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Synthesis of various acid dyes from benzthiazole derivative

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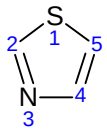
ABSTRACT

Various Benzthiazole Derivative were synthesized using Para Amino Benzoic Acid, 2- Amino Thiophenol, Poly Phosphoric Acid and Diazonium Salt of Resulting Amino Compound coupling with various Naphthoic acid to form various Acid Dyes.

Keywords: Para Amino Benzoic Acid, 2- Amino Thiophenol, Poly Phosphoric Acid, various Naphthoic acids.

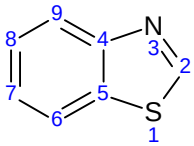
INTRODUCTION

Thiazole (1) is structurally related to Thiophene and pyridine but in most of its properties it resembles the latter **[1,2]** structure (2) is Benzthiazole. 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.

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 Follow. **[5-7]**

Primuline, Thioflavin-T, Pantamine Brilliant Yellow 5G

ACID DYES

Acid dyes are divided into three groups based on their difference in affinity, which is primarily a function of the molecular size **[8]**.

1. Leveling dyes are relatively small molecules.

2. Milling dyes are large volume dye molecule.
3. Dyes with intermediate molecular size.

Acid dyes are water soluble anionic dyes that are applied to by direct printing on protein fibers and by the vigorous process; selected dyes may be printed on viscose from a paste containing area, other important uses includes the dyeing of leather, paper, jute, straw and anodized aluminum the coloring of food and drink, drugs, cosmetics, insecticides, fertilizers, wood, stains, varnishes, inks, plastics, resins and the manufacture of toners and pigments of the lake types **[9]**.

we wish to describe a simple and efficient protocol for the rapid preparation of Acid dyes were probably originally so named because of the presence of one or more sulphonic acid or other acidic groups in the molecules. These dyes give very bright hues and have a wide range of fastness properties from very poor to very good **[10,11]**.

Chemically the acid dyes consist of azo **[12]**, anthraquinone **[13]**, azine **[14]**, pyrazolone **[15]**, nitro and nitroso compounds.

R. S. Patel and K. C. Patel **[16]** have synthesized some novel acid dyes and evaluate their dyeing application on various fibers.

MATERIALS AND METHODS

We wish to describe a simple and efficient protocol for the rapid preparation of Various Acid Dyes from the Diazotization of 4-Benzthiazole-2-yl-phenylamine with various Naphthoic acids.

General
All the melting points were taken in open capillaries tube and are uncorrected. The purity of compounds was checked routinely by TLC (0.5 mm thickness)Using silica gel – G coated Al – plates (Merck) and spots were visualized by exposing the dry plates in iodine vapours. IR spectra were recorded on FTIR spectrophotometer using KBr or Nujol technique.^{1}H NMR spectra on a Varian 400 FT MHz NMR instrument at using $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal reference.UV- Visible Spectra and microbiological Activity.

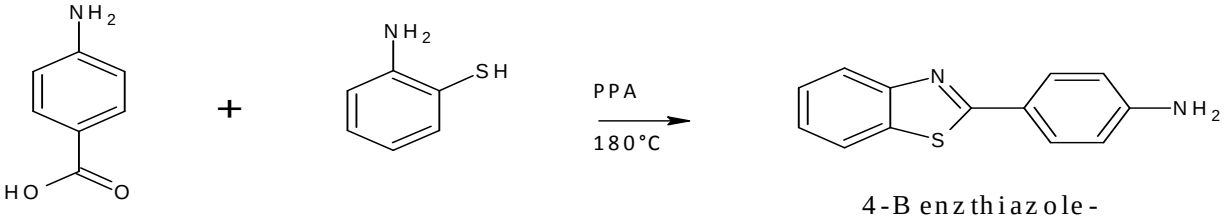
Scheme:
Step-1
Preparation Of 4-Benzthiazole-2-yl-phenylamine
Para Amino Benzoic Acid (0.05 mole) was dissolved in poly phosphoric Acid (15 ml). 2-Amino phenol was added to this mixture slowly with stirring. The mixture was heated to 180°C for 2 hrs. The solution was poured on crushed ice. The solid 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 diazotised by hydrochloric acid(0.15mole) at 0-5ºC and Sodium nitrite(0.05 mole) was added as an aqueous solution at 0-5ºC for 1 hrs to form **2-{4-[(*E*)-chlorodiazenyl]phenyl}-benzthiazole(B)**

