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Synthesis of various Reactive Dyes from Benzothiazole Derivative

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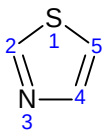
ABSTRACT: Various benzothiazole derivatives were synthesized using para amino benzoic acid, 2- amino thiophenol, poly phosphoric acid and diazonium salt of resulting amino Compound was coupled with various primaryamine. which on further added in a well stirred solution of cyanuric chloride in acetone at 0-5°C. After the completion of reaction, Phenylurea dissolved in acetone added in this solution with maintaining the temperature at 40°C to form various reactive dyes.

KEYWORDS: Para amino benzoic acid, 2- Amino thiophenol, Poly phosphoric acid, various primary amine, cyanuric chloride and phenyl urea.

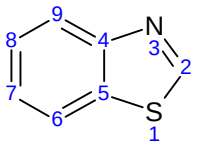
I. INTRODUCTION

Thiazole (1) is structurally related to thiophene and pyridine but in most of its properties it resembles the latter **[1,2]** structure (2) is benzothiazole. Thiazole was first described by Hantzsch and Weber in 1887. Popp Confirmed its structure in 1889.



1,3-thiazole

(1)



1,3-benzothiazole

(2)

The numbering in thiazole starts from the sulphur atom. The thiazole ring has been extensively studied and it forms a part of vitamin-B, penicillin and the antibacterial thiazole. Reduced thiazoles serve in the study of polypeptides and proteins and occur as structural units in compounds of Biological importance.

Thiazole are structural compounds of a number of peptide derived natural products among them are Antibiotics**[3]** Siomycin, Thiostereption and Micrococin, Antitumor**[4]** , Antibiotics, Phleonycin and Bleomcycin.

A.Thiazole dyes

This group of dyes has the thiazole ring system, The presence of this ring system, Increases the substantivity for cellulosic fibers. The important examples of Thiazole dyes are as follows. **[5,7]** Primuline, Thioflavin-T, Pantamine Brilliant Yellow 5G

B.Reactive dyes

Reactive dyes are coloured compounds which contain one or two groups capable of forming covalent bonds between a carbon atom of the dye ion or molecule and an oxygen, nitrogen or sulpher atom of a hydroxy, an amino or a mercapto

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group, respectively, of the substrate. Such covalent bonds are formed with the amino, hydroxyl groups of cellulosic fibres, with the amino, hydroxyl and mercapto groups of protein fibres and with the amino groups of polyamides **[8]**. In general, reactive dyes are the only textile colourants designed to bond covalently with the substrate on application. They are used for the dyeing and printing of cellulose and to a lesser extent polyamide fibres. They are valued for their brilliance and variety of hue, versatility and high wet fastness profiles **[9-16].**

II. MATERIALS AND METHODS

We wish to describe a simple and efficient protocol for the rapid preparation of various reactive dyes from the diazotization of 4-Benzthiazole-2-yl-phenylamine and coupling various primary amine which added in well stirred solution of cyanuric chloride at 0-5°C . after the completion of reaction, Phenylurea added in this solution with maintaining the temperature at 40°C.

A.General

All the melting points were taken in open capillary tube and are uncorrected. The purity of compounds were checked and characterized by IR spectra recorded on FTIR spectrophotometer, ^{1}H NMR spectra , UV- Visible spectra and microbiological activity was checked.

III. SCHEME

Step-1 Preparation Of 4-benzthiazole-2-yl-phenylamine

Para amino benzoic acid (0.05 mole) was dissolved in poly phosphoric acid (15 ml). 2-amino thiophenol was added to this mixture slowly with stirring. The mixture was heated to 180°C for 2 hrs. The solution was poured on crushed ice. The solid product obtained was filtered and dried. The crude product was purified by crystallization from DMF to form 4-benzthiazole-2-yl-phenylamine **(A)** in 70-80% yield**[17-26].**

Step-2 Diazotization Of 4-benzthiazole-2-yl-phenylamine

4-Benzthiazole-2-yl-phenylamine(0.05 mole) was dissolved in hydrochloric acid(0.15mole) and cooled to 0-5°C . Sodium nitrite(0.05 mole) was added as an aqueous solution at 0-5°C within 1 hr to form **2-{4-[(*E*)-chlorodiazenyl]phenyl}- benzthiazole(B).**

Step-3 Coupling Of 2-{4-[(*E*)-chlorodiazenyl]phenyl}- benzthiazole(B) with various Primaryamine.

