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Synthesis, Spectral Properties and Applications of Some Mordant and Disperse Mono Azo Dyes Derived from 2-amino-1, 3-benzothiazole

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Abstract

Mono azo dyes were synthesized using diazotized 2-amino-1, 3-benzothiazole followed by coupling with different substituted anilines and phenols in appropriate reaction condition. Dyes were readily obtained in 65-85 % yield in very pure form. The structures of newly prepared dyes were confirmed from FT-IR, 1H-NMR, LC-MS, UV-Vis spectroscopic technique. The UV-Visible spectras of new mono azo dyes in suitable solvent was investigated in terms of structural property relationship. The dyeing assessment of all the dyes was evaluated on various fabrics. The results revealed that a better hue is obtained on cotton mordant fibres. The prepared azo dyes were tested as an indicator for different types of titrations. It was found that some of the dyes are very good indicators for acid – base titrations, giving a very sharp and distinct end point. Antimicrobial evaluation revealed that the dyes show good antibacterial activity.

Keywords: Heterocycles, benzothiazole, coupling with phenols and anilines, diazo compounds, substituent effects, antimicrobial activity.

Introduction

Benzothiazole azo dyes are well established as mordant and disperse dyes. Azo dyes are the single largest synthetic chemical class of industrial colorants[1]. Azo dyes account for approximately 60-70% of all dyes used in food and textile manufacture[2]. Azo dyes can different set of colours in which yellow/red dyes are more common as blue/brown dyes. The different colours of azo dyes can be attributed to the extra stability of azo groups and substituent by extended conjugation Figure-1 through aromatic ring[3]. The extended conjugation in azo dyes helps to absorb the light in visible range which makes most of the azo compounds coloured.

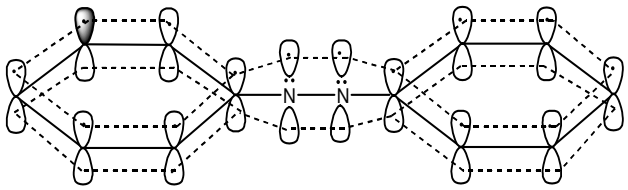


Figure-1
Extended delocalization of π- electrons

The process involved in the synthesis is very simple and the raw materials used are readily available and cheap which leads to the manufacture of azo dyes at a larger scale. The reactions are generally carried out at lower temperature and the solvent mostly used is water which reduces the environmental impact. All these factors contributes to the cheap production of azo dyes[4-8].

Azo dyes show better stability than a natural dyes in the whole pH range of foods, are heat stable and do not fade when exposed to light[9] or oxygen[10-11]. Because of low toxicity, less allergic reactions and no hyperactivity effect, azo dyes are used in food stuffs (eg. tartrazine, yellow2G, sunset yellow, azorubin, etc)[12-13]. Azo dyes have also been utilised in non-textile application such as lasers, nonlinear optical systems[14], reprography[15], dye sensitized solar cells[16] and metallochromic indicators[17]. Among all benzothiazole azo dyes are more popular one in production of red azodye due to their better fastness properties [18-21] and high level dyeing properties[22-27]. Azo dyes are also used as indicators for acidimetry and alkalimetry.

In alkaline medium the dye is in azo form and solution is in particular color. In acidic medium the color deepens to different colour as an azo nitrogen atom takes a proton and then give resonance hybrid shown in (figure-2)

