)O_4$ tetrahedral with all four oxygen shared by adjacent tetrahedral [23]. As the result, they have a channel structure with molecular dimensions of 4Å [24]. Some of the Si^{4+} are substituted by Al^{3+}, the total net negative charge is balanced by framework containing exchangeable cations mainly Na^{+}, K^{+}, Ca^{2+} or Mg^{2+} [25]. These cations are loosely held within the central cavities and surrounded by water molecules from sides [26]. These water molecules are loosely held in the pores. The Zeolite 4A can be reversibly dehydrated and their cations can be

readily exchanged [27]. Unlike most other tectosilicates, Zeolite 4A has large vacant spaces or cages in their structures that allow space for large cations and even for relatively large molecules or cations groups such as water, ammonia, carbonate and nitrate ions [28]. Due to these properties, Zeolite 4A is an ideal material for sorption based separation of nitrogenous material. It would provide superior sorption capacity and would be perfect material for separation of nitrogenous material from aquaculture waste water.

Ammonium nitrate contains both ammonium and nitrate group of nitrogenous material in single molecule. Its toxicity is one of the critical factors, contributed by enormous demand for high quality water by hatcheries and other freshwater phases of aquaculture. In practice there is a potential initial build up of ammonia, nitrite and nitrate during biological treatment of aquaculture water. Concentration levels of nitrate-nitrogen in excess of 0.2 mg/1 (ppm) lead to methemoglobinemia and heavy mortalities [29]. Hence we thought it would be necessary to study the sorption of ammonium nitrate as a representative of nitrogenous compounds using zeolites.

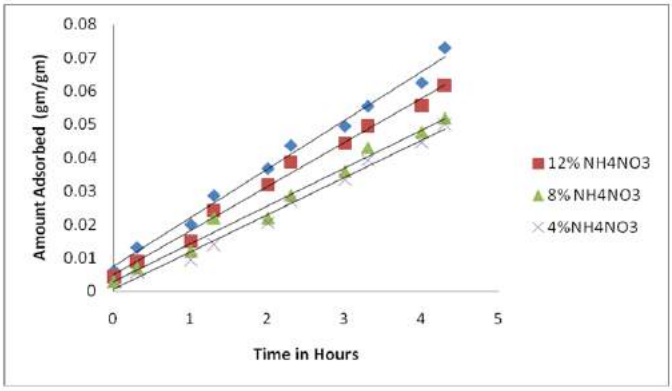

Figure 2 : Sorption of ammonium nitrate on Zeolite Vs Time

It can be seen from Figure that sorption increased linearly with increase in contact period. This is obvious that with increase in contact tim, more and more amount of nitrogenous material. This would lead to interaction between zeolite and increase . Higher concentration lead to higher sorption, due to increase in interaction.

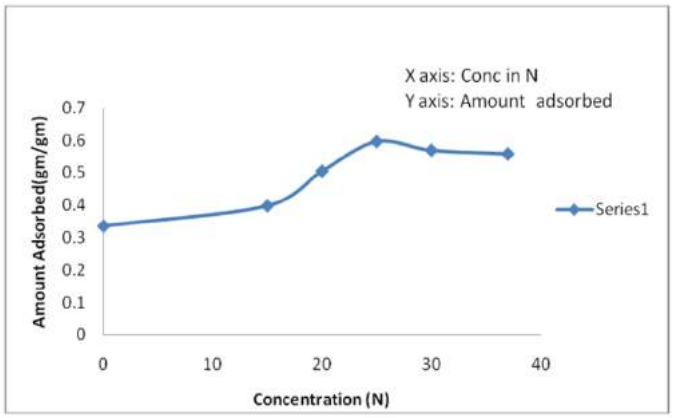

Figure 3. Graph of Amount Adsorbed(gm/gm)Vs Concentration H_2SO_4 (N)

This graph was obtained by taking amount adsorbed v/s concentration of H_2SO_4. Bell like structure is observed adsorption increases at the 25N and at other concentrations the adsorption is decreased this is due to the change in the structure of Zeolite by acid treatment. The removal efficiency of ammonium ion decreases with an increase in concentration [30] **.** Adsorption isotherm for NH^{4+} ion exchange data on zeolites 4A fitted better to Langmuir model at the concentration of 15N to 25N .This might have occur due to the change in the surface adsorption . The change in surface structure was seen due to the acidic treatment crystallization was occurred, due to this the adsorption capacity might have been changed [31].

