Heterocyclic Letters
Vol. 12| No.2|415-443|February -April|2022
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

COUPLING REACTIONS OF ARYLDIAZONIUM SALT. PART-XII: REVIEW ON COUPLING OF ARYLDIAZONIUM SALT OF AMINOBENZOTHIAZOLES WITH AROMATIC OR HETEROAROMATIC MOFITS

Amol N. Dhake[a], [*]Chandrashekhar J. Patil[a] ,
Ganesh R. Chaudhari[b]

[a] *MTES's Smt. G. G. Khadse College, Muktainagar, Tal. - Muktainagar, Dist. - Jalgaon, M. S. India.*
[b]*P. G. Research Center, Department of Chemistry, Arts and Science College, Bhalod, Tal. - Yawal, Dist. - Jalgaon, M. S. India.*
(amoldhake29@gmail.com, [*]drcjpatil@yahoo.com, drgrc76@gmail.com)

ABSTRACT: The Aminobenzothiazole-azo compounds are industrially very important for technical purposes. Azo group compounds are commonly used in preparation of or as synthetic colour molecules. They are prepared beginning with primary aromatic amines by diazotization and coupling on aromatic mofits. The compounds were studied to arrive at their skeleton using different type of data (spectroscopic and the analytical) using spectroscopies such as UV-Vis., FT-IR, ^{1}H-NMR. Azo compounds of amino benzothiazole have varied applications in pigments, many used in food, cosmetics and drug industry as well.

KEYWORDS: Aminobenzothiazole, azo, diazotization, dyes, Antibacterial and Antioxidant Activity

INTRODUCTION:

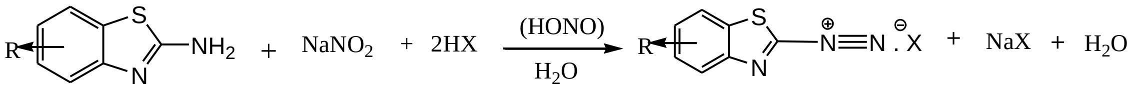
The compounds of azo class or dyes are analyzed by occurrence of the azo (-N=N-) moiety in their skeleton, conjugated with different or identical, mono or dicyclic aromatic, polycyclic aromatic or hetero-aromatic systems. Due to their precise physio-chemical properties and biological activities, they have found a broad application viz. in cosmetic, pharmaceutical, dyeing or textile, food industry and also in analytical field.

The diazonium compounds, epitomize a main group of organic compounds having functional formula $R\text{-}N{\equiv}N^{\oplus}X^{\ominus}$ in which R = alkyl or aryl and X = organic or inorganic anion such as a F, Cl, Br and or I group. Diazonium salts, where R is an aryl group, are precious intermediates and have many applications in organic chemistry synthesis. Since, their discovery in 1858[1] many protruding named reactions associated with diazonium salts of arene moiety and have evolved throughout development of one century plus. In 1884, Sandmeyer found out that by treating with copper chloride, benzene diazonium salt was converted into chlorobenzene[2]. Pschorr reported a preparation method for of biaryl tricyclics by intramolecular substitution of an aryl radical with one arene, which is formed from an aryl diazonium salt by copper catalysis[3] by in-situ mode.

Diazonium salts found more useful as starting materials for a wide range of conversions, which are divided into the three major sub-groups. First group, viz. ionic reactions, comprises azo couplings and triazene formations, Japp-Klingemann reaction and Balz Schiemann. Diazonium salts radical reactions, that representing the second subgroup, contain Gomberg-Bachmann- and Pschorr type aryl-aryl couplings, Meerwein type alkene functionalization's, Sandmeyer reactions and hydrogen atom transfer reactions, and some others. In addition, aryldiazonium salts have been successfully employed in Pd-catalysed cross-couplings also in closely related transition-metal mediated reactions, thereby constituting the third subgroup.

Since from the discovery of aryl diazonium salts[1-3] many developments in the dye and other industry have benefited for more than a century in 1884. Doyle et. al.,[4-5] reported no need of aqueous acid for the formation of these intermediate. Scientist, Sandmeyer treated copper(I) chloride with benzene diazonium salt to convert it to chlorobenzene[6-7]. After the work of Kikukawa and Matsuda[8] in the next 50 years the coupling reactions of C-C and C-B bonds have been well elaborated. Usually, they are synthesized by the process of diazotization[2], a process in which aromatic amine - primary nature is reacted with nitrous acid. Instead of all securities development of products due to presence of HNO_2 and its aromatic amine is mandatory, forming dark decomposition, thus by decreasing yield and thus the product is made tough to isolate[9].

In addition to dye and pigment industry[10] the azo compounds also relevant for biocidal treatment of textile materials since they show biological activity also Azo compounds has medicinal importance and they are recognized for its applications as - antineoplastics[11], antibacterial[12-13] antidiabetics[14] and antitumor[15]. The azo compounds are also valuable in the pharmaceutical and medicinal fields[16] and possibly the azo-imine linkage would be accountable for biological activities showed by some Schiff bases as reported[17]. Some of the azo compounds are studied as antibacterial activity[18]. The presence of the azo moiety shows pesticidal and antibacterial activities. The diazonium salt reacts with other arene (coupling agents) to show diazo coupling reaction[19]. The azo compounds, act as antimicrobial agents that has been subject of many reports[20-30]. Preparation of most of the azo compounds includes diazotization of a primary (aromatic or heteroaromatic) amine, along with by coupling with coupling agents[19] viz. pentane-2,4-dione (or acetylacetone)[21], phenols[23-28]. Thus naphtholic, phenolic and salicylic compounds undergo diazotization process and as of variety applications, so it is exciting to study preparation of such azo compounds. Literature shows studies on the derivatives in order to explain the newer aptitudes of similar type of compounds. Sometimes azo compounds are frequently described as a chromogen in the literature[25]. The hydroxy[23-28] or amino-[29] groups are common functional group of organic compounds used as coupling agents[30]. The appearance of various classes of synthetic dyes[31] containing azo dyes occurred due to constant effort. Azo dyes are industrial importance which include textile fabric[32], silk, wool and nylon[33] fabrics. Moreover, azo compounds are also many applications in photo-industry like photographic or electro-photographic systems, photodynamic therapy and dominant organic photoconductives[25]. Recently, from our laboratory a review is published[34] pertaining to the reaction of varied diazonium salt with salicylic acid and Phenolic compounds. Recently, the diazotization proceeds with easy processes and ecologically benign situations with high yields of the products[35]. Reaction of primary aromatic amine, **1** with nitrous acid formed from sodium nitrite and hydrochloric acid cooled (0-5°C) to forms diazonium salt, **2** which is highly unstable and hence very reactive moiety. **Scheme-1** shows the general reaction of formation of diazonium salt, **2**. The **Scheme-2** shows the general reaction of diazonium chloride, **2** with aromatic compound, **3** to form the aromatic-azo compound, **4**.



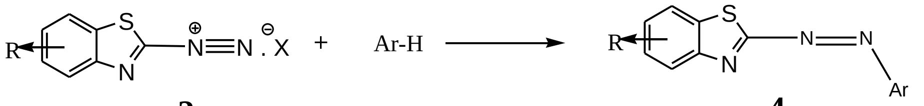
2

1

2-Amino-benzo[*d*]thiazol-2-amine

Diazonium salt of 2-Amino-benzothiazole(highly unstable)

Scheme-1: General reaction of Diazonium salt formation.



2 **3** **4**

Diazonium salt of 2-Amino-benzothiazole(highly unstable)

Azo derivative of 2-Aminobenzothiazole

Scheme-2: General Reaction of Diazonium salt with Phenolic compound.

LITERATURE SURVEY:

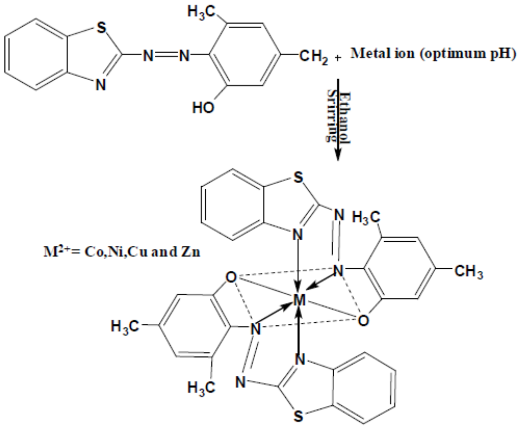
Literature marked that the synthesis of 2-aminobenzothiazole and its derivatives via. treatment of aromatic amine derivatives in presence of potassium thiocyanate and molecular bromine and glacial acetic acid and latter defuse by conc. ammonia solution or by 50 % sodium hydroxide. These molecules were used for synthesis of diazonium salts as per the reaction with sodium nitrite and hydrochloric acid, the diazonium salts were used for specific interaction[36] with 4-amino-3-hydroxy-1-naphthalene sulphonic acid and 4-amino antipyrine in basic medium to produce dyes with azo group. These were characterized by spectroscopic information FT-IR, ^{13}C-NMR, ^{1}H-NMR and C.H.N.S. elemental characterization. Biological activity assessed for four of synthesized compounds towards four types of bacteria.

Photochemical and electrochemical experiments[37] in ethanol shows that the tendency to reduce the azo dyes prepared from 2-aminobenzothiazole is similar for both processes. This is assigned to the one-electron reduction of the dyes and protonation of the resultant radical anions.