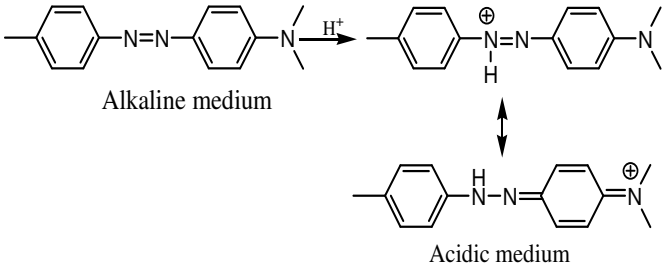
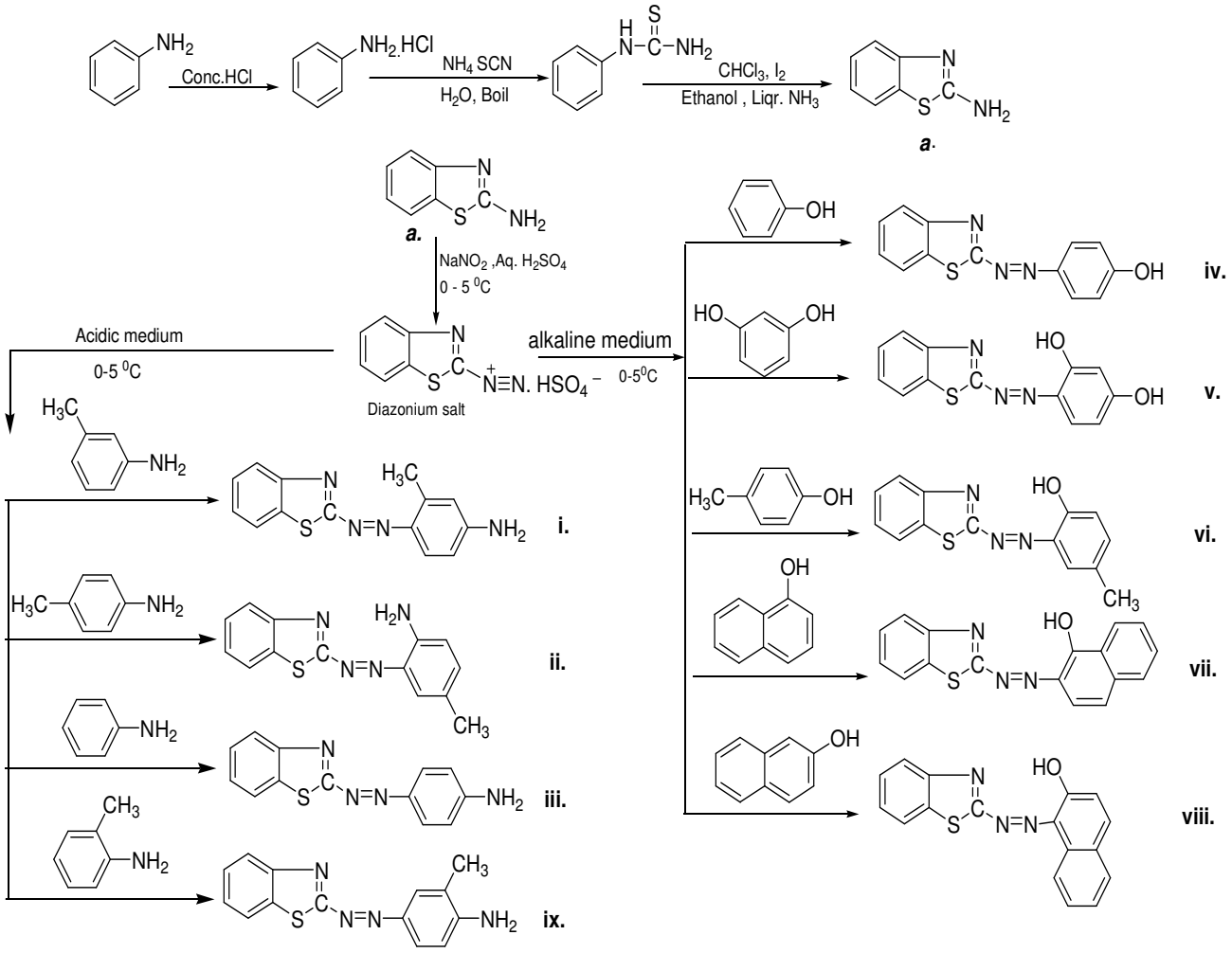


Figure-2
In acidic medium the color deepens to different colour as an azo nitrogen atom