Regeneration and reuse of zeolites: we have regenerated the Zeolite column by treating it with 0.1 M NaCl by passing through it for 3 hours. Regeneration of zeolites bed can be done by NaCl solution sodium ion gets exchanged with the ammonium ion. [32] . Regeneration of the zeolite is important because we cannot replace the zeolite by using it once so for the commercial purpose we have to regenerate it .The cost of regeneration of the zeolite is less than that of the replacement of the zeolite [33].we have recycles it 7 times but the adsorption capacity decreases after 3rd time, so we can regenerate it only 3 times zeolites can be regenerated upto certain times [34].

Modification of zeolite: Adsorption of Ammonium nitrate is observed in zeolites if we want to increase more adsorption capacity it should be modified with acid treatment[35]. As we have to adsorb ammonium nitrate we have modified zeolite with strong acid i.e. H_2SO_4 .With modified zeolite we have got 0.2602 more adsorption rate

than normal zeolite 4A . Adsorption in terms of gm of NH_4NO_3/gm of modified zeolite was seen more in 25N (0.5951) than 37N (0.5570), 30N (0.5682), 20N (0.5039) and 15N (0.3914). Change in adsorption is there due to modifications done in the zeolite which increases its adsorption capacity .[36] Crystallization of zeolite structure have occurred due to treatment with the strong acid the colour of zeolite changed from white to yellowish brown .Structural changes occurs when zeolites are treated with different solutions [37].

Figure 4 (a). zeolite just added to strong acid

Figure 4 (b). crystallization after treatment

Figure 4 (c). crystallized and colour changed zeolite

Crystallized and colour changed zeolite.To ensure a high-quality product, diagrams and lettering MUST be either computer-drafted or drawn using India ink. Figure captions appear below the figure, are flush left, and are in lower case letters. When referring to a figure in the body of the text, the abbreviation "Fig." is used. Figures should be numbered in the order they appear in the text. Table captions appear centered above the table in upper and lower case letters. When referring to a table in the text, no abbreviation is used and "Table" is capitalized.

IV.CONCLUSION

Zeolite was found to be excellent materials for removal of niteogeneous material from aquaculture waste waters. They have excellent ammonium nitrate removal but the chemisorptions lead to permanent sorption of nitrogenous material on surface of reducing its sorption capacity. Modification of zeolite with concentrated acid lead to large (0.2602 times) increase in sorption capacity for ammonia. This makes the sorption based removal of ammonium components using zeolite an attractive method.

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Synthesis and Characterizations of N^2,N^4-bis(5-nitro-1,3-benzothiazol-2-yl)-N^6-aryl-1,3,5-triazine-2,4,6-triamine,as Biological Agents

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ABSTRACT

Some novel N^2, N^4-bis (5-nitro-1,3-benzothiazol-2-yl) - N^6- aryl-1, 3, 5-triazine-2, 4, 6-triamine 1a-1l have been synthesized and characterized by elemental analyses IR and NMR spectra. The products tested for their antibacterial activity against gram (+)ve and gram (-)ve bacteria. Introduction of –OH, -NO_2, -Cl and –Br groups to the heterocyclic frame work enhanced antibacterial activities.

Keywords: 1, 3, 5-triazine-2, 4, 6-triamines; Antibacterial activity.

I. INTRODUCTION

Antibacterial and Antiviral diseases are very common in all over the world. The s-triazine based chalcones and their derivatives have been studied extensively because of their wide range of biological activity. The s-triazine[1-6] have been linked with a wide range of therapeutic activities[7-12] such as Antibacterial, Fungicidal, Anticancer, Antitubercular.

Among all heterocycles, nitrogen based heterocycles have specific and unique identity in the world. Pyrimidine, oxadiazole, coumarin, pyrimidine, s-triazine are some of the examples. The research work described here is humble effort to synthesis the nitrogen based novel heterocycles. And study of their pharmaceutical importance in medicinal chemistry.

The study of pyrazoline derivatives has been a developing field within the heterocyclic chemistrybroad spectrum of biological activity[13-20]. Pyrazoline derivatives have been found to be bactericidal[13,14], fungicidal[15,16], and insecticidal agents[17,18]. Asurveyof more recent literature reveals that some pyrazoline derivatives possess cerebroprotective properties[19] and antidepressant activity[20,21].