In Step-3 , The diazonium salt prepapered in step-2 was coupled with aniline at P^{H} 4-5 and at 0-5°C for 1 hr to form 4-(4-benzothiazol-2-yl-phenylazo)-phenylamine (C). After the completion of reaction, solution was poured into ice cold water. The solid product obtained was filtered and dried. In the same way 2-{4-[(*E*)-chlorodiazenyl]phenyl}-benzthiazole coupled with various primaryamine.

Step-4 Preparation of [4-(4-benzothiazol-2-yl-phenylazo)-phenyl]-(4,6-dicholoro-[1,3,5]triazin-2-yl)-amine

To a stirred solution of cyanuric chloride in acetone at 0-5°C, the solution of (C) was added and P^{H} was maintained neutral by the addition of 10% sodium carbonate solution. The stirring was continued at 0-5°C for four hours. After the completion of reaction, solution was poured into ice cold water. The solid product obtained was filtered and dried.

Step-5 Preparation of various reactive dyes

Phenylurea dissolved in acetone. (35 ml) was slowly added to a well-stirred solution of (D) in acetone. maintaining the temperature at 40°C. The P^{H} was adjusted neutral by the addition of 10% sodium carbonate solution. The stirring was

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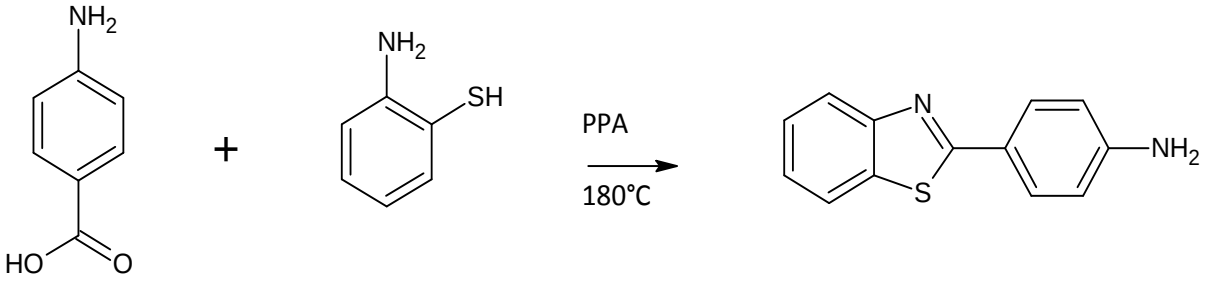
continued at 40°C for four hours. After the completion of reaction, solution was poured into ice cold water. The solid product obtained was filtered and dried. The crude product was purified by crystallization from acetone. to form reactive dye. In the same way, different coupling compounds were used to form various reactive dyes as per given in Table-1.

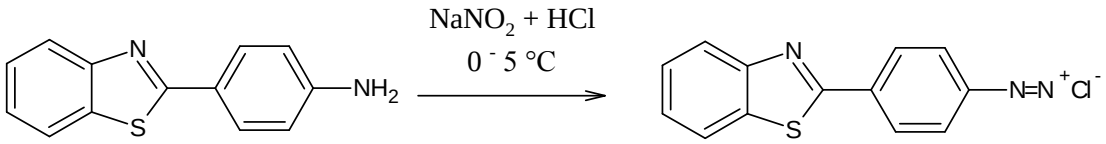
Route of synthesis :

Step-1



Para amino benzoic acid | 2-Amino thiophenol | Benzthiazole-2-yl -phenylamine **(A)**