The azo linkage is the most labile portion of azo dyes molecule and easily undergo enzymatic breakdown in mammals including man. The azo linkage may be reduced and cleaved, resulting in the splitting of the molecule in two parts by non-specific enzyme named ado - reductase found in various microorganisms (such as in intestinal bacteria) and in all tested mammals.[28-33], so we thought to test biological activity of newly synthesized azo dyes. In view of the mentioned facts and in continuation of our interest in the synthesis of mono azo dyes containing benzothiazole moiety, to identify synthetic strategies in designing new, selective and less toxic , effective azo dyes, we thought to design a new series of azo dyes using 2-amino derivative of benzothiazole. We report herein the synthesis, structural properties, applications, dyeing properties and antimicrobial evaluation of some novel mono azo dyes incorporating both benzothiazole moiety and various substituted anilines and phenols through azo linkages at 2-position of benzothiazole. The substitution pattern in benzothiazole , anilines and phenols was carefully selected so as to confer different electronic environment to the molecule.

Chemistry: The synthetic strategies adopted for the synthesis of the intermediates and target compounds are depicted in (scheme-I). The starting compound (a), 2-amino-1, 3-benzothiazole was prepared from phenylthiourea in presence of I_2. The product obtained was recrystallised from 50% ethanol and vacuum dried. The data obtained with test compounds was found to be in good agreement with the reported literature values. The structures were confirmed by LCMS, IR, NMR, UV-Vis, etc. Compound (a) was diazotized and then added drop wise to a solution of substituted anilines and phenols below 5^0C to get a desire dye (i - ix).

A solid product was isolated at pH 7.0-7.5, washed with cold water, recrystallised by using suitable solvent and air dried. The dyeing ability of prepared dyes was tested as reported in literature [34-35]. The chemical structures of (i - ix) were confirmed from LC-MS and various spectral analysis.



Scheme-I

Material and Methods

All melting points were measured on a Gallenklamp electrothermal melting point apparatus. IR spectra were recorded for KBr disc on a FT-IR BRUKER ALPHA-200455. ^{1}H NMR spectra was measured on a Bruker AC 300 (300 MHz) in $CDCl_3$ or DMSO-d_6 as solvent, using TMS as an internal standard, and chemical shifts are expressed as δppm. LC- Mass spectra were determined on Finnigan Incos 500 (70 ev).The progress of the reaction was monitored by thin layer chromatography with F254 silica gel pre-coated sheets (MERCK) using petroleum ether / ethyl acetate 55/45 solvent system. Solvents unless specified, were of analytical reagent grade or of the highest quality commercially available. The fastness to light, sublimation and perspiration of dye pattern was asserted according to British standard: 100-1978 and the wash fastness test according to Indian standard IS: 765-1979. The rubbing fastness was analysed by Crock Meter (Atlas) AATCC-1961, as shown in table. 2 The dye bath percentage exhaustion and fixation of the dyed cotton fabric was determined by known reported method [36].

General procedure for the synthesis of 2-amino-1, 3-benzothiazole (a): Aniline was treated with conc.HCl to get water soluble salt of aniline. The mixture of aniline hydrochloride salt and ammonium thiocyanate solution in water refluxed till turbidity was found and then cooled to room temperature and poured in ice cold water. White crystals of phenylthiourea obtained were filtered, washed and vacuum dried. The phenylthiourea and iodine in chloroform was stirred for four hours at lower temperature. After completion of reaction, ethanol was added to the reaction mixture and then basified with liquor ammonia. A solid product of compound (a) obtained was filtered , washed, recrystallised from 50% ethanol and vacuum dried. Gray color crystals; yield 78 % mp. 126-128^{0}C Mol. formula $C_7H_6N_2S$ Mol. mass. 150. Mass [M/Z (rel. Int)] , M^+150 (100), 123, 95, 69, expected 150. IR-KBr ν (cm-1). 3399-3274 (1^{0}amine N-H str.) 3037 (ArC-H Str.), 1590 (C=N thiazole str.), 1646-1648 (ArC=C str.) ^{1}H NMR (300 MHz, $CDCl_3$, δppm)
δ 5.8 (s, 2H Ar-NH_2), δ 7-7.7 (m, 4H Ar-H).