It is our project to produce new bioactive molecules. Currently used antibacterial agents are not effective due to the resistance developed by the bacterial. And therefore, it is an ongoing effort to synthesize new antibacterial agents.

In view of these observations we have synthesized s-triazine, 4a-m (scheme-1, Table -1) by the condensation of triazine with different aromatic amines. 6-chloro-N,N'-bis (5-nitro-1,3-benzothiazol-2-yl)-1,3,5-triazine-2,4-diamineafforded the title compounds 1a-1l respectively (scheme -1) the series of compounds were characterization by IR and NMR analysis.

II. METHODS AND MATERIAL

Biological Activity

Antibacterial Activity: Antibacterial activity was carried out by broth dilution method. Antibacterial activity was carried out by broth dilution method[22]. Concentrations of 1000, 200, 100, 50, µg/ml respectively (Table 2) of compound 1a-1l.

Antifungal Activity: Same compounds were tested for antifungal activity against *C. Albicans A.Niger and A. Clavatus* at concentrations of 1000, 500, 200, and 100 and 50 µg/ml respectively (Table 2) of compound 1a-1l. The results are recorded in the form of primary and secondary screening. Each synthesized drug was diluted to obtain 1000 µg/mL concentration, as a stock solution.

Experimental Section

Melting points were taken in paraffin bath and are uncorrected. IR spectra were recorded on FTIR-BRUKER spectrometer (V_{max} in cm^{-1}); Purity was checked by TLC using TLC aluminum sheets silica gel 60, supplied by E.Merck. The spots were located by keeping the plates in iodine vapor. 5-nitro-1,3-benzothiazol was prepared by methods as described in contain[23-25].

For 1a compound: IR (kbr): 3454 (-N-H str., sec.amine), 3083(-C-H str., aromatic), 1527 (> C = N- str., ter. Amine), 1350 (C-NO_2 STR.), 1122 (C-S-C str., thiazol), 952 (C-Cl str., aromatic), 808 (disubstituted aromatic),1431 (C = N str., sec.amine).
NMR Spectra: 1H NMR spectra, were recorded in CDCl3 solution on a Bruker Avance DPX 200 MHz spectrometer Chemical shifts are reported as δ (ppm) relative to TMS as internal standard.10.08δ (s, -NH, 2H), 9.29 δ (s, -NH, 1H), 9.44 δ (s, -NH, 2H), 6.54 δ (s, Ar-H, 8H).

Preparation of 6-chloro-N, N'-bis (5-nitro-1,3-benzothiazol-2-yl)-1,3,5-triazine-2,4-diamine:

In a conical flask, 1,3,5-triazine (1) (0.01 mol) was taken acetone (40 ml) and 5-nitro-1,3-benzothiazol-2-amine (2) (0.02 mol) was added to it. To this mixture, 4% NaOH was added drop wise at room temperature. Stirred the solution for 5 h. The reaction mixture was pour onto crushed ice with constant stirring. And it was neutralized with dil. HCl. The solid was filtered and washed with water. The product was recrystallized from acetone. M.p. 196ºc; yield 71.00%.

Preparation of N^2,N^4-bis(5-nitro-1,3-benzothiazol-2-yl)-N^6-aryl-1,3,5-triazine-2,4,6-triamine:

In a round bottom flask, 6-chloro-N, N'-bis (5-nitro-1, 3-benzothiazol-2-yl)-1, 3, 5-triazine-2, 4-diamine. (3) (0.01 mol) and 1,4-dioxane (10 ml) was taken. To this mixture, aniline (0.01 mol) was added. The pHwas adjusted to neutral by adding 8% NaOHin it . The reaction mixture was refluxed for 2.5 h. And was poured onto crushed ice with constant stirring. The mixture was then neutralized with dil. HCl. The product was filtered and washed with cold water. The product was dried and recrystallized from methanol. M.p. 286ºc; Yield 69%.