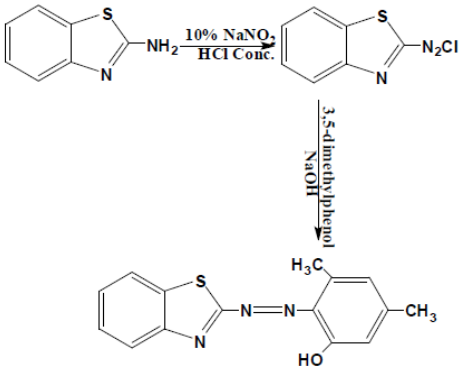
The 2-Amino-6-substituted benzothiazoles are prepared by the one pot reaction[38] of substituted-anilines with thiocyanogen and consumed to synthesize the particular 2-phenylazo-6-substituted benzothiazoles in fair yields by usual diazotization followed by coupling with 2 N,N-dialkyl anilines. Amino benzothiazoles existence absorption in UV region, while dyes having absorption maxima in the visible region. In case of the amino benzothiazoles and particular azo dyes, variations in donor-acceptor character of substituent affect absorption maxima. The azo dyes show large variations in absorption spectra with changing pH (blue to red colour), indicated optical sensors potential at low pH values. Solvent effects are involved by PCM formalism with acetonitrile and dichloromethane.

A new azo compound 2-(2'-hydroxynaphthylazo) benzothiazole[39] has been synthesized, bands of the ligand and the formed complexes of Cu II, Co II and Fe III are assigned using FT-IR spectra. Electronic absorption spectra of pure ligands in organic solvents of diverse polarity and also in buffer solution of changing pH are studied. The sensitive spectral procedure for micro evaluation of metals employing azo compound, as a new chromogenic ligand is also established. The method is successfully used for determination of the Cu II, Co II and Fe III with foreign ions and in solution form.

6-(2-benzathiazolyl azo)-3,5-dimethylphenol[40] have been prepared by reacting the 2-benzothiazole diazonium chloride with 3,5-dimethylphenol. Azo ligand have been characterized by FT-IR, UV-Vis, ^{13}C-NMR and ^{1}H NMR spectral evaluation. Complexation of tridentate ligand with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in aqueous of ethanol with a 1: 2 (metal: ligand) and at ideal pH. The preparation of metal chelates are set using flame atomic absorption, FT-IR and UV-Vis spectral evaluation, along with magnetic estates and conductivity. Nature of complex remained supported out by mole ratio and constant difference mechanism, Beer's law followed rate 0.0001 - 0.0003 M) concentration, where in molar absorptivity for complex solutions was detected.



Scheme 2: The expected geometry of the metal chelates.



Varied azo benzothiazole chromophore based liquid crystalline compounds having various substituents at 6th position on benzothiazole moiety[41] with methacrylate terminal group were prepared and characterized by FT-IR, ^{13}C-NMR, ^{1}H-NMR. DSC and TGA evaluations exhibited that all studied compounds are thermally stable and exhibited liquid crystal behaviours. The temperature varies of Mesophase formation was seriously inclined by 6th position electron donating substituent on benzothiazole ring and terminal methacrylate function. In UV-Vis spectra absorption maxima are bathochromically shifted with removal of 6th position H by electron donating function on benzothiazole chromophore.

Some of azo-benzothiazole dyes are prepared by coupling reaction[42] of 8-hydroxy-quinoline, 2-naphthol and 2,6-diamino-pyridine through diazotized 2-Amino-6-nitrobenzothiazole. Azo dyes were prepared in fair yields and are characterized by ^{1}H-NMR, UV-Vis and FT-IR spectral methods and these azo compounds screened for the biological activity i.e., antimicrobial agents.

The diverse derivatives of 4-methoxy-2[H/substituted-4-(N-N-disubstituted amino) phenylazo] benzothiazole are synthesized coupling[43] with diazotized 2-amino-4methoxy-benzothiazole (II) through substituted aniline. The dyes furnished bright dying with reasonable to light fastness and fair to excellent fastness to, rubbing perspiration, washing and sublimation.

Coupling of diazotized[44] 2-aminobenzothiazole and 2-aminothiazole with cyclohexane-1,3-dione gives a new class of tridentate ligand system. Analytical, FTIR, ^{1}H-NMR, mass spectral and ^{13}C-NMR data indicate presence of compounds in intramolecularly hydrogen bonded azo-enol tautomeric form. Normal paramagnetic moment by Ni(II) and Cu(II) complexes while Zn(II) chelates are diamagnetic was displayed.

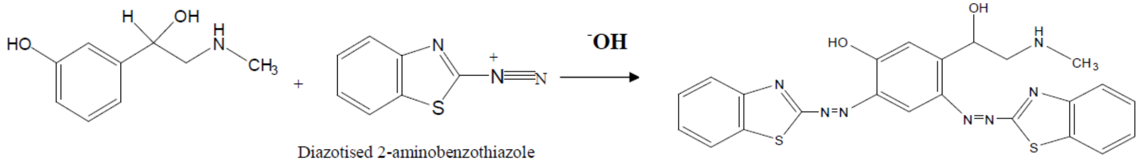
Varied 2-aminobenzothiazole[45] has been reacted with acetyl acetone and different hydrazine to give several (3,5-dimethyl-1-phenyl-1H-pyrazol-4-yl)-(substituted benzothiazole-2-yl)-

diazenes. The spectral data viz. ^{1}H-NMR, IR, mass and elemental analysis have confirmed structure of compound, assessed for antifungal activity.

The liquid crystals[46], containing 2-[4-(4′-n-alkoxybenzoyloxy) naphtha-1-ylazo]-6-fluorobenzothiazoles and 2-[4-(4′-n-alkoxybenzoyloxy) phenylazo]-6-fluorobenzothiazoles were prepared and characterized. Each section includes Thirteen homologous members diversely length of alkoxy chain. Substances with C-1 to C-7 chain are found to show enantiotropic smectic C (SmC) and nematic (N) mesophases. Homologue, C-8 had enantiotropic SmC, N mesophases and smectic A (SmA), whereas longer chain homologues (C-10 to C-14) exhibited enantiotropic SmA and SmC mesophases. C-16 and C-18 homologues had only SmA mesophases while in F series all molecules (C-1 to C-18) showed only the enantiotropic nematic mesophase.

Heteroaryl amines have diazotized and coupled to 3-amino croton nitrile to give 2-hetaryl hydrazone-3-ketiminobutyronitrile[47] it can react with hydrazine hydrate and phenyl hydrazine to afford matching 5-amino-3-methyl-4-hetarylazo-1-phenylpyrazoles and 5-amino-3-methyl-4-hetarylazo-1H-pyrazoles. Some newer diazo dyes and were prepared and characterized by elemental analysis and spectral data, also studied the solvatochromic performance of dyes in different solvents.

A spectrophotometric method[48] for the determination of microgram volumes of phenylphrin-HCl has been proposed. The process is based on coupling of the phenylphrin-HCl with diazotized 2-aminobenzothiazole in alkaline medium. The molar absorptivity of the formed dye LDL and HDL is evaluated.



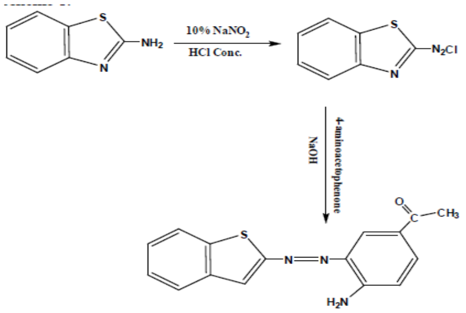
Emission and absorption spectra of three hetaryl azo quinoline compounds having varied substituents are observed in liquids and liquid crystalline solvents[49]. Spectral structures of hetaryl azo quinoline dyes are elucidated giving to azo/hydrazone tautomerism in conjunction through the solvatochromic characteristic. Extent of solute-solvent interactions are explained by using Kamlete Taft and Katritzky multiparameter polarity scales. It was determined that anisotropic hosts avoid shift of tautomeric equilibrium to hydrazone.

Varied 2-aminobenzothiazole based dichromophoric cationic azo dyes are prepared and studied photo physical properties[50]. Azo dyes are violet to blue with high molecular extinction coefficient and showed exclusive fluorescence emission in the range of 409-494 nm. Antibacterial activities of these dyes are reported against bacteria including, *S. aureus*, *S. epidermidis*, *E. coli* and *P. aeruginosa* and diverse concentrations of dyes exhibited bacterial activity.

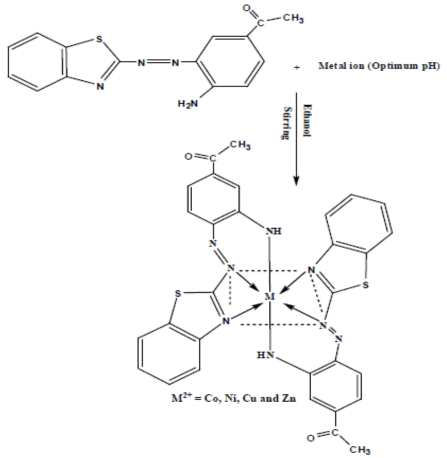
The coupling component 1-(2-benzothiazolyl)-3-methylpyrazol-5-one synthesized and treated with diazotized heterocyclic amines to give 6 hetarylazo-pyrazolone dyes[51]. Azo dyes of benzimidazole and benzothiazole ring systems are studied for elemental analysis and spectral data. Solvatochromic performances of these dyes in several solvents are studied. Ground state geometries of synthesized compounds were optimized by Time-dependent density functional theory (TD-DFT) and density functional theory (DFT) calculations are executed to get absorption spectra.

