



Synthesis and spectroscopic studies of alkali clearable azo dye of 3-amino-5-nitrophthalic acid

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ABSTRACT

The present work describes the synthesis of alkali clearable azo dye stuffs (**6a-c**) derived from naphthanilides. The dyes (**6a-c**) were synthesized from 3-amino-5-nitro-phthalic acid (3,5-ANPA) as diazo component and 3-carboxy-2-hydroxy naphthanilides (**5a-c**) as coupling agent, under suitable experimental conditions. The dyes were characterized by using FT-IR, ¹H and ¹³C NMR, UV-Visible, fluorescent and LC-MS techniques. The thermal behavior of compounds have been determined by means of differential thermal analysis (DTA) and thermo gravimetric analysis (TGA). The electrochemical properties of dyes were studied by cyclic voltametry.

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KEYWORDS

Alkali clearable azo dyes;
3-amino-5-nitro-phthalic acid;
3-carboxy-2-hydroxy
naphthanilides;
Absorption spectra;
Thermal studies.

INTRODUCTION

The development of new disperse dyes must take into account in order to minimize the effect of dyeing effluent on the environment. Temporary solubilised dyes containing β -sulphatoethylsulphone group have been investigated for the dispersant-free dyeing of polyester^[1]. The sodium sulphonate group of the dye structure gives sufficient water solubility at the early stage of dyeing without any dispersant. Even, alkali-clearable disperse dyes have been studied since 30 years in order to reduce the impact of dyeing processes on the environment through reduction in effluent discharge as well as in the use of energy and materials^[2-6]. The alkali clearable disperse dyes facilitate alkaline treatment to be substituted for costly and environmentally damaging

reduction clearing process since, the dyes can be easily hydrolyzed and washed-off under relatively mild alkaline condition. Moreover, naphthaimide based dyes have been investigated in a number of ways to examine their use as dyes intermediates on both synthetic and natural fabrics as well as on the other polymeric materials. Pioneering work on naphthalimide and their derivatives have been investigated to assess their role as the intermediates for dye stuffs preparation^[7-11]. Heterocyclic derivatives such as naphthlimides, phenylazo phthalimides and 1, 8-naphthalic anhydrides have been considered for the preparation of disperse dyestuffs^[12-14] for other polymer fibers, and dye stuffs capable of copolymerization.

In the present paper we report a facile method for the synthesis of alkali clearable azo disperse dyes (**6a-**

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c) from 3-carboxy-2-hydroxy naphthanilides (**5a-h**) as coupling agent, and 3, 5-ANPA (**4**) as diazo component. The diazo component 3, 5-ANPA (**4**) was prepared by reduction of 3, 5-dinitrophthalic acid (3, 5-DNPA). The 3, 5-DNPA (**3**) was prepared from 3, 5 dinitro-*o*-toluic acid (3, 5-DNTA), which in turn was synthesized by the nitration of *o*-toluic acid. The diazotization was carried out under suitable experimental conditions to get the dye stuffs in good yield.

EXPERIMENTAL

Infrared spectra of azo dyes were recorded in the region of 4000 cm^{-1} – 400 cm^{-1} on a FT-IR 8400s SHIMADZU spectrometer in KBr pellets. The ^1H and ^{13}C -NMR spectra were recorded in $\text{DMSO}-d_6$ at 400 MHz using amx400 FT-NMR spectrometer with TMS as internal standard. The mass spectra were recorded with a LC-MSD-trap-XCTplus mass spectrometer. The UV-Visible absorption spectra were recorded in various of solvents, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), pyridine, methanol (MeOH), acetone, acetic acid, acetonitrile, tetrahydrofuran (THF), 0.1N sodium hydroxide (NaOH), MeOH+0.1N

NaOH and MeOH +0.1N hydrochloric acid (HCl), with a SHIMADZU UV-Visible 1650 spectrometer in the wavelength range of 400–800 nm. Thermal analysis was carried out in SHIMADZU TA-60WS Thermal analyzer in air at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. Redox properties of dyes were studied by Electro Analyzer-206 Cyclic voltametry. Fluorescence measurements were performed on a Shimadzu spectrofluorimeter Model RF-5300 equipped with a 150 W Xenon lamp and slit width of 10 nm.

Coupling components (5a-c)