III. RESULTS AND DISCUSSION

Scheme 1:

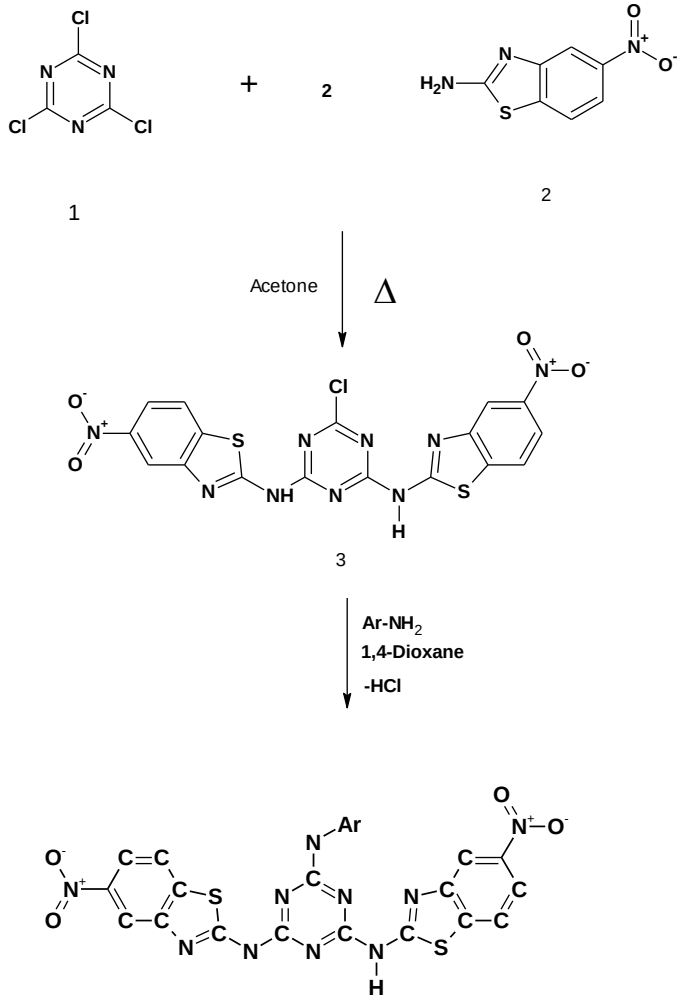

Figure 1. 1a-1l

Table 1 : Physical constant of the compounds (1a-1l):

Compd.	-Ar	Molecular Formula	m.p. (ºC)	Yield (%)	C (%) Found	C (%) Reqd.	N (%) Found	N (%) Reqd.
1a	$-C_6H_5$	$C_{23}H_{14}N_{10}O_4S_2$	220	65	49.44	49.46	25.06	25.08
1b	$-3-Cl-C_6H_4$	$C_{23}H_{13}ClN_{10}O_4S_2$	160	59	46.52	46.58	23.60	23.62
1c	$-4-Cl-C_6H_4$	$C_{23}H_{13}ClN_{10}O_4S_2$	226	54	46.54	46.58	23.59	23.62
1d	$-3-NO_2-C_6H_4$	$C_{23}H_{13}N_{11}O_6S_2$	210	65	45.70	45.77	25.51	25.53
1e	$-4-NO_2-C_6H_4$	$C_{23}H_{13}N_{11}O_6S_2$	245	62	45.71	45.77	25.49	25.53
1f	$-4-Br-C_6H_4$	$C_{23}H_{13}BrN_{10}O_4S_2$	170	57	43.30	43.34	21.95	21.97
1g	$-4-F-C_6H_4$	$C_{23}H_{13}FN_{10}O_4S_2$	184	64	47.85	47.91	24.20	24.29
1h	$-2-C_5H_4N_2$	$C_{22}H_{13}N_{11}O_4S_2$	196	65	47.19	47.22	27.50	27.54
1i	$-4-C_5H_4N_2$	$C_{22}H_{13}N_{11}O_4S_2$	223	68	47.20	47.22	27.49	27.54
1j	$-N-CH_3-C_6H_4$	$C_{24}H_{16}N_{10}O_4S_2$	290	59	50.30	50.34	24.40	24.46
1k	$-4-CH_3-C_6H_4$	$C_{24}H_{16}N_{10}O_4S_2$	288	56	50.29	50.34	24.41	24.46
1l	$-2-NO_2-C_6H_4$	$C_{23}H_{13}N_{11}O_6S_2$	256	55	45.74	45.77	25.50	25.53