Synthesis of 2-Diazo (4'-amino-2'-methyl phenyl)-1, 3-benzothiazole (i): Compound a. (0.5g, 33 mmol) was dissolved in 15mL of 50% H_2SO_4 and then cooled to 0-5^{0}C. A cold solution of $NaNO_2$ (0.25g, 36mmol in 5mL water) was added drop wise at 0-5^{0}C. A reaction mixture was stirred for half an hour at the same temperature to obtain diazonium salt of compound a. The diazonium salt solution was added very slowly and drops wise to a previously cooled solution of m-toluidine (0.353g, 33mmol in 5mL 30% H_2SO_4) below 5^{0}C. The reaction mixture was stirred for 3-4 hrs and then at room temperature for 1 hr. The pH of reaction mixture was adjusted to 7-7.5 with sodium acetate. A precipitate of dye obtained was filtered, washed with cold water, recrystallised from acetone-ethanol mixture and air dried to give compound (i).

Brown colour crystals; yield 66%; mp 195-198^{0}C, mol. formula $C_{14}H_{12}N_4S$, mol. mass 268, Mass [M/Z (rel.Int)] M^+, 269.151, 124, 106 . UV-Vis λmax (nm). 528.84 IR-KBr ν (cm^{-1}).542.12 (N=N str), 1607.48 (C=N str thiazole,), 3316 , 3180 (N-H str), 3059 (ArC-H str), 857- 667 (Ar def)^{1}H NMR, (300MHz, $CDCl_3$, δppm)2.2 (s , 3H, $ArCH_3$) , 2.8 (s, 2H, ArNH2) 7.4-7.6 (m, 3H, ArC-H), 7.8-8.2 (m, 4H, ArC-H).

Synthesis of 2-Diazo (2'-amino-5'-methyl phenyl)-1, 3-benzothiazole (ii): Compound (ii) was prepared from compound (a) and p-toluidine by using the same procedure including stoichiometry of reagents as described in i,

Dark brown crystals; yield 63%; mp 98-100^{0}C, mol. formula $C_{14}H_{12}N_4S$, mol. mass 268, Mass [M/Z (rel.Int)] M^+269.15, UV-Vis λmax (nm). 443.51 IR-KBr ν (cm^{-1}). 1410.94 (N=N str), 1558, (C=N str thiazole,), 3174.07 (N-H str), 3086 (ArC-H str), 763.18-632.22 (Ar def), 1H NMR, (300MHz, CDCl3, δ ppm) 2.4 (s 3H, $ArCH_3$) 2.6 (s 2H, $ArNH_2$), 7.0-7.4 (dd, t, d, 4H, ArC-H), 7.5-8.1 (m, 3H, ArC-H).

Synthesis of 2-Diazo (4'-amino phenyl)-1, 3-benzothiazole (iii): Compound (a). (0.5 g, 33mmol) was diazotized with NaNO2 and coupled with aniline (0.307g, 33mmol) by using same procedure and stoichiometry of reagents as described in i to obtain compound (iii)

Dark red crystals; yield 68%; mp 152-154^{0}C, mol. formula $C1_3H_{10}N_4S$, mol. mass 254. Mass [M/Z (rel. Int)] M^+ 254 , UV-Vis λmax (nm). 487.06. IR-KBr ν (cm^{-1}).1646.85 (N=N str), 603.02 (C=N str thiazole,), 3348.05, 3211.05 (N-H str), 3000 (ArC-H str), 889.90-631 (Ar def) (C=N str thiazole,), 3348.05, 3211.05 (N-H str), 3000 (ArC-H str), 889.90-631 (Ar def). ^{1}HNMR, (300MHz, $CDCl_3$, δ ppm) 2.6 (s 2H, $ArNH_2$) 7.3-7.5 (m, 4H, ArC-H), 6.7-6.8, (d, 2H, ArC-H),
7.8-8.1 (m, 2H, ArC-H).

Synthesis of 2-Diazo (4'-hydroxy phenyl)-1, 3-benzothiazole (iv): Compound a. (0.5 g, 33mmol) was dissolved in 15mL of 50% H_2SO_4 and then cooled to 0-5^{0}C. A cold solution of $NaNO_2$ (0.25g, 36mmol in 5mL in water) was added drop wise at 0-5^{0}C. A reaction mixture was stirred for half an hour at the same temperature to obtain diazonium salt of compound a.