Diazotized 2-Aminobenzothiazole and coupled with 1- Naphthol, 1-Naphthylamine, and 2-Napthol mono azo-heterocyclic disperse dyes were prepared[52]. These dyes were applied to polyester, nylon and acrylic fabrics. Fastness properties of dyed fabrics to wash and light was evaluated, also the physical characteristics i.e., light absorption in the visible spectrum a melting temperature has been determined. These dyes have fastness to light is poor and all the dyes were absorbed at the visible region.

Aromatic ketone, 1-(4-amino-3-(benzo[d]thiazol-2-yldiazenyl) phenyl) ethenone was prepared by treating diazonium salt of 2-aminobenzothiazole with 4-aminoacetophenone[53]. Spectroscopic studies such as, UV-Vis, ^{1}H and ^{13}C NMR, FT-IR and elemental analysis were done to confirm ligand. Metal chelates of some transition metals were performed as well as depicted. Complexes were characterized by using elemental analysis, atomic absorption of flame, conductivity and magnetic quantifications. The analytical data exhibited that all complexes are in 1:2 metal-ligand ratio. Biological studies of all prepared compounds were assessed against diverse kinds of strain of microbe.

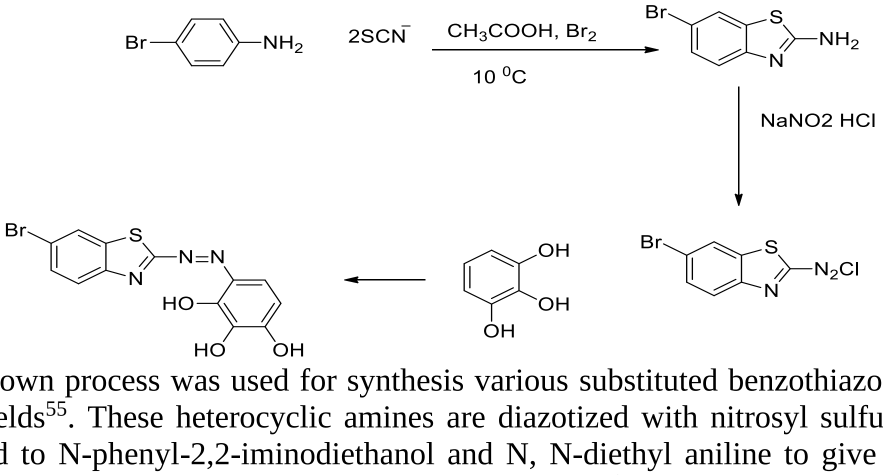


Scheme 1: Synthesis of azo ligand (L).



Scheme 2: Suggested structure of the metal (II) complexes of azo ligand (L).

Organic reagent, 4-(6-bromo-2-benzothiazolylazo) pyrogallol (4-Br-BTAP), was prepared by coupling of diazotized 2-amino-6-bromobenzothiazole with pyrogallol[54] and improved by recrystallization. Synthesized molecules were analyzed by using physical constant, elemental analysis, ^{1}H-NMR and FT-IR spectra. Dissociation constant of organic reagent was evaluated by spectrophotometry. Absorption spectra of 4-Br-BTAP in solvent of diverse polarities were reported. Analytical uses of 4-Br-BTAP are established with Pd II and Cu II.



A known process was used for synthesis various substituted benzothiazole amines in moderate yields[55]. These heterocyclic amines are diazotized with nitrosyl sulfuric acid and later coupled to N-phenyl-2,2-iminodiethanol and N, N-diethyl aniline to give azo dyes in suitable yields. These dyes are studied by UV-Vis, FT-IR, ^{1}H-NMR and elemental analysis. Solvatochromism performance of azo compounds is examined by studying their spectra in mixed and pure organic solvents of different characteristics. Effects of base and acid on absorption maxima of dyes were also studied.

Azo dyes are prepared by diazotization of 2-amino-1,3-benzothiazole and coupled to varied phenols and anilines. Newly synthesized[56] dyes are characterized by UV-Vis, ^{1}H-NMR, FT-IR and LC-MS spectral technique. UV-Visible spectra of these dyes were studied for SPR. Dyeing assessment of these dyes were investigated on different fabrics. Better hue is found on cotton mordant fibres. These azo dyes are reported as efficient indicators in acid - base titrations. Few of them show fine sharp end point to distinct level. In addition to this, antimicrobial evaluation of these dyes showed antibacterial activity.

One pot reaction was optimized to synthesize heterocyclic azo[57] dyes using silica-supported $BF_3.SiO_2$ as a catalyst. Nano inks were prepared by microencapsulation were applied in digital printing methods to cotton and polyamide fabrics. Fastness properties of prints are measured and printed fabrics have a brilliant washing and light fastness.

The 2-aminobenzothiazole diazotized and coupled with 1,3-dicarbonyl compounds[58] viz. methyl acetoacetate, acetoacetanilide and benzoyl acetone yielded a novel group of tridentate ligand systems. Compounds were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data. It concludes that the intramolecular hydrogen bond in azo-enol tautomeric form in which one >C=O groups had enolized and H bonded to one azo (-N=N-) N atoms. Compounds formed stable complexes with Zn II, Cu II and Ni II. Analytical data, FT-IR, ^{13}C-NMR, ^{1}H-NMR and mass spectral data of complexes are dependable with removal of chelated enol proton of ligand with a metal ion, thus leads to a stable 6-membered ring chelate including a cyclic N, one of azo nitrogen's and the enolate O. The Zn II chelates are diamagnetic in nature while Cu II and Ni II chelates exhibited paramagnetic behaviour.

(E)-2-(benzo[d]thiazol-2-yliazenyl)-4-methoxyaniline[59] was prepared by reacting diazonium salt of 2-aminobenzothiazole with 4-methoxyaniline. These ligands were characterized by spectral techniques such as UV-Vis, ^{1}H-NMR, FT-IR and LC-MS with micro elemental analysis. Complexes of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were prepared and characterized using elemental analysis, A.A.S. (Atomic absorption Spectrometer), UV-Vis and infrared spectral methods. The height molar absorptivity of synthesized compound solutions has been examined. Analytical data exhibited that all the complexes out to 1:2 metal-ligand ratio. Biological studies of all molecules were assessed verses different types of antimicrobial strains.

The different types of azo-bridged benzothiazole-phenyl ethers 4-((6-ethoxybenzothiazol-2-yl)diazenyl)bromoalkoxybenzene[60] in which N=N exocyclic group is present in between ethoxy-substituted benzothiazole and a Bromo alkoxy phenyl have been prepared and studied. Phase transition behaviour of the azo compound was associated with the difference of flexible alkyl chain with n units of CH_2 group (5-12). Thermal stability as replicated by temperature transition in range of homologues under study is dependent on length of the CH_2 units.

Reaction of aliphatic diamines [1,6-diaminohexane, 1,2-diaminoethane and 1,3-diaminopropane] to 3-[2-(1,3-benzothiazol-2-yl) hydrazinylidene] pentane-2,4-dione under specific conditions gave a new group of polydentate Schiff base ligands[61]. Analytical data, FT-IR, 1 H-NMR and mass spectra exhibited existence of intramolecular H bond in the form of keto-imine. The dibasic tetradentate N4 coordination of molecules in their complexes [M = Cu (II), Ni (II) and Zn (II)] has shown based on spectral and analytical studies output.

Azo dyes are synthesized by reacting substituted aromatic amines and phenols with 2-amino-1,3-benzothiazole[62]. The structures of azo dyes and Schiff bases were confirmed by a spectroscopic technique such as ^{1}H-NMR, FT-IR, Mass and UV-Vis. Dyeing ability of azo dyes was performed by using azo dyes on several fabrics. These molecules were also tried against selected of gram-negative and gram-positive bacteria using agar diffusion method.

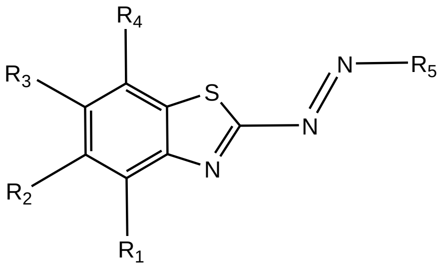
The heterocyclic dyes (azo) and their consistent Schiff bases were synthesized by diazotization and Schiff-base formation reactions between the substituted 2-aminobenzothiazoles[63], to get some disperse red dyes with high performance and compare spectral and structural differences between azo dyes and Schiff bases. Azo dyes and Schiff bases studied have same benzothiazole/phenol and but varied substituent groups in phenyl ring.

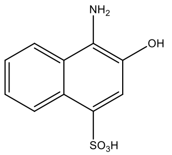
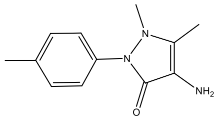
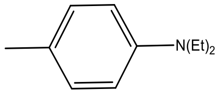
The azo-phenyl benzothiazole skeleton based liquid crystals having diverse substituents at 3rd position of central benzene ring are synthesized[64] and characterized. The compounds were characterized by using FT-IR and ^{1}H-NMR, mass spectrometry, also elemental analysis. Thermal behaviour of mesophase of these liquid crystal molecules are analyzed to show an enantiotropic nematic phase excluding for compounds containing OH group. Mesomorphic properties of azo-phenyl benzothiazole liquid crystalline molecules are compared to these compounds to assess effect of nature of substituents on their mesomorphic behaviour.