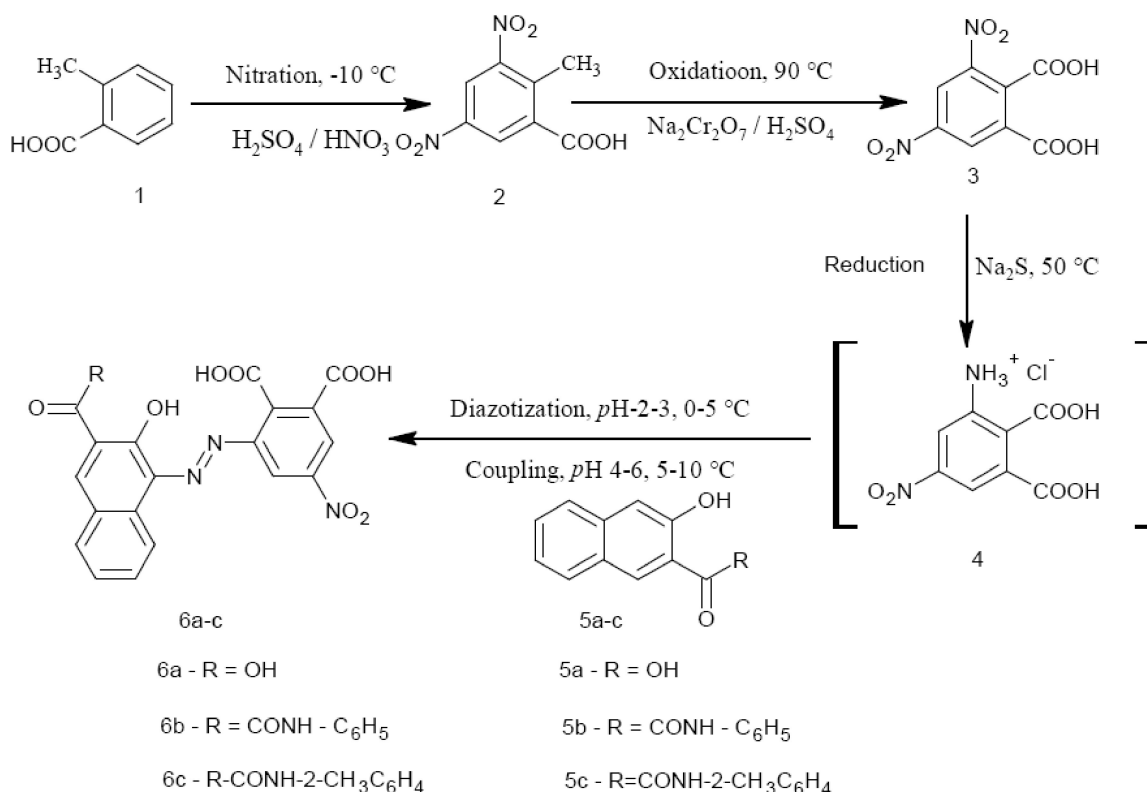
All the coupling components were purchased and recrystallized in ethanol.

Synthesis of 3, 5-DNTA (2) and 3, 5-DNPA (3)

The compound (2) and (3) were synthesized from the documented procedure available in the literature^[15]

Synthesis of 3, 5-ANPA (4)

The compound (3) (2.56 g, 0.01 mol) was added to a solution containing 50 cm^3 of 5% NaOH and sodium sulfide nanohydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) (1.58 g, 0.04 mol) with continues stirring for 1 hr at $60\text{ }^\circ\text{C}$. The resulting mixture was to be allowed cool and filtered. The



Scheme 1

filtrate thus obtained was acidified HCl and allowed to stand over night and filtered. The filtrate thus obtained was used for the synthesis of dye stuffs^[15].

3-(3-carboxy-2-hydroxy-naphthalen-1-ylazo)-5-nitro-phthalic acid

Diazotization

The filtrate containing 3, 5-ANPA (**4**) was cooled at 0-5 °C and an equimolar solution of aqueous sodium nitrite (NaNO₂, 0.7g 0.01 mol) was added drop wise with constant stirring. After complete addition, the stirring was continued for 30 min. The excess NaNO₂ was destroyed by adding 1-2 g of urea. The pH of the reaction mixture was maintained in the range of 6-7 by adding chilled aqueous solution of sodium carbonate. To this solution, the compound (**5a**) (1.44 g, 0.01 mol, taken in 20 ml DMF) was added in portions while the temperature 0-5 °C at pH-6 for 2 hr. The dye obtained was filtered, wash and recrystallized from appropriate solvent. The purity of the compound was checked by thin layer chromatography. All other dyes (**6b-c**) were

synthesized with similar method by using different coupling components (**5b-c**) as given in the Scheme 1^[16]

RESULTS AND DISCUSSION

The most convenient method for the preparation of desired dyes involves the synthesis of 3,5-ANPA that was readily synthesized from easily available starting material, *o*-toluic acid (**1**). *o*-toluic acid upon nitration under appropriate experimental conditions yield 3,5-DNTA (**2**). The resulting 3,5-DNTA was oxidized to corresponding 3,5-DNPA and nitro group was reduced in the presence of aqueous sodium sulphide under controlled reaction conditions to get 3, 5-ANPA. Efforts to isolate the 3,5-ANPA was not succeed, hence the diazotization and coupling reactions were carried out *in situ* with a series of 3-hydroxy-2-naphthanilides (**5a-c**) to obtain the corresponding dyes (**6a-c**) respectively. Their yield, solubility and color are summarized in the TABLE 1. The FT-IR, ¹H and ¹³C-NMR data of these compounds are given in experimental section.

TABLE 1 : Physical characteristics and structure of (6a-c)

Compound	Mol.formula Mol. Wt	Structure	Solubility	Color Appearance	Yield (%)
6a	C ₁₉ H ₁₁ N ₃ O ₉ 425.30		MeOH, DMF Acetone, DMSO	Scarlet red (amorphous)	65
6b	C ₂₅ H ₁₆ N ₄ O ₈ 500.41		MeOH, DMF Acetone, DMSO	Orange red (amorphous)	72
6c	C ₂₆ H ₁₈ N ₄ O ₈ 514.44		MeOH, DMF Acetone, DMSO	Red (amorphous)	68

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The FT-IR spectra of the compound (**6c**) exhibited a broad band in 3500-3200 cm^{-1} region and could be attributed to -OH and -NH of amide group and an intense strong band at 1624 cm^{-1} was assigned to C=O of carboxylic groups. Further, a band at region 1554, and 1590 