Step-3
Preparation of Various Acid Dyes.
In Step-3 , 2-{4-[(E)-chlorodiazenyl]phenyl}- Benzthiazole ,the diazonium salt was coupled with H-Acid at 0-5ºC for 1 hrs to form Acid Dye in 70-75% yield. Different coupling compounds were used to form various Acid Dyes.

ROUTE OF SYNTHESIS :

Step-1



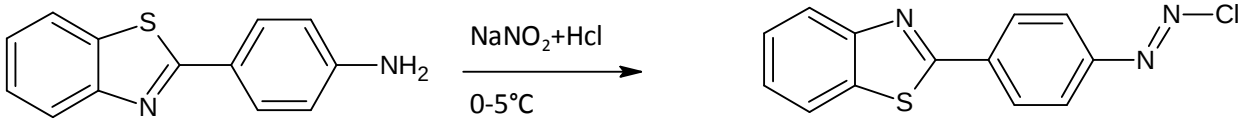
Para Amino Benzoic Acid

2-Amino Thiophenol

4-Benzthiazole-2-yl-phenylamine

(A)

Step-2

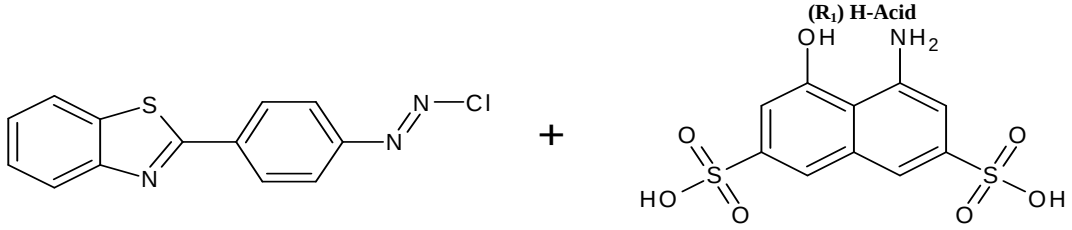


4-Benzthiazole-2-yl-phenylamine **2-{4-[(E)-chlorodiazenyl] phenyl}-Benzthiazole**

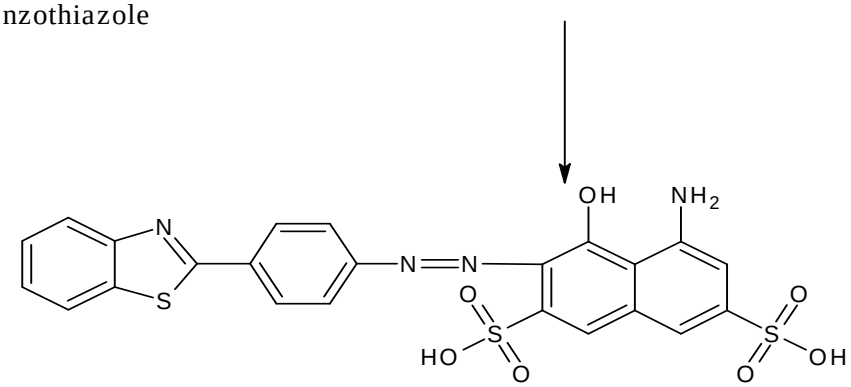
(B)

Step-3

(R_1) H-Acid



2-{4-[(*E*)-chlorodiazenyl]phenyl}-1,3-benzothiazole



5-Amino-3-(4-Benzthiazol-2-yl-Phenylazo)-4-Hydroxy-Naphthalene-2,7- Disulphonic Acid