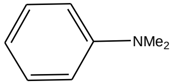
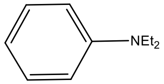
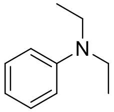
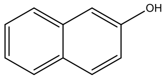
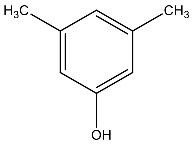
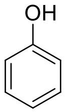
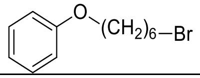
The metal complexes of Fe^{+3}, Cr^{+3}, Cu^{+2}, Ni^{+2}, and Co^{+2} with ligand dye starting from 2-aminobenzothiazole were prepared[65] and analyzed by atomic Absorption, microelement analysis, spectral methods also the magnetic behaviour of complexes and molars conductance measured. From data show that all the complexes have octahedral geometries in the formula $[ML_2(H_2O)_2]X$, where M = Cu^{+2} / Co^{+2}, X = Cl^{-1} for Fe^{+3} / Cr^{+3} except $[NiL_2]$ Cl_2 which was square planer. Biological activity of ligand and complexes were evaluated against different types of bacteria and fungi viz. Serratia marcescens, Pseudomonas aeruginosa, Staphylococcus, and Klebsiella.

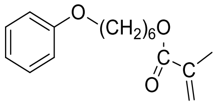
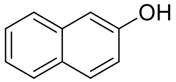
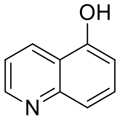
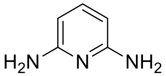
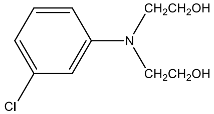
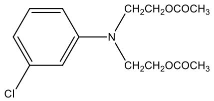
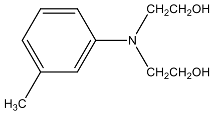
The **Table 1** indicates some of the derivatives of amino-benzothiazole azo compounds, their uses, metal complexes and the applications

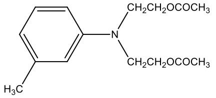
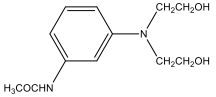
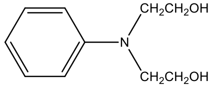
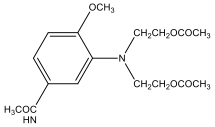
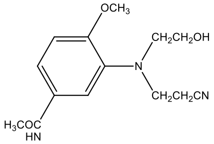
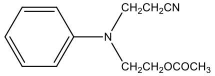
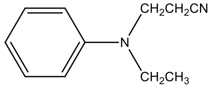
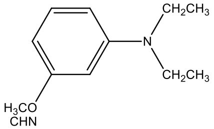
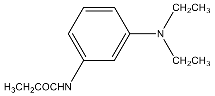
Table 1: Derivatives of amino benzothiazole-azo compounds, their metal complexes uses and applications.

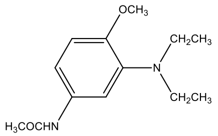
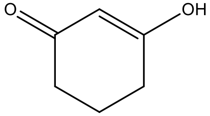
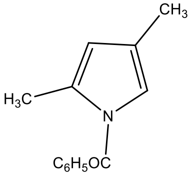
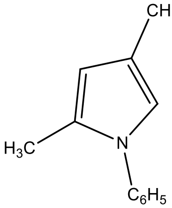
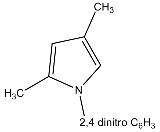


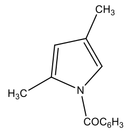
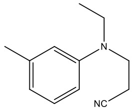
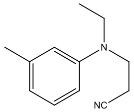
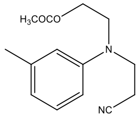
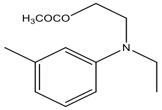
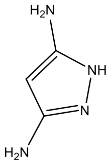
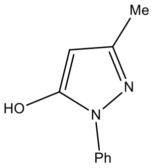
Sr. No.	**R$_1$**	**R$_2$**	**R$_3$**	**R$_4$**	**R$_5$**	**Use**	**Bioactivity**	**Studies made**	**Metal used**	**Ref**
1	H	H	F	H		Substituted 2-Amino benzothiazoles with substituted diazonium salt and coupling with newer reagents, 4-amino -3-hydroxy-1-naphthalene sulphonic acid and 4-amino antipyrine.	Synthesized compounds showed moderate activity against *E. coli* and highly significant activity against *B. subtilis*, they have electronegative groups compared to compounds with halogen groups against *B. subtilis.* Compounds showed moderate to good activity against *Eterobactern* and good effect against *S. aureus* and *E. coli*.	Elemental Analysis ^{13}C-NMR ^{1}H-NMR FT-IR	-	36
2	H	H	Cl	H						
3	Cl	H	Cl	H						
4	H	NO$_2$	H	H						
5	H	H	F	H						
6	H	H	Cl	H						
7	Cl	H	Cl	H						
8	H	NO$_2$	H	H						
9	H	H	F	H						
10	H	H	Cl	H						
11	Cl	H	Cl	H						
12	H	NO$_2$	H	H						
13	H	H	H	H		Tendency to electrochem., photochem., reduction of azo dyes in alcohol was correlated to quantum chemical calculations of e-affinities in GS and ES.	The NO$_2$ group plays important role in one e- reduction process, azo bond which accommodates mainly an additional electron and is protonated into hydrazyl radical.	TLC, UV ^{1}H-NMR	-	37
14	H	H	OCH$_3$	H						
15	H	H	NO$_2$	H						

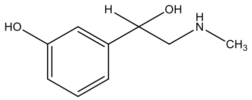
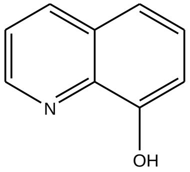
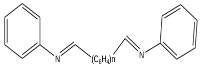
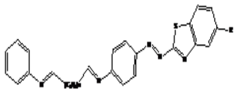
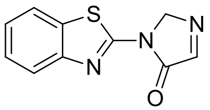
16	H	H	OCH_3	H		The photo-physical characterization of these molecules displayed comparable and complementary output, allow to understand the photo-physical behavior improves application.	-	UV-Vis FT-IR ^{13}C-NMR HRMS-ESI	-	38
17	H	H	OCH_3	H						
18	H	H	NO_2	H						
19	H	H	Br	H						
20	H	H	COOEt	H						
21	H	H	OCH_3	H						
22	H	H	H	H		Deep colored complexes are formed at optimum conditions. For micro determination of metals applying Beer's law method several advantages good selectivity and high sensitivity.	-	Elemental Analysis FT-IR pH	Co (II) Cu (II) Fe (III)	39
23	H	H	H	H		Metal chelates formed with azo ligand.	All compound shows good antibacterial activity against *S. Aureus, Pseudomonas and E. coli.*	UV-Vis FT-IR ^{13}C NMR ^{1}H-NMR Molar absorptivity	Co Ni Cu Zn	40
24	H	H	H	H		Thermally stable compounds, displayed liquid crystal mesophase characteristics using DSC and POM. Effect of 6th position electron donating substituent on benzothiazole skeleton produced	-	FT-IR ^{1}H NMR ^{13}C NMR TGA POM DSC	-	41
25	H	H	CH_3	H						
26	H	H	OCH_3	H						
27	H	H	OC_2H_5	H						
28	H	H	H	H						
29	H	H	CH_3	H						

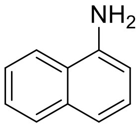
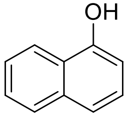
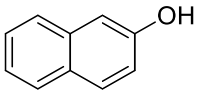
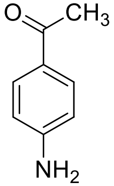
30	H	H	OCH_3	H		considerable variation for mesophase formation and temperature ranges. Absorption maxima of ultraviolet spectra shifted bathochromically with existence of electron donar groups on benzothiazole skeleton exposed highest fluorescence emission.				
31	H	H	OC_2H_5	H						
32	H	H	H	H						
33	H	H	CH_3	H						
34	H	H	OCH_3	H						
35	H	H	OC_2H_5	H						
36	H	H	H	H		Method for synthesis of het-azo dyes, coupled with 2-naphthol, 8-hydroxy quinoline and 2,6-diaminopyridine.	Biologically active molecules with safer antimicrobial and in vitro antioxidant property. Dyes of azo-benzothiazole are safer up to upper dosage. Antimicrobial activity studies revealed that azo dye with benzothiazole moiety exhibited a potential antimicrobial activity. Azo compounds certainly hold a greater promise in discovering a safer antimicrobial and antioxidant agent.	Elemental analysis FT-IR UV-Vis ^{1}H NMR and mass	-	42
37	H	H	H	H						
38	H	H	H	H						
39	OCH_3	H	H	H		Compounds having good substantivity to polyester fibre and exhaust well to produce dyeing with efficient fastness to washing, moderate light fastness, pur-spiration and rubbing with moderate sublimation fastness.	-	FT-IR NMR UV-Vis M.P.	-	43
40	OCH_3	H	H	H						
41	OCH_3	H	88H							