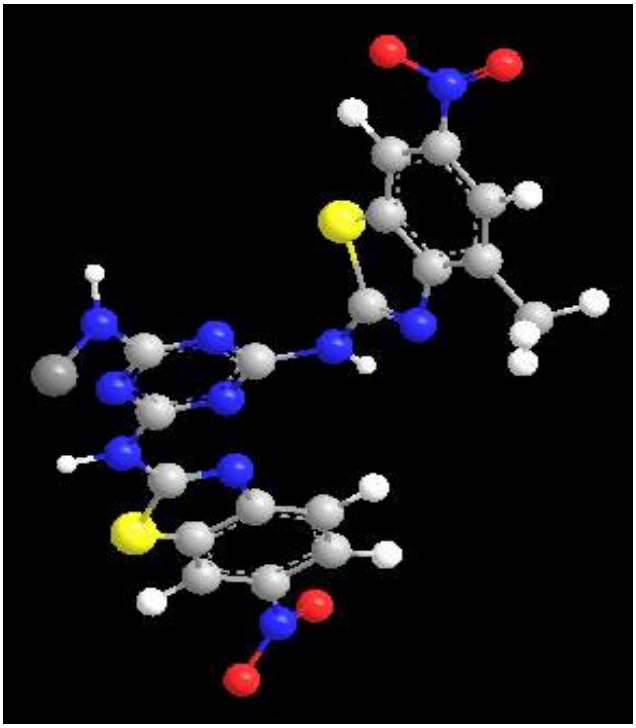

Figure 2. 3d-structure of : 1a

Table 2 : Antibacterial and Antifungal Activities:

SR NO.	Minimal bactericidal concentration (MBC) in µg/ml				Minimal fungicidal concentration (MFC) in µg/ml		
	E.coli	*P.aeru ginosa*	*S.aureus*	*S.pyogenus*	*C.albicans*	*A.nigar*	*A.clavatus*
	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC
	- 443	-1688	-96	- 442	-227	-282	-1323
1a	100	50	100	200	500	500	500
1b	100	100	500	500	100	100	500
1c	100	250	25	500	100	100	100
1d	50	500	500	500	50	50	50
1e	500	500	100	250	50	50	100
1f	100	250	250	500	100	100	100
1g	500	250	250	500	500	1000	1000
1h	50	500	500	500	500	500	500
1i	50	500	1000	1000	50	50	50
1j	100	500	100	100	200	200	200
1k	250	250	100	250	50	100	100
1l	500	250	100	200	100	100	500

IV.CONCLUSION

In this work, a series of compounds comprising of S-triazine based chalcone were successfully synthesized using this method. s-triazine provided a versatile synthetic approach for the synthesis of differently bioactive substituted triazine. The synthetic yields of the generated products are ranged from 50 to 70 % and their structures were established by spectral data (IR and NMR). Finally, all of synthesized compounds have been tested by elemental and spectral analysis.

V. ACKNOWLEDGEMENT

We are thankful to the principal of M. G. Science Institute, Ahmadabad to providing research facilities, IR data collection and North America Institute of Pharmaceutical Technology, Toronto for NMR data collection.

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Synthesis and Characterizations of Some New S-Triazine Based Derivatives as Potent Antimicrobial and Antiinfective Agents

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ABSTRACT

1,2,4-Triazines are the six membered heterocyclic compounds containing three nitrogen in its structure with general formula $C_3H_3N_3$ .Some novel N^2,N^4-bis(6-nitro-1,3-benzothiazol-2-yl)-N^6-aryl-1,3,5-triazine-2,4,6-triamine 1a-m have been synthesized and characterized by elemental analyses. Introduction of -OCH_3, -F, -NO_2, -Cl and –Br groups to the heterocyclic frame work enhanced antibacterial and antifungal activities.The products have been tested for their antibacterial activity against gram (+)ve(POSITIVE) and gram (-)ve(NEGATIVE) bacteria and also on different strains of fungi.

Keywords : 1, 3, 5-triazine-2, 4, 6-Triamines; Antibacterial Activity; Antifungal Activity.

I. INTRODUCTION

Organic chemistry is the chemistry of compounds that contains the element carbon. Medicinal chemistry has its womb in several armlets of chemistry and biology. However, incumbent it concerns with the rubric of mechanisms of function and action of drugs. It link biodynamic behavior with chemical reactivityand mechanisms. Rightly, therefore, medicinal chemistry is also called therapeutic chemistry in present.

The Chemistry of Heterocyclic Compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications. A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt.