Table 1 Different coupling compounds to form various acid dyes at pH 8

Sr. No.	R, Compounds	Molecular formula	Molecular Weight	% Yield	M.P. in °c
1	R_1, H-Acid	$C_{23}H_{16}N_4O_7S_3$	556.59074	70-75%	340 °c
2	R_2, J-Acid	$C_{23}H_{16}N_4O_4S_2$	476.52754	75%	330
3	R_3, Gamma Acid	$C_{23}H_{16}N_4O_4S_2$	476.52754	75%	240
4	R_4, Chromotropic Acid	$C_{23}H_{15}N_3O_8S_3$	557.5755	68%	330
5	R_5, N-Benzoyl-J-Acid	$C_{30}H_{20}N_4O_4S_2$	564.6342	74%	250
6	R_6,Phenyl-J-Acid	$C_{29}H_{20}N_4O_3S_2$	536.6241	74%	240

Table 2 Different coupling compounds to form various acid dyes at pH 4

Sr. No.	R, Compounds	Molecular formula	Molecular Weight	% Yield	M.P. in °c
7	R_4, Peri Acid	$C_{23}H_{16}N_4O_3S_2$	460.52814	72%	180
8	R_5, Laurent Acid	$C_{23}H_{16}N_4O_3S_2$	460.52814	70%	180
9	R_6, Tobias Acid	$C_{23}H_{16}N_4O_3S_2$	460.52814	75%	170
10	R_7, Naphthionic Acid	$C_{23}H_{16}N_4O_3S_2$	460.52814	65%	170
11	R_8, Bronner Acid	$C_{23}H_{16}N_4O_3S_2$	460.52814	78%	160
12	R_9, Acetyl Bronner Acid	$C_{25}H_{18}N_4O_4S_2$	502.56482	77%	180
13	R_{10}, mix Cleve Acid	$C_{23}H_{16}N_4O_3S_2$	460.52814	70%	160

Table-3: IR Spectra of comound-R_1

Position of absorption band wave number cm^{-1} R_1	Bond & its mode of vibration	Functional group
3015	C-H stretching	Aromatic, =CH- bond
1650	-C=N Stretching	>C=N- stretching of thiazole ring
650	C-S-C stretching	C-S-C Stretching of thiazole ring
1470	C-H bending	$-CH_2-$ group
1620	N=N stretching	Azo group
1510	C=C stretching	Aromatic ring
3480	N-H stretching	Primary amine
3600	O-H stretching	Phenol
1160	S=O stretching	sulphonic acid, RSO_3H

Table-4: IR Spectra of compound-R_2

Position of absorption band wave number cm^{-1} R_2	Bond & its mode of vibration	Functional group
3020	C-H stretching	Aromatic, =CH- bond
1670	-C=N Stretching	>C=N- stretching of thiazole ring
650	C-S-C stretching	C-S-C Stretching of thiazole ring
1450	C-H bending	$-CH_2-$ group
1620	N=N stretching	Azo group
1500	C=C stretching	Aromatic ring
3450	N-H stretching	Primary amine
3590	O-H stretching	Phenol
1170	S=O stretching	sulphonic acid, RSO_3H

TABLE -5: ^{1}HNMR spectral characteristics of compound- R_1

Chemical Shifts (δ in ppm)	Multiplicities	Relative number of protons	Assignment
6.30-8.50	m	11	Aromatic protons
5.00	s	1	-OH group
3.30	s	1	-NH group
2.00-2.50	s	2	$-SO_3H$ group

TABLE -6: ^{1}HNMR spectral characteristics of compound- R_2

Chemical Shifts (δ in ppm)	Multiplicities	Relative number of protons	Assignment
6.30-8.20	m	10	Aromatic protons
5.30	s	1	-OH group
3.30	s	1	-NH group
2.00	s	1	$-SO_3H$ group

CONCLUSION

All the synthesized compounds were characterized by UV- Visible Spectra, Infrared Spectroscopy and some representatives by Nuclear Magnetic Resonance Spectroscopy and by anti microbiological activity.

The synthesized dyes sample were applied to polyester, silk, wool and cotton in 2% shade and their dyeing performance on each fabric was evaluated.

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