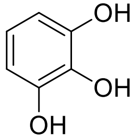
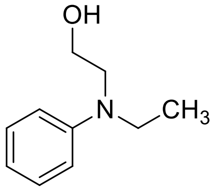
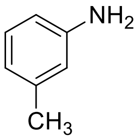
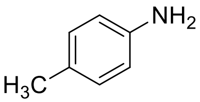
42	OCH_3	H	H							
43	OCH_3	H	H							
44	OCH_3	H	H							
45	OCH_3	H	H							
46	OCH_3	H	H							
47	OCH_3	H	H	H						
48	OCH_3	H	H	H						
49	OCH_3	H	H	H						
50	OCH_3	H	H	H						

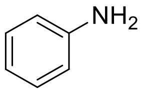
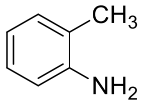
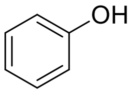
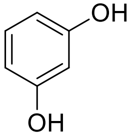
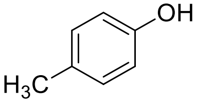
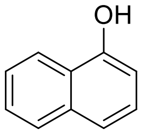
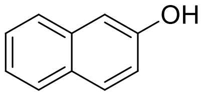
51	OCH_3	H	H	H						
52	H	H	H	H		Complexes of Zn II and Ni II are tridentate monobasic N_2O coordination including azo Ns, ring N and enolized carbonyl O. Cu II complexes conform to [CuL(OAc)] stoichiometry. Zn II chelates are diamagnetic in behavior, Cu II and Ni II complexes paramagnetic in nature.	-	^1H-NMR FT-IR ^{13}C-NMR Mass spectra	Cu II Ni II Zn II	44
53	H	H	F	H		R-2-aminobenzothiazole reacts with acetyl acetone, various hydrazine to give different compounds.	All studied compounds are biologically active.	FT-IR ^{13}C-NMR ^1H-NMR Mass spectra	-	45
54	Cl	H	H	H						
55	Cl	H	H	H						

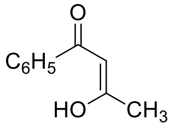
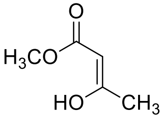
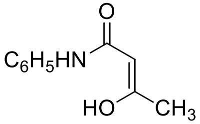
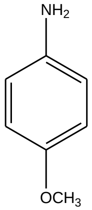
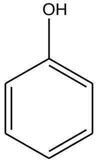
56	Cl	H	H	H						
57	H	H	NO_2	H		Dyes have a low potential to accumulate in the lipid tissue.	-	NMR Mass spectra DSC	-	46
58	H	Cl	Cl	H						
59	H	H	NO_2	H						
60	H	H	Cl	H						
61	H	H	H	H		The solvatochromic nature of dyes in (diverse solvents) have been estimated. substituent, base and acid effects on absorption maxima of dyes.	-	FTIR ^{1}H-NMR ^{13}C-NMR Mass spectra	-	47
62	H	H	H	H						
63	H	H	EtO	H						

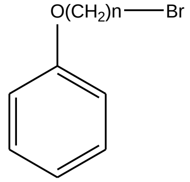
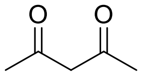
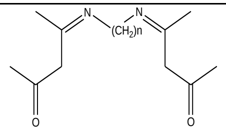
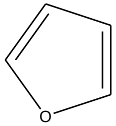
64	H	H	H	H		Proposed method was a simple and has good sensitivity. proposed method has advantageous over some of reported visible spectrophotometric methods.	Accuracy precision, and stability of coloured species were studied. The proposed method is suitable for evaluation of phenylphrine in neat form and in nose drop-formulation without excipients interference.	UV-Vis	-	48
65	H	H	H	H		Emission and absorption spectra for het-aryl-azo-quinoline molecules were observed in liquids and liquid crystalline solvents.	Spectra Het-aryl-azo-quinoline dyes were described according to azo/hydrazone tautomerism in conjunction and solvatochromic characteristic of preferred tautomer.	TLC UV-Vis FT-IR ^{1}H NMR	-	49
66	H	H	OCH_3	H						
67	H	H	NO_2	H						
68	H	H	Cl	H						
69	H	H	OCH_3	H						
70	H	CH_3	CH_3	H						
71	H	OMe	H	H		Colours of the studied azo dyes are violet to blue having high molecular extinction coefficient between 2.6 - 4.7. Dyes showed unique fluorescence emission at a range of wavelength 409–494 nm. Emission and absorption spectra changes of some dyes - analysed in solvents with different polarity.	Antibacterial activities of dyes are assessed against gram negative and positive bacteria involving *E. coli*, S. *aureus*, *P. aeruginosa*, and *S. epidermidis* and varied concentrations of dyes exhibited an anti-gram-positive bacterial potential.	FT-IR ^{1}H-NMR ^{13}C-NMR	-	50
72	H	OEt	H	H						
73	H	H	H	H						
74	H	NO_2	H	H						
75	H	OMe	H	H						
76	H	OEt	H	H						
77	H	H	H	H						
78	H	NO_2	H	H						
79	H	H	H	H		Absorption spectra of dyes are described experimentally and theoretically by TD-DFT methods. Absorption maxima for het-aryl-azo-pyrazolone dyes having benzothiazolyl diazo moiety displayed bathochromic shifts because these dyes	-	Elemental analysis FT-IR ^{1}H NMR DFT	-	51
80	H	H	Cl	H						
81	H	H	OCH_3	H						
82	H	Me	Me	H						

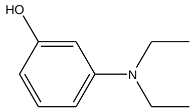
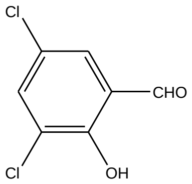
						give easily acidic H to DMSO and DMF. Maximum absorption was obtained with TD-DFT/B3LYP calculations using nonequilibrium method.				
83	H	H	H	H		Dyes from 1-Naphthol and 2-Naphthol have same melting point temperatures, same molecular weight and formula but different appearance and have different wavelength of absorption all these changes were due to position of the HO- group in each dye molecule. Heterocyclic disperse dyes have high wash fastness for polyester, nylon and acrylics fibers, while their fastness to light is poor and that all the dyes absorbed at the visible region of the spectrum.	-	Drapkira's method Melting Temperature Light Absorption	-	52
84	H	H	H	H						
85	H	H	H	H						
86	H	H	H	H		Metal chelates complexes have been prepared with ligand. Exploration of antibacterial and antifungal potential was lifted out opposite experimented organism. According result data an octahedral structure was suggested.	Synthesized new metal complexes exhibited potential antifungal and antibacterial activity against: *S. aureus, E. Coli, C. albicans* and *C. tropicalis.*	FT-IR UV-Vis ^{13}CNMR ^{1}H NMR Elemental analysis	Cu II Zn II Co II Ni II	53

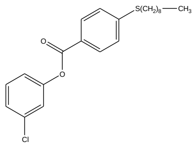
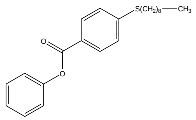
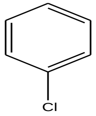
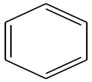
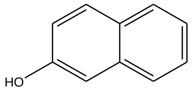
87	H	H	Br	H		The diazotized 2-amino-6-bromobenzothiazole is coupled with pyrogallol to form organic reagent, 4-(6-bromo-2-benzothiazolylazo) pyrogallol (4-Br-BTAP).	-	FT-IR, UV-Vis ^{1}H-NMR	Cu (II) Pd (II)	54
88	H	H	Me	H		Solvatochromic behavior of azo molecule was studied by visible spectra in some mixed and pure organic solvents. Azo compounds showed one band in electronic absorption spectra in all organic media, except acetic acid. It was attributed to varying of electronic transition in aromatic and hetero-aromatic skeleton including all electronic system of the molecule. However, in acetic acid a second band at longer λmax for few molecules.	-	UV–Vis FT-IR ^{1}H NMR Elemental analysis	-	55
89	H	H	Br	H						
90	H	H	Cl	H						
91	H	H	H	H		Synthesized dyes have studied fastness to light, perspiration, sublimation and fairly rubbing fastness properties. These compounds used as an indicator in acid-base titrations. Dyes were	Dyes show good antibacterial activity against *B. subtilis, S. aureus.*	FT-IR ^{1}H-NMR LC-MS UV-Vis	-	56
92	H	H	H	H						

93	H	H	H	H		screened for their antimicrobial potential. Result shows that benzothiazole skeleton having azo linkages and aromatic moiety with electron donating group at p-position may be important enough for study for the antimicrobial potential.				
94	H	H	H	H						
95	H	H	H	H						
96	H	H	H	H						
97	H	H	H	H						
98	H	H	H	H						
99	H	H	H	H						
100	H	H	H	H	Ph	Molecules were used for inks for printing cotton, polyamide fabrics. All these compounds have good light fastness properties.	-	M.P. NMR	-	57
101	H	H	H	H	Me					