In recent decades, problems of multi-drug resistantmicroorganisms have reached on alarming level in many countries around the world. A numbersof recent clinical reports describe the increasingccurrence of meticillin-resistant S. aureus and other antibiotic-resistant human pathogenic microorganisms in United State, European countries and other developing countries. Infections caused by those microorganisms pose a serious challenge to the medical community and the need for an effective therapy has led to a search for novel antimicrobialagentsand antifungleagents[1]. In this work, we report the synthesis and biological activity of some newly synthesized cyanuric chloride based derivatives. Several derivatives of s-triazine show antimicrobial[2], antibacterial[3], and herbicidal activities[4]. They are also used for the treatmentof HIV infection[5-6]. Cyanuric chloride derivatives are widely used in commercial chemicals. Some trisubstituted-1,3,5-triazines are also used as liposome[7].

Several investigators found s-triazine nucleus as potential therapeutic agents for diseases due to bacteria, malaria and cancer[8]. Trichlorotriazine derivatives have found extensive use in the synthesis of “activated”dyes. 1,3,5-Triazine derivatives also possess biological activities like antitubercular,antitumor[9], anti-inflammatory[10]. 1,3,5-triazines represent a widely used lead structure with multitude of interesting applications in numerous field[11]. Cyanuric chloride is a heterocyclic organic compound commonly used for immobilization of proteins[12-14].

It has been reported that s-triazine derivatives are used as templates for molecular imprinting and for the construction of three-helix bundle protein[15]. Cyanuric chloride is an essential organic intermediate of which three chlorines can be replaced by –NH2, –OH, –SH or –NHR step by step with high yield. Cyanuric chloride derivatives have been studied for decades, especially its amino derivatives, which depends on the activity of amine nucleophiles[16]. Thiourea and Urea derivatives possess antibacterial[17] and antifungal activity. It is also lead a human immuno deficiency virus type (HIV-1)[18], and found as antagonist[19-20].

Over the last few years, the thiourea moiety has been of interest to design molecules as receptor antagonists, as natural product mimics or as synthetic intermediates to amidinesorguanidines[21]. Thiourea not only confers antibacterial, antitubercular or antileprotic activity also urea confers antibacterial and antifungle activity, antibacterial, anticancer, anticonvulsant, antithyroidal, antibacterial[22-28], diuretic[29] and insecticidal activity[30].
We are going to make some new kind of synthesis and characterization of some triazine based cyanuric derivatives carrying the above biodynamic heterocyclic systems with the hope to achieve enhanced biological activity[31-32].

II. METHODS AND MATERIAL

Biological Activity

Antibacterial activity: Antibacterial activity was carried out by broth dilution method[17]. The strains used for the activity were secured from Institute of Microbial Technology. The compounds 1a-1l were observed for their antibacterial activity against *E. coli, S. aureus, E. pyogenes and P. aeruginosa*,at concentrations of 1000, 500, 200, 100, 50, 25, 12.5 µg/mL respectively (Table 2).

Antifungal activity: Same compounds were tested for antifungal activity against *C. Albicans A. Niger and A. Clavatus* at a concentrations of 1000, 500, 200, 100 and 50 µg/ml respectively (Table 2).

The result of this test is affected by the size of the inoculums. The test mixture should contain 10^8 organisms/ml. "K. *Nystatin*" was used as the standard drug for antifungal activity which showed 100µg/ml MFC against fungi, used for the antifungal activity[32].

Experimental Section

Melting points were taken in open capillaries using paraffin bath. IR spectra were recorded on FTIR-BRUKER ALPHA-E (10044239) spectrometer (V_{max} in cm^{-1}); Purity was checked by TLC using TLC aluminum sheets silica gel 60, supplied by E.Merck. The spots were located by keeping the plates in iodine vapor. 6-nitro-1,3-benzothiazol-2-amine was prepared by methods as described in our paper and literature.

For 1a compound: IR (kbr): 3083(-C-H str., aromatic), 1527 (> C = N- str., ter. Amine), 1350 (C-NO_2 STR.), 1122 (C-S-C str., thiazol), 952 (C-Cl str., aromatic),808 (disubstituted aromatic),1431 (C = N str., sec.amine).

NMR Spectra: 1H NMR spectra, were recorded in CDCl3 solution on a Bruker Avance DPX 200 MHz spectrometer Chemical shifts are reported as δ (ppm) relative to TMS as internal standard.10.08δ (s, -NH, 2H), 9.29 δ 8048 (s, C-NO_2), (s, -NH, 1H), 8.48 6.54 δ (s, Ar-H, 8H).