The diazonium salt solution was added very slowly and drops wise to a previously cooled solution of phenol (0.310g, 33mmol in 10mL dil. NaOH) below 5^{0}C in alkaline medium. A viscous mass of azo dye was obtained towards the end of addition; cold water was added gradually in order to get a non-sticky precipitate. The reaction mixture was stirred for 3-4 hrs and then at RT for 1 hr. The pH of reaction mixture was adjusted to 7-7.5 with sodium acetate. A precipitate of dye obtained was filtered, washed with cold water, recrystallised from acetone-alcohol mixture and air dried to give compound (iv).

Dark brown crystals; yield 71%; mp 240-242 ^{0}C, mol. formula $C_{13}H_9N_3SO$, mol. mass 255

Mass [M/Z (rel.Int)] , M^+255. UV-Vis λ max (nm). 421.32 IR-KBr, ν (cm^{-1})1465.73 (N=N str), 1603.91 (C=N str thiazole,), 3631.30 (O-H str), 3055.67 (ArC-H str), 839.05-722.95 (Ar def)^{1}H NMR, (300MHz, $CDCl_3$, δ ppm). 2.8 (s , 1H, PhO-H), 7.0-7.5 (m, 4H, ArC-H), 7.8-8.0 (dd 4H, ArC-H).

Synthesis of 2-Diazo (2', 4'-dihydroxy phenyl)-1, 3-benzothiazole (v): A compound (v) was prepared by diazotization of compound a . (0.5 g, 33mmol) with $NaNO_2$ followed by coupling with resorcinol (0.363g, 33mmol) in slightly alkaline medium by the same method and stoichiometry of reagents employed in iv.

Brown colour crystals; yield 72 %; mp 310-312 ^{0}C, mol. formula $C_{13}H_9N_3SO_2$, mol. mass 271. Mass [M/Z (rel.Int)] , M^+271 UV-Vis λ max (nm). 492.08. IR-KBr ν (cm^{-1}). 1454.97 (N=N str), 1599.12 (C=N str thiazole,), 3239.71 (O-H str),
2927.33 (ArC-H str), 843.11-624.20 (Ar def). ^{1}H NMR (300MHz, $CDCl_3$, δ ppm) 3.9 (s , 2H, PhO-H) 7.4-7.8 (m, 4H, ArC-H), 7.8-8.2 (m, 3H, ArC-H).

Synthesis of 2-Diazo (2'-hydroxy-5'-methyl phenyl)-1, 3-benzothiazole (vi): A compound (vi) was prepared by diazotization of compound a . (0.5 g, 33mmol) with $NaNO_2$ followed by coupling with p-cresol (0.356g, 33mmol) in slightly alkaline medium by the same method and stoichiometry of reagents employed in iv.

Dark brown crystals; yield 68%;mp 130-132 ^{0}C, mol. formula $C_{14}H_{11}N_3SO$, mol. mass 269. Mass [M/Z (rel.Int)] , M^+269 UV-Vis λ max (nm). 422.17, IR-KBr ν (cm^{-1}). 1487.83 (N=N str), 1578.24 (C=N str thiazole,), 3464.52 (O-H str), 3000 (ArC-H str), 881.84-721.31 (Ar def) ^{1}H NMR, (300MHz, $CDCl_3$, δ ppm)
1.6 (s 3H, $ArCH_3$) 2.5 (s , 1H, PhO-H) 7.4-7.8 (m, 4H, ArC-H), 7.0-7.8 (m, 3H, ArC-H).

Synthesis of 2-Diazo (1'-hydroxy naphthyl)-1, 3-benzothiazole (vii): A compound (vii) was prepared by diazotization of compound a . (0.5 g, 33mmol) with $NaNO_2$ followed by coupling with 1-naphthol (0.475g, 33mmol) in slightly alkaline medium by the same method and stoichiometry of reagents employed in iv.