102	H	H	H	H		Arylazo product was synthesized by coupling 2-benzothiazole diazonium ion on active methylene group of the *β*->C=O molecule like benzoyl acetone, methyl acetoacetate, acetoacetanilide.	-	FTIR ^{1}H-NMR ^{13}C-NMR Mass spectra	Ni (II), Cu (II) Zn (II)	58
103	H	H	H	H						
104	H	H	H	H						
105	H	H	H	H		Metal chelates were synthesized with compounds. Screening of antimicrobial potential were lifted out opposite experimental strains. Antibacterial potential and antifungal potential of ligand and metal complexes was explored.	Antibacterial potential and antifungal potential of ligand and its complexes was studied, between all complexes Zn (II) complex exhibited higher antibacterial potential through inhibition zone of 15 mm against, *E. coli*, *Steptococcus sp.* and *S. epidermidis* related with ligand and other complexes. Zn (II) molecule antifungal potential of *C. albicans* shows higher inhibition area of 18 mm with higher activity from ligand and other complexes.	M.P. Atomic absorption FTIR UV-vis	Co^{2+} Ni^{2+} Cu^{2+} Zn^{2+}	59
106	H	H	OCH_2CH_3	H		Transition phase temperature and enthalpy values are examined by a differential scanning calorimeter (DSC). Transition phase	-	FT-IR, ^{1}H-NMR ^{13}C-NMR DSC POM	-	60

107	H	H	OCH_2CH_3	H	 n=5,6,8,9,10,11,12	temperatures and corresponding change of enthalpy for all molecules measured by DSC. Molecules in this series indicate enantiotropic N phase. While, some of them also exhibit monotropic SmA phase.				
108	H	H	H	H		Complexes displayed dibasic tetradentate coordination having imino and hydrazone nitrogen's whereas >C=O groups are exempted from coordination.	-	^{1}H NMR FTIR Mass spectra	Ni (II), Cu (II) Zn (II)	61
109	H	H	H	H						
110	H	H	H	H	C_6H_5	Synthesized compounds were potentially biologically active and the dyeing ability of these azo dyes were checked by applying azo dyes to different nature.	All the compounds show fair antibacterial potential when compared to ampicillin as a standard control, also all the azo dyes exhibited good dyeing ability for cotton fabric and gives a bright brilliant shade. Fastness to light, hot press and wash are fair. Dyeing was dischargeable and it's highly resistant to acid fading and light.	FT-IR ^{1}H-NMR Mass UV	-	62
111	H	H	H	H	2-OHC_6H_4					
112	H	H	H	H	4-ClC_6H_4					
113	H	H	H	H	4-BrC_6H_4					
114	H	H	H	H	4-$OCH_3C_6H_4$					
115	H	H	H	H	4-NO_2 C_6H_4					
116	H	H	H	H	$N(CH_3)_2$ 4- C_6H_4					
117	H	H	H	H						
118	H	H	H	H	2- CH_3, 4-$NH_2C_6H_3$					

119	H	H	H	H	3- CH_3, 2- $NH_2C_6H_3$					
120	H	H	H	H	4-$NH_2C_6H_4$					
121	H	H	H	H	3- CH_3, 4- $NH_2C_6H_3$					
122	H	H	H	H	4-OH C_6H_4					
123	H	H	H	H	2,4-$(OH)_2C_6H_3$					
124	H	H	H	H	5-CH_3, 2-OHC_6H_3					
125	H	H	H	H	4-$OHC_{10}H_6$					
126	H	H	H	H	3-$OHC_{10}H_6$					
127	H	CH_3	H	H		X-ray single-crystal diffraction characterization of some molecules reveal that they are similar planar conformation between the phenol and benzothiazole units but dissimilar dimeric crystal pack. Electronic spectra of dyes demonstrate that presence of N=N and C=N chromophore units in addition to with substituent effects of varied auxochrome moiety in benzothiazole backbone makes significant variation of bathochromic and hypsochromic shifts although only slight differences in their molecular skeleton.	-	^{1}H-NMR FT-IR UV-Vis Elemental analysis X-ray single-crystal diffraction	-	63
128	H	H	H	H						
129	H	NO_2	H	H						
130	H	H	CH_3	H						
131	H	H	H	H						
132	H	H	NO_2	H						
133	H	CH_3	H	H						
134	H	H	H	H						
135	H	NO_2	H	H						
136	H	H	CH_3	H						
137	H	H	H	H						
138	H	H	NO_2	H						

139	H	H	H	H		Mesomorphic properties of substituted molecules are compared with those of unsubstituted parent molecules to estimate effect of nature of lateral substituents. All prepared compounds showed enantiotropic nematic phase except EB$_1$-OH.	-	^{1}H-NMR Mass spectra Elemental analysis	-	64
140	H	H	H	H						
141	H	H	H	H						
142	H	H	H	H						
143	H	H	H	H		Metal ion chelate molecules are more toxic to same micro-organism under experimental conditions. The increase in antifungal potential of metal chelates might be due to effect of metal ion on normal cell process.	Biological activity of ligand and complexes were studied against different types of fungi and bacteria which included Staphylococcus, S. marcescens, Klebsiella and P. aeruginosa.	UV-Vis FTIR ^{1}HNMR	Fe^{+3} Cr^{+3} Co^{+2} Ni^{+2} Cu^{+2}	65

Abbreviations:

E. coli : *Escherichia coli*
S. pyogenes : *Streptococcus pyogenes*
P. vulgaris : *Proteus vulgaris*
E. faecalis : *Enterococcus faecalis*
B. subtilis : *Bacillus subtilis*
C. albicans : *Candida albicans*
S. aureus : *Staphylococcus aureus*
P. aeruginosa : *Pseudomonas aeruginosa*
CT : Charge Transfer
DC : Direct Current
GS : ground states
ES : excited states
M.P. : Melting Point
IR : Infra-Red
UV-Vis : Ultra Violet Visible
NMR : Nuclear Magnetic Resonance
TGA : Thermogravimetric Analysis
POM : Polyoxymethylene
DSC : Differential Scanning Calorimetry
SAR : Structural Activity Relationship
SmC : Smectic C
SmA : Smectic A
N : Nematic
LDL : Low-density lipoproteins
HDL : Heigh-density lipoproteins
DFT : Density Functional Theory
TD-DFT : Time Dependent Density Functional Theory
HRS : Hyper-Rayleigh scattering
SAXS : Small-angle X-ray Scattering
FMO : Frontier Molecular Orbitals
SPR : Structural Property Relationship

CONCLUSION:

Molecules prepared from azo transforms of 2-aminobenothiazole are useful for varied uses such as colours of dyes containing azo mofits include varied applications for wool dying in for animal textile fibres dyeing, for chelation ion-exchanging properties of different polymeric compounds. The pharma-wise regularity and readily dissolvable salts, polymeric biodegradable pro-drug, anti-helmentic, antifungal potential and their dye process ability, for potential antioxidant ability. For basic solution these will normally form more easily soluble salts having a deep coloration. Azo variants also used as prodrugs. The present review paper gives an overview or detailed account of azo-benzothiazole synthesized and its use in various reactions.

The molecules synthesized containing azo mofits in azo- benzothiazole are useful for many applications dying industry, for ion-exchanging applications of polymers. The antimicrobial (antibacterial, antifungal) and antioxidant activities. Azo derivatives of benzothiazole serve as a building block for many intermediates.

On conclusion we found that the present review covers the study or applications as tabulated below…

Description	**No.**	**Description**	**No.**
Biological Activity Antibacterial	4	Liquid Crystal Behaviour	5
Synthesis & Characterization	15	Antimicrobial	4
Reduction	1	Dyes	11
Sensor	1	Antifungal	1
Dichroism	1	Analytical	5
Complex	6	Tautomerism	3
Metal Determination	1	Computational Studies	1
UV-Vis Study	7		

This can be graphically represented as below…

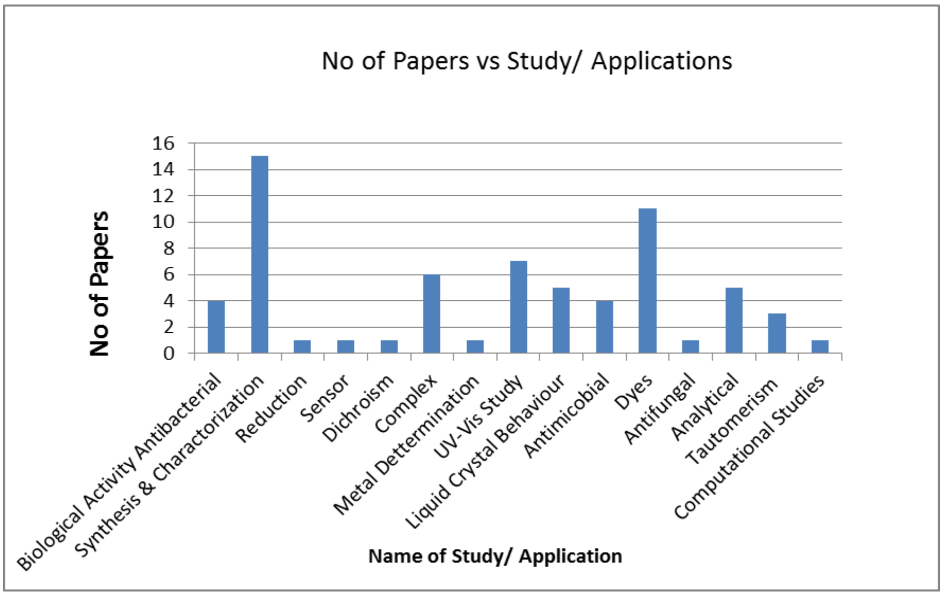


Fig. 1: Histogram presenting the number of papers vs use or applications recorded in review.

FUTURE SCOPE: -

Thus, this review may be useful to many researchers for further developments of azo-benzothiazole and their varied reactions to form different applied derivatives in near future.