13C-NMR (100 MHz, DMSO-*d*6): δ ppm, 20.67 (CH3), 22.47 (CH3), 60.14 (CH).

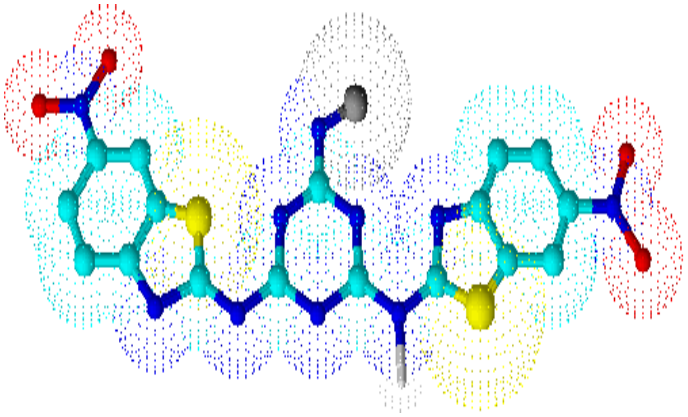
Preparation of 6-chloro-N, N'-bis (6-nitro-1,3-benzothiazol-2-yl)-1,3,5-triazine-2,4-diamine

2,4,6-trichloro-1,3,5-triazine (1) (0.01 mol) was taken in a flask add acetone (30-40 ml) in it. Mix that solution and add 6-nitro-1,3-benzothiazol-2-amine (2) (0.02 mol). 4% NaOH was added drop by drop wise at room temperature in this solution. The solution was stirred for 4 to 5 hour. The reaction mixture was poured onto crushed ice with constant stirring. The solution was neutralized byadding drop by drop dil. HCl. The precipitate was filtered and washed with cold water or cold distilled water. The compound was recrystallized from acetone or alcohol. M.p.200ºc; yield 79.00%. Anal. Found: C,43.05; N, 21.50; cal. For $C_7H_5N_3O_2S$: C, 43.07; N, 21.53%.

Preparation of N^2,N^4-bis(6-nitro-1,3-benzothiazol-2-yl)-N^6-aryl-1,3,5-triazine-2,4,6-triamine (4a)

6-chloro-N, N'-bis (6-nitro-1, 3-benzothiazol-2-yl)-1, 3, 5-triazine-2, 4-diamine. (3) (0.01 mol) and 1,4-dioxane (10 ml) was taken in RBF(Round Bottom Flask). To this

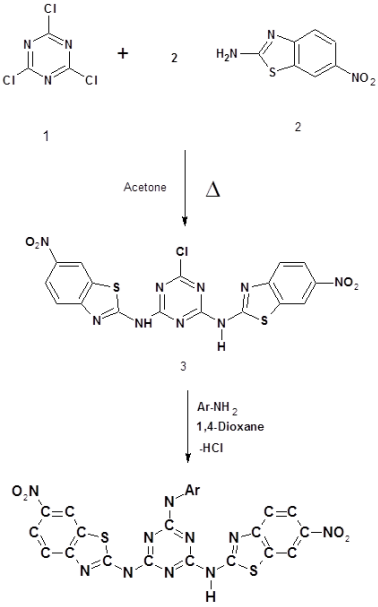
mixture, aniline (0.01 mol) was added. The pH was adjusted to neutral by adding 8% NaOH drop by drop. The reaction mixture was refluxed for 2.5 to 3 h. And was poured onto crushed ice with constant stirring. The mixture was then neutralized with dil. HCl. The product was filtered and washed with cold water. The product was dried and recrystallized from methanol. M.p. 287ºc; Yield 68% .Anal. Found: C,49.41; N, 25.06; cal. For: $C_{23}H_{14}N_{10}O_4S_2$; C, 49.46; N, 25.08% (1a).