Violet colour crystals; yield 70%; mp 240-242 ^{0}C, mol. formula $C_{17}H_{11}N_3SO$, mol. mass 305. Mass [M/Z (rel. Int)] , M^+305, UV-Vis λ max (nm). 323.25. IR-KBr ν (cm^{-1}).1455.80 (N=N str), 1595.47 (C=N str thiazole,), 3296.35 (O-H str), 3050 (ArC-H str), 874.62-624.30 (Ar def)[1]. H NMR, (300MHz, $CDCl_3$, δ ppm) 2.8 (s , 1H, PhO-H) 7.4-8.4 (m, 6H, ArC-H), 6.5-7.2 (m, 4H, ArC-H).

Synthesis of 2-Diazo (2'-hydroxy naphthyl)-1, 3-benzothiazole (viii): A compound (viii) was prepared by diazotization of compound a . (0.5 g, 33mmol) with $NaNO_2$ followed by coupling with 2-naphthol (0.475g, 33mmol) in slightly alkaline medium by the same method and stoichiometry of reagents employed in iv.

Dark brown color crystals; yield 70%; mp 160-162 ^{0}C, mol. formula $C_{17}H_{11}N_3SO$, mol. mass 305

Mass [M/Z (rel.Int)]M^+305, UV-Vis λmax (nm).330.12 IR-KBr ν (cm^{-1}). 1462.19 (N=N str), 1596.80 (C=N str thiazole,), 3273.03 (O-H str), 3052 (ArC-H str), 846.61-618.65 (Ar def)
^{1}H NMR, (300MHz, $CDCl_3$, δ ppm) 2.5 (s , 1H, PhO-H) 7.2-7.4 (m, 6H, ArC-H), 7.6-7.8 (m, 4H, ArC-H).

Synthesis of 2-Diazo (4'-amino-3'-methyl phenyl)-1, 3-benzothiazole (ix): Compound (ix) was prepared from compound (a) and o-toluidine (0.353g, 33mmol)by using the same procedure including stoichiometry of reagents as described in i

Brown colour crystals; yield 66%; mp 270-272^{0}C, mol. formula $C_{14}H_{12}N_4S$, mol. mass 268

Mass [M/Z (rel.Int)] M^+269.15, UV-Vis λmax (nm). 351.92 IR-KBr ν (cm^{-1}). 1438.64 (N=N str), 1596.66 (C=N str thiazole,), 3464.10 (N-H str), 3059.92 (ArC-H str), 822-614 (Ar def) ^{1}H NMR, (300MHz, CDCl3, δ ppm) 2.2 (s 3H, ArCH3) 2.8 (s, 2H, ArNH2), 7.2-7.4 (m, 4H, ArC-H), 7.8-8.4 (m, 3H, ArC-H).

Results and Discussions

The structures of newly described compounds (i- ix) were confirmed from FT-IR, ^{1}H-NMR, LC-MS, UV-Vis spectroscopic methods. Physical, chemical, IR, NMR, Mass relevant data of the compounds are reported in experimental section separately. The experimental data obtained for each target molecule matches significantly with the reported data in literature and calculated.

UV-Vis absorption spectra of dyes were recorded in methanol. The absorption maxima (λ max) of all dyes was found in range of 323.25 - 528.84 nm as shown in (Table-1)

It was found that N=N is an electron withdrawing group and auxochrome like $–NH_2$, $-NR_2$, -OH and electron releasing groups, when conjugated through double bonds, electrons move from auxochrome to N=N. This increases the resonance and causes the change in dipole moment leading to higher intensity of colour. Result also revealed that, if the separation between N=N and auxochrome is increased then resonance increases and intensity of colour also increases.

Dyeing properties of dyes : The dyes were applied at 2% depth on cotton fabric and found that wide range of colours varying from orange to reddish brown shades are obtained with excellent smoothness, brightness and depth on cotton fabric. Dyeing properties are recorded in (table-2). The variation in shades of dye fabrics can be attributed to the nature and position of substituent (auxochrome) present with respect to N=N in dye structure. The dyeing showed an excellent fastness to light and good to excellent

fastness to washing, perspiration and sublimation. Rubbing fastness of the dyes was found fairly well. It was observed that the dye fabric showed remarkable degree of smoothness which can be attributed to the association of cotton molecule with the dye. The prepared dyes were tested as indicators for acid-base titrations and found dye (i, iii, iv, vi, vii, viii) as excellent indicators giving very sharp and distinct end point.