ACKNOWLEDGEMENT: Authors are thankful to the Management and Principal of Smt. G. G. Khadse College, Muktainagar and Management and Principal of Art and Science College, Bhalod and the Management, for the facility given for the present work.

PERSONAL IDENTITY: - **Google Scholar:** C. J. Patil; **ORCID ID:** orcid.org/0000-0002-7535-698X; **Researcher ID:** G-6274-2015; **Scopus ID:** 56810689600, **Google Scholar:** Ganesh R. Chaudhary; **ORCID ID:** orcid.org/0000-0002-9020-0828; **Google Scholar:** A. N. Dhake; **ORCID ID:** orcid.org/0000-0001-5993-1676.

DECLARATION: The work done without any kind of funding. No any conflict of interest.

REFERENCES:

i. Griess J. P.; Vorläufige Notiz über die Einwirkung von salpetriger Säure auf Amidinitro- und Aminitrophenylsäure; Annalen Der Chemie Und Pharmacie; 1858, **106(1)**, 123-125 , doi: 10.1002/jlac.18581060114.
ii. Griess J. P.; Philos. Trans. R. Soc. London; 1864, **164**, 667-731.
iii. Griess J. P.; Ann. Chem. Justus Liebigs; 1866, **137**, 3991.
iv. Doyle M. P.; Siegfried B.; Dellaria J. J. F.; Alkyl Nitrite-Metal Halide Deamination Reactions. Substitutive Deamination of Arylamines by Alkyl Nitrites and Copper (II) Halides. A Direct and Remarkably Efficient Conversion of Arylamines to Aryl Halides; J. Org. Chem.; 1977, **42**, 2426-2431.
v. Doyle M. P.; Dellaria J. J. F.; Siegfried B.; Bishop S. W.; Reductive Deamination of Arylamines by Alkyl Nitrites in N, N-Dimethylformamide. A Direct Conversion of Arylamines to Aromatic Hydrocarbons; J. Org. Chem.; 1977**, 42**, 3494-3498.
vi. a) Sandmeyer T. Ber. Dtsch. Chem. Ges., 1884; 17(4) 2650–2653. doi:10.1002/cber.188401702202, Ueber die Ersetzung der Amid-gruppe durch Chlor, Brom und Cyan in den aromatischen Substanzen; b) www.name-reaction.com/sandmeyer-reaction (visited on 11-12-2021).
vii. Sandmeyer T. Ber. Dtsch. Chem. Ges., 1884; 17(3) 1633-1635, doi: 10.1002/cber.18840170219, Ueber die Ersetzung der Amidgruppe durch Chlor in den aromatischen Substanzen.
viii. Kikukawa K.; T. Matsuda.; Chem. Lett.; 1977, 159-162.
ix. Kikukawa K.; Nagira, K.; Matsuda, T.; Palladium(O)-Catalyzed Arylation of Unsaturated Compounds with Arenediazoium Salts; Tetrahedron; 1981, **37**, 31-36.
x. Zollinger H.; Colour Chemistry-Synthesis, Properties of Organic Dyes and Pigments. VCH Publishers; New York; 1987, 92-100.
xi. Browing C. H.; Cohen J. B.; Ellingworth S.; Gulbransen R.; The antiseptic properties of the amino derivatives of styryl and anil quinoline; Journal Storage; 1926, **100**, 293-325
xii. Child R. G.; Wilkinson R. G.; Tomcu-Fucik A.; Effect of substrate orientation of the adhesion of polymer joints; Chem. Abstr.; 1977, **87**, 6031.
xiii. Pagga U.; Brown D.; The degradation of dyestuffs in aerobic biodegradation tests, Chemosphere; 1986, **15**, 479-491.
xiv. Khalid A.; Arshad M.; Crowley D. E.; Accelerated decolorization of structurally different azo dyes by newly isolated bacterial strains; Appl. Microbiol. Biotech; 2008, **78**, 361-369. doi: 10.1007/s00253-007-1302-4.
xv. Garg H. G.; Prakash C.; Preparation of 4-arylazo-3,5-disubstituted-(2H)-1,2,6-thiadiazine 1,1-dioxides; J. Med. Chem.; 1972, **15**(4) 435-436.
xvi. Park C.; Lim J.; Lee Y.; Lee B.; Kim S.; Lee J.; Kim S.; Optimization and morphology for decolorization of reactive black 5 by Funalia trogii; Enzy. Microb. Tech.; 2007, **40**, 1758-1764. doi: 10.1016/j.enzmictec.2006.12.005.

xvii. Chandravadivelu G.; Senniappan P.; In-vitro antimicrobial activity of novel derivative of azo dye from cyano ester; Int. J. Res. Pharm. Chem.; 2011, **1**(4) 1082-1086.

xviii. Chopde H. N.; Meshram J. S.; Pagadala R.; Mungole A. J.; Synthesis, characterization and antibacterial activity of some novel azo-azoimine dyes of 6-bromo-2-naphthol; Int. J. Chem. Tech. Res.; 2010, **2**(3) 1823-830.

xix. Swati G.; Karnawat R.; Sharma I. K.; Verma P. S.; Synthesis, Characterisation and Antimicrobial Screening of Some Azo Compounds; Int J. Appl. Biol Pharma. Techn.; 2011, **2**(2) 332-338.

xx. Wilson C. O.; Givold O.; Text book of Organic Medicinal and pharmaceutical Chemistry; Pitman Medical Publishing Co. ltd, London; UK; 1966.

xxi. Patil C. J.; Patil P. A.; Patil P. B.; Patil M. C.; Coupling Reactions Involving Aryldiazonium Salt: Part-I. Chemoselective Synthesis of 3-Oxo-(substituted-2-phenylazo)-butyricacid ethyl ester derivatives and their Antibacterial Activity; Der. Chemica. Sinica; 2015, **6**(5) 108-114.

xxii. Patil C. J.; Patil M. C.; Pachpol N. R.; Waykole V. S.; Coupling Reactions Involving Aryldiazonium Salt: Part-II. Chemoselective Condensation with Acetylacetone and Antibacterial Activity; Der. Chemica. Sinica; 2015, **6**(5) 115-121.

xxiii. Patil C. J.; Talele D. S.; Talele S. P.; Pohekar P. R.; Patil A. S.; Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-IV. Chemoselective Synthesize and Antibacterial Activity of 3-(Substituted-phenylazo)-pentane-2,4-done; Int. J. Pharm. Sci. Rev. Res.; 2017, **45**(1), 64-73.

xxiv. Patil C. J.; Talele D. S.; Talele S. P.; Pohekar P. R.; Kolhe D. S.; Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-VII. Product of reaction of aryl diazonium chloride with active methylene group containing moiety; J. Pharm. Sci. Res.; 2019, **11** (6) 2213-2219.

xxv. Patil C. J.; Patil M. C.; Rane V.; Mahajan K.; Nehete C. A.; Coupling Reactions Involving Reactions of Aryldizonium Salts: Part-III. Chemoselective condensation with β-napthol to Synthesize Sudan-I, its Nitro Derivaties and Antibacterial Potential; Int. J. Chem. Biol. Phy. Envir. Sci.; 2015, **5**(4) 3860-3867.

xxvi. Patil C. J.; Waghulade G. P.; Patil M. C.; Patil Mru. C.; Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-V. Chemoselective Synthesis of 1-(Substituted-phenyl)-azo-naphthalene-2-ol; Int. J. Pharm. Res. Rev.; 2017, **45**(2), 21-28.

xxvii. Patil C. J.; Waghulade G. P.; Patil M. C.; Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-VI. Chemoselective Condensation with Resorcinol; Int. J. Green Herbal Chem.; 2017, **6**(2) 5-14. doi: 10.24214/IJGHC/GC/6/2/0514.

xxviii. Al-Rubaie L. A. R.; Mhessn R. J.; Synthesis and characterization of azo dye para red and new derivatives; E-J. Chem.; 2012, **9**(1) 465-470.

xxix. Shridhar A. H.; Keshavayya H.; Hoskeri H. J.; Ras A.; Synthesis of some novel bis 1,3,4-oxadiazole fused azo dye derivatives as potent antimicrobial agents; Int. Res. J. Pure Appl. Chem.; 2011, **1**(3) 119-129. doi: 10.9734/IRJPAC/2011/493.

xxx. Nehete C. A.; Patil C. J.; Coupling Reactions Involving Reactions of Aryldiazonium Salt: Part-IV. Synthesis of Novel Azo-Aniline from Different Substituted Anilines and study of their Biological Activity; Int. J. Pharma Biol. Arch.; 2017, **8** (1) 20-26.

xxxi. Heinrich Z.; Color Chemistry; Synthesis, Properties and Applications of Organic Dyes and Pigments; VCH, Angew. Chem. Int. Ed.; 2004, **43**, 5290 – 5292.

xxxii. Brode W. R. ; Gould J. H. ; Wyman G. M.; The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXV. Phototropism and cis-trans Isomerism in Aromatic Azo Compounds; J. Am. Chem. Soc.; 1952, **74**(18).

xxxiii. Elisangela F.; Andrea Z.; Fabio D. G.; Cristiano R. M.; Regina D. L.; Artur C. P.; Biodegradation of textile azo dyes by a facultative Staphylococcus arlettae strain VN-11 using a sequential microaerophilic/aerobic process; Int. Biodeter. Biodegrad.; 2009, **63**, 280-288.