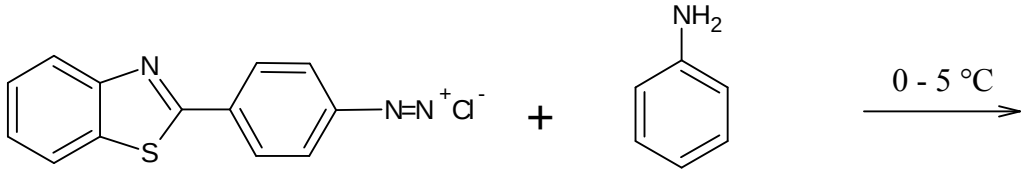
Step-2



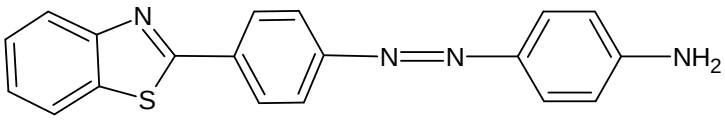
4-Benzthiazole-2-yl-phenylamine **(A)**

2-[4-(chlorodiazenyl)phenyl] -1,3-benzothiazole **(B)**

Step-3



2-[4-(chlorodiazenyl)phenyl] -1,3-benzothiazole | Aniline



4-(4-Benzothiazol-2-yl-phenylazo)-phenylamine **(C)**

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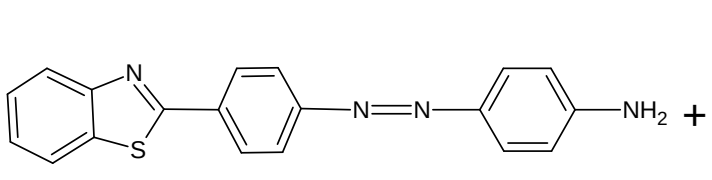
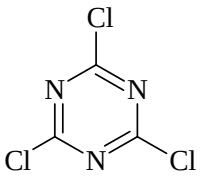
Step-4

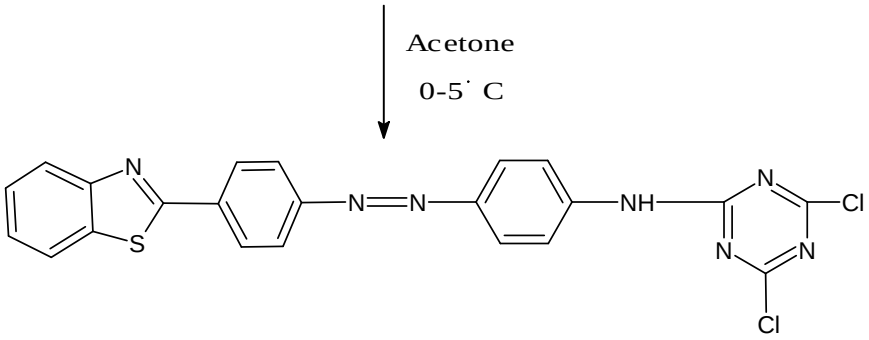


4-(4-Benzothiazol-2-yl-phenylazo)-phenylamine



2,4,6-trichloro-1,3,5-triazine

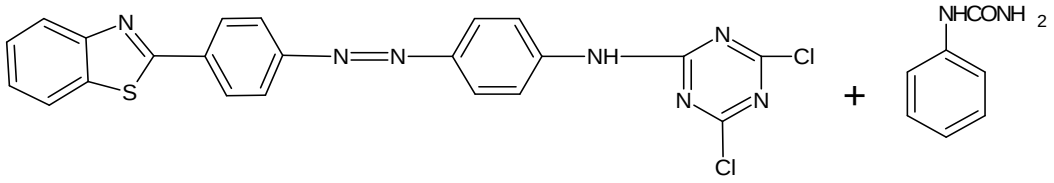
(C)



[4-(4-Benzothiazol-2-yl-phenylazo)-phenyl]-(4,6-dichloro-[1,3,5]triazin-2-yl)-amine

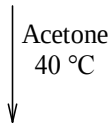
(D)

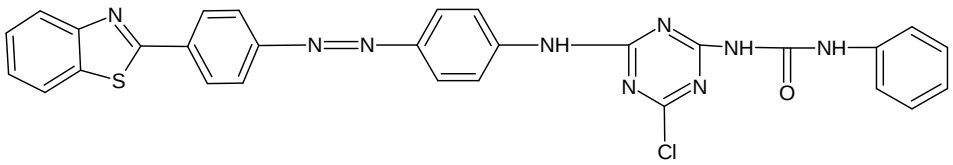
Step-5



4-(4-Benzothiazol-2-yl-phenylazo)-phenylamine

1-phenylurea





1-{4-[3-(3-Benzothiazol-2-yl-phenylazo)-phenylamino]-6-chloro-[1,3,5]triazin-2-yl}-3-phenyl-urea

(E)

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Table 1. Different coupling compounds to form various reactive dyes

Sr. No.	R, Compounds	Molecular formula	Molecular Weight	% Yield	M.P. in °c
1R	4-phenylene diamine	$C_{29}H_{21}ClN_{10}OS$	593.06	75%	240 °c
2R	2-phenylene diamine	$C_{29}H_{21}ClN_{10}OS$	593.06	80%	220 °c
3R	3-amino phenol	$C_{29}H_{20}ClN_9O_2S$	594.05	75%	250 °c
4R	2-amino phenol	$C_{29}H_{20}ClN_9O_2S$	594.05	78%	240 °c
5R	4-amino phenol	$C_{29}H_{20}ClN_9O_2S$	594.05	72%	260 °c
6R	2-nitro aniline	$C_{29}H_{19}ClN_{10}O_3S$	623.05	70%	210 °c
7R	3-nitro aniline	$C_{29}H_{19}ClN_{10}O_3S$	623.05	70%	200 °c
8R	4-nitro aniline	$C_{29}H_{19}ClN_{10}O_3S$	623.05	75%	240 °c
9R	2-anisidine	$C_{30}H_{22}ClN_9O_2S$	608.00	72%	270 °c
10R	4-anisidine	$C_{30}H_{22}ClN_9O_2S$	608.00	68%	260 °c
11R	2-amino pyridine	$C_{28}H_{19}ClN_{10}OS$	579.00	78%	280 °c
12R	2-toludine	$C_{30}H_{22}ClN_9OS$	592.00	65%	210 °c
13R	4-toludine	$C_{30}H_{22}ClN_9OS$	592.00	68%	220 °c
14R	2-Bromo aniline	$C_{29}H_{19}BrClN_9OS$	657.00	80%	230 °c
15R	Aniline	$C_{29}H_{20}ClN_9OS$	578.05	70%	200 °c

Table-2. IR Spectra of comound-R_1

Position of absorption band wave number cm^{-1} (1R)	Bond & its mode of vibration	Functional group
3100	C-H stretching	Aromatic, =CH- bond
1673	-C=N Stretching	>C=N- stretching of thiazole ring
698	C-S-C stretching	C-S-C Stretching of thiazole ring
1612	N=N stretching	Azo group
1547	C=C stretching	Aromatic ring
3400	N-H stretching	Primary amine
3308	N-H stretching	Secondary amine
1673	N-H deformation in urea	Secondary amine
1700	>C=O stretching	>C=O stretching in urea

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Table-3. IR Spectra of compound-R_4

Position of absorption band wave number cm^{-1} (4R)	Bond & its mode of vibration	Functional group
3150	C-H stretching	Aromatic, =CH- bond
1650	-C=N Stretching	-C=N- stretching of thiazole ring
696	C-S-C stretching	C-S-C Stretching of thiazole ring
1650	N=N stretching	Azo group
1554	C=C stretching	Aromatic ring
3430	O-H stretching	Phenol
3314	N-H stretching	Secondary amine
1592	N-H deformation in urea	Secondary amine
1742	>C=O stretching	>C=O stretching in urea

TABLE -4. ^{1}H NMR spectral characteristics of compound- R_1

Chemical Shifts (δ in ppm)	Multiplicities	Relative number of protons	*Assignment*
6.85-8.00	m	16	Aromatic protons
2.10-3.14	1) s	2	-NH group in Ar ring
5.60	2) s	2	-NH group in urea

TABLE -5. ^{1}H NMR spectral characteristics of compound- R_4

Chemical Shifts (δ in ppm)	Multiplicities	Relative number of protons	*Assignment*
6.80-8.00	m	16	Aromatic protons
3.20	8	1	-OH group
2.50	8	1	-NH group in Ar ring
5.60	8	2	-NH group in urea

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IV. CONCLUSION

All the synthesized compounds were characterized by UV- Visible Spectra, Infrared Spectroscopy and some representatives by Nuclear Magnetic Resonance Spectroscopy. The IR and NMR data of some dyes are given in table-2,3,4 and5.
The synthesized dyes samples were applied to polyester, silk and cotton in 2% shade and their dyeing performance on each fabric was evaluated.

V.ACKNOWLEDGEMENTS

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