1a-1l

III. RESULTS AND DISCUSSION

Scheme 1:



1a-1l

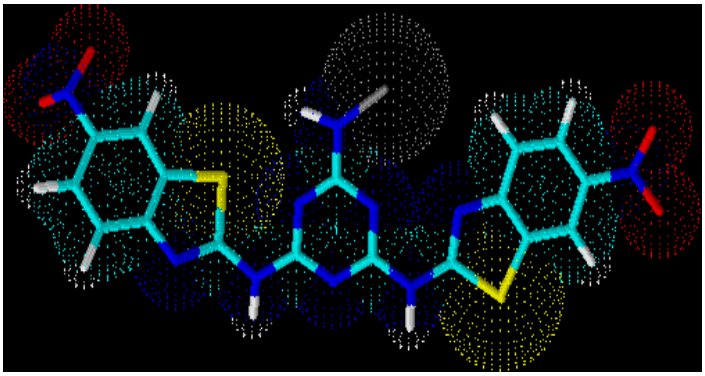


Table I. Physical constant of the compounds (1a-1l)

Sr No.	-Ar	MOLECULAR FORMULA	M. P. ^{O}C	YIELD (%)	% OF CARBON		% OF NITROGEN		Mol. Wt
					FOUND	REQD.	FOUND	REQD.	
1a	-C_6H_5	$C_{23}H_{14}N_{10}O_4S_2$	240	65	49.41	49.46	25.06	25.08	558.55
1b	-3-Cl-C_6H_4	$C_{23}H_{13}ClN_{10}O_4S_2$	186	59	46.56	46.58	23.60	23.62	592.99
1c	-4-Cl-C_6H_4	$C_{23}H_{13}ClN_{10}O_4S_2$	255	54	46.54	46.58	23.59	23.62	592.99
1d	-3-NO_2-C_6H_4	$C_{23}H_{13}N_{11}O_6S_2$	320	65	45.74	45.77	25.51	25.53	603.54
1e	-4-NO_2-C_6H_4	$C_{23}H_{13}N_{11}O_6S_2$	265	62	45.76	45.77	25.48	25.53	603.54
1f	-4-Br-C_6H_4	$C_{23}H_{13}BrN_{10}O_4S_2$	193	57	43.31	43.34	21.96	21.97	637.44
1g	-4-F-C_6H_4	$C_{23}H_{13}FN_{10}O_4S_2$	251	64	47.89	47.91	24.24	24.29	576.54
1h	-2-$C_5H_4N_2$	$C_{22}H_{13}N_{11}O_4S_2$	197	65	47.19	47.22	27.51	27.54	559.53
1i	-4-$C_5H_4N_2$	$C_{22}H_{13}N_{11}O_4S_2$	218	68	47.20	47.22	27.50	27.54	559.53
1j	-N-CH_3-C_6H_4	$C_{24}H_{16}N_{10}O_4S_2$	270	59	50.32	50.34	24.43	24.46	572.57
1k	-4-CH_3-C_6H_4	$C_{24}H_{16}N_{10}O_4S_2$	179	56	50.29	50.34	24.40	24.46	572.57
1l	-2-NO_2-C_6H_4	$C_{23}H_{13}N_{11}O_6S_2$	196	55	45.71	45.77	25.50	25.53	603.54

Table 2: Antibacterial and Antifungal Activities

SR NO.	Minimal bactericidal concentration (MBC) in µg/ml				Minimal fungicidal concentration (MFC) in µg/ml		
	E.coli	***P.aeruginosa***	***S.aureus***	***S.pyogenus***	***C.albicans***	***A.nigar***	***A.clavatus***
	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC	MTCC
	- 443	-1688	-96	- 442	-227	-282	-1323
1a	100	50	100	200	100	250	500
1b	100	100	500	500	100	100	500
1c	100	250	25	500	100	100	100
1d	50	500	500	500	50	50	50
1e	500	250	100	250	50	50	100
1f	100	250	250	500	100	100	100
1g	500	200	250	500	500	250	1000
1h	50	500	500	500	500	500	500
1i	50	500	1000	1000	50	50	50
1j	100	100	100	100	200	200	200
1k	50	50	200	50	50	50	100
1l	500	250	100	200	50	50	500

IV.CONCLUSION

As outline in Scheme-1, an important novel s-triazine derivatives, N^2, N^4-bis (6-nitro-1,3-benzothiazol-2-yl)- N^6 -aryl-1,3,5-triazine- 2,4,6-triamine has been synthesized. In this work, a series of compounds comprising of s-triazine based chalcone were successfully synthesized using this method. s-triazine provided a versatile synthetic approach for the synthesis of differently bioactive substituted triazine. The synthetic yields of the generated products ranged from 55 to 70 % and their structures were established by spectral data (IR and NMR). Finally, all of synthesized compounds have been tested by elemental and spectral analysis.

V. ACKNOWLEDGEMENT

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