xxxiv. Patil C. J.; Nehete C. A.; The Azo Derivatives of Salicylic Acid; Int. J. Pharm. Sci. Rev. Res.; 2015, **33**(2) 248-256.

xxxv. Kyriaki G.; Ioannis E.; Tsatsaroni E.; Colour and dyeing properties of hetarylazo disperse dyes, Visual and instrumental evaluation; Am. J. Appl. Chem.; 2014, **2**(2) 33-37.

xxxvi. Hamzah M. A. M.; Jebur I. K.; Ahmed A. K.; Synthesis, Characterization and Biological Activity Evaluation of Some New Azo Derivatives from 2-Amino Benzothiazole and their Derivatives; KUJSS; 2018, **13**(1) 212- 227.

xxxvii. Podsiadły R.; Sokołowska J.; Marcinek A.; Zielonka J.; Socha A.; Kazmiersk M.; The relationship between the electrochemical and photochemical reduction of some azo dyes derived from 2-aminobenzothiazole; J. Photochem. Photobio.; 2005, **171**, 69–76.

xxxviii. Coelho F. L.; Braga C. de Á.; Zanotto G. M.; Gil. E. S.; Campo L. F.; Gonçalves P. F.; Rodembusch F. S.; Santos F.; Low pH optical sensor based on benzothiazole azo dyes; Compu. Photochem. Photophy.; 2018, 259, 514-525. doi: 10.1016/j.snb.2017.12.097.

xxxix. Mohamed T. Y.; Synthesis and Spectral Studies of Co (II), Cu (II) and Fe (III) Ions with 2(2'-Hydroxynaphthyl azo-) Benzothiazole; Egypt. J. Chem.; 2014, **57**(1) 1-10.

xl. Jarad A. J.; Majeed I. Y.; Hussein A. O.; Synthesis and spectral studies of heterocyclic azo dye complexes with some transition metals; J. Phy. Conf. Series; 2018, **1003**, 012021, doi: 10.1088/1742-6596/1003/1/012021.

xli. Karim Md. R.; Sheikh K. R. Md.; Salleh N. M.; Hassan R. Y. A.; Hoque Md. A.; Synthesis and characterization of azo benzothiazole chromophore based liquid crystal macromers: Effects of substituents on benzothiazole ring and terminal group on mesomorphic, thermal and optical properties; Materials Chem. Phy.; 2013, **140,** 543-552.

xlii. Keerthi Kumar C. T.; Keshavayya J.; Ravi B. N.; Patil S. R.; Synthesis, Characterization and Biological Studies of Azobenzothiazole Dyes; Int. J. Inno. Res. Delop.; 2016, **5**(11).

xliii. Dalal M. M.; Desai K. R.; Heteroaryl disperse dyes derived from 2-aminobenzothiazole and their application on polyester fibre; Ind. J. Fibre Tex. R.; 1996, **21**, 161-164.

xliv. Ummathur M. B.; Babu D. K.; Krishnankutty K.; Heteroaryl azo derivatives of cyclohexane-1,3-dione and their metal complexes; J. Serb. Chem. Soc.; 2014, **79** (3) 303–311.

xlv. Sareen V.; Khatri V.; Shinde D.; Sareen S.; Synthesis of some new derivatives of dimethyl azopyrazole as antifungal agent; Ind. J. Chem.; 2011, **50B**, 937-940.

xlvi. Makwana U. C.; Thaker B. T.; Patel B. S.; Dhimmar Y.; Chothani N. J.; Solanki D.B.; Patel N.; Patel K. B.; Mesomorphic studies of novel azomesogens having a benzothiazole core: Synthesis and characterisation; Liq. Cryst.; 2012, **40**(40) 237-248. doi: 10.1080/02678292.2012.737478.

xlvii. Karcı F.; Karcı F.; Synthesis and absorption spectra of some novel heterocyclic disazo dyes derived from pyridone and pyrazolone derivatives; Dyes and Pigments; 2008, **76**(1) 147-157. doi: 10.1016/j.dyepig.2006.07.029.

xlviii. Othman N. S.; Noha T. H.; Fatah A.; Spectrophotometric Determination of Phenylephrine Hydrochloride by Coupling with Diazotized 2-Aminobenzothiazole; J. Raf. Sci.; 2009, **20**(4), 69-81.

xlix. Gilani A. G.; Moghadam M.; Zakerhamidi M.S.; Moradi E.; Solvatochromism, tautomerism and dichroism of some azo quinoline dyes in liquids and liquid crystals; Dyes and Pigments; 2012, **92**, 1320-1330.

l. Nourmohammadian F.; Alikhani M. Y.; Gholami M. D.; Abdi A. A.; Benzothiazole-Based Bis-azo Cationic Fluorescent Dyes with Extended Conjugated Systems: Synthesis and Properties; J. Appl. Sol. Chem. Mode.; 2015, **4**, 83-94.

li. Aktan E.; Uyar T.; Hetarylazo pyrazolone Dyes Based on Benzothiazole and Benzimidazole Ring Systems: Synthesis, Spectroscopic Investigation, and Computational Study; J. Chem.; 2017, Article ID 8659346. doi: 10.1155/2017/8659346.

lii. Abdullahi H. J.; Synthesis and study of dyeing properties of heterocyclic dis derived from 2-aminobenzothiazole; Int. J. Adv. Res.; 2019, **7**(5) 1054-1059. doi:10.21474/IJAR01/9135.

liii. Al-Zinkee J. M. M.; Jarad A. J.; Synthesis, Spectral Studies and Microbial Evaluation of Azo Dye Ligand Complexes with Some Transition Metals; J. Pharm. Sci. Res.; 2019, **11**(1) 98-103.

liv. Naser N. A.; Kahdim K. H.; Taha D. N.; Synthesis characterization of an organic reagent 4-(6-bromo-2benzothiazolylazo) pyrogallol and its analytical application; J. Oleo Sci.;2012, **60**(7) 387-392.

lv. Moradie E. O.; Rufchahi H. Y.; Mohammadini M.; Synthesis and spectral properties of some azo disperse dyes containing a benzothiazole moiety; J. Mol. Liq.; 2013, **188**, 173-177. doi: 10:1016/jmolliq.2013.08.21.

lvi. Awale A. G.; Gholse S. B.; Utale P. S.; Synthesis, Spectral Properties and Applications of Some Mordent and Disperse mono azo dyes derived from2-Amino-1,3-benzothiazole; Res. J. Chem. Sci.; 2013, **3**(10) 81-87.

lvii. Ahmed K.; Shahin A; Ragheb A. El-Hennawi H.; A Facile Synthesis with One Step of Disperse Azo Dyes to be Applied as Nano-Inks in Textile Printing; Biointerface Res. Apple. Chem.; 2021, **11**(4) 11713-11723.

lviii. Krishnankutty K.; Ummathur M. B.; Babu D. K.; Benzothiazolyl azo derivatives of some β-dicarbonyl compounds and their Cu (II), Ni (II) and Zn (II) complexes; J. Serb. Chem. Soc.; 2010, **75**(5) 639–648. doi: 10.2298/JSC090816040K.

lix. Dahi M. A.; Jarad A. J.; Synthesis, characterization and biological evaluation of thiazolyl azo ligand complexes with some metal ions; J. Phy. Conf.; 2020, **1664**, 012090, doi:10.1088/1742-6596/1664/1/012090.

lx. Alshargabi A; Yeap G. Y.; Takeuchi D.; Masato M.; Synthesis and Terminal Chain Effect on the Phase Transition Behaviour of Azo- Bridged Benzothiazole-Phenyl Ethers; Mol. Cryst. Liq. Cryst.; 2013, **575**, 128–139. doi: 10.1080/15421406.2013.766919.

lxi. Basheer U. M.; Sayudevi P.; Krishnankutty K.; Schiff Bases of 3-[2-(1,3-benzothiazol-2-yl) hydrazinylidene] pentane-2,4-dione with aliphatic diamines and their metal Complexes; J. Argentine Chem. Soc.; 2009, **97(**2) 31-39.
Awale A. G.; Gholse S. B.; Utale P. S.; Synthesis, Characterization and Antimicrobial activity of 2- Amino-1,3-benzothiazole, Schiff bases and Azo dyes of 2-Amino- 1,3-benzothiazole; IOSR-JPBS 2013, **6**(2) 01-07.

lxii. Tao T; Xu F.; Chen X.C.; Liu Q. Q; Huang W; Xiao Z. Y.; Comparisons between azo dyes and Schiff bases having the same benzothiazole/phenol skeleton: Syntheses, crystal structures and spectroscopic properties; Dyes and Pigments; 2012, **92**, 916-922. doi: -10.1016/j.dyepig.2011.09.008.

lxiii. Al-Hamdani U. J.; Abbo H. S.; Al-Jaber A. A.; Salam J. J. T.; New azo-benzothiazole based liquid crystals: synthesis and study of the effect of lateral substituents on their liquid crystalline behaviour; Liq. Cryst.; 2020, **47**, 2257-2267. doi: -10.1080/02678292.2020.1766134.

lxiv. Mohammed H. H.; Mageed Z. N.; Najim M.; Synthesis and biological activity study of 1-[4,5,6,7-tetrahydro-1,3-benzothiazol-(2-yldiazenyl)]-2-naphthol complexes; J. Chem. Pharm. Res.; 2013, **5**(11), 711-720.

Received on October 13, 2021.