The newly synthesized target compounds were evaluated for their in vitro bacterial activity against gram-positive bacteria (staphylococcus aureus and Bacillus subtilis). Agar diffusion method was used for the determination of preliminary antibacterial activity using ampicillin as reference drug.

The results were recorded for each tested compounds as the average diameter of inhibition zones (IZ) of bacterial growth around the disks in cm. The minimum inhibitory concentration (MIC) measurement was determined for compounds showed significant growth inhibition zones using serial dilution method. The MIC and inhibition diameters values are recorded in (table –3)

Table-1
Absorption maxima (λ_{max}) , exhaustion (E) and fixation (F) of azo dyes on cotton fabric

Dye. No	(λ_{max}) nm, methanol	Rf cm	Dyeing on cotton %	
			Exhaustion E	Fixation F
i	528.84	0.6	73	90
ii	443.51	0.5	71	91
iii	487.06	0.5	80	90
Iv	421.32	0.4	83	94
v	492.08	0.2	81	92
vi	422.17	0.3	71	96
vii	323.25	0.4	76	92
viii	330.12	0.4	75	95
ix	351.92	0.3	78	92

Table-2
Dyeing and various fastness properties of the dye on cotton

Dye No.	Colour shades on cotton	Light fastness	Washing fastness	Sublimation fastness	Perspiration fastness		Rubbing fastness	
					Acid	Alkaline	Dry	Wet
i	Brown	5	4	5	5	4	4	3.5
ii	Dark orange	5	5	5	4	4	5	3.5
iii	Orange	5	4	5	4	4	4	3.5
iv	Red	5	5	5	4	5	5	4.5
v	Violet	5	5	5	5	5	5	4.5
vi	Dark Red	5	5	5	4	5	5	5.0
vii	Violet	5	5	5	4	4	5	4.5
viii	Brown	5	5	5	4	5	5	4.0
ix	Red	5	4	5	5	4	4	3.5

Table–3
Minimum Inhibitory Concentration of Compound (i-ix); zone inhibition diameter in (cm)

Compound	Basillus subtilis			Staphylococcus aureus		
	Concentration (µg / ml)			Concentration (µg / ml)		
	50	100	200	50	100	200
i	0.9	0.8	1.0	1.1	1.2	1.5
ii	1.7	1.7	1.8	1.3	1.3	0.9
iii	0.8	1.1	0.8	1.5	1.8	1.9
iv	1.7	1.4	1.5	1.7	1.5	1.5
v	1.2	1.4	1.1	2.0	1.5	2.1
vi	1.2	1.0	0.8	1.2	1.0	0.9
vii	1.4	1.3	1.6	1.3	0.9	1.5
viii	0.9	1.0	1.1	1.5	1.6	1.6
ix	1.5	1.5	1.6	1.2	1.5	1.3

In general observation it is found that among all the compounds prepared, compound (ii bearing 1, 4-methyl amino group) showed the highest antibacterial activity followed by compound (iv) and (ix). Surprisingly compound (vii) showed appreciable activity against bacillus subtilis and moderate activity against staphylococcus aureus. The results reveal that benzothiazole moiety having azo linkages with aromatic nuclei and electron releasing group at preferably p-position might be interesting enough for further investigation on potential antimicrobial effects.

Conclusion

The method employed in preparation of benzothiazole moiety and its azo dyes (i- ix) gives excellent practical yield and high purity with simple method. The newly synthesized dyes have good fastness to light, sublimation, perspiration and fairly good rubbing fastness properties. The prepared dyes can also be used as an indicator for acid-base titrations. A series of dyes synthesized screened for their antimicrobial activity. Result reveals that the benzothiazole moiety having azo linkages with aromatic nuclei having electron releasing group at preferably p-position might be interesting enough for further investigation on potential antimicrobial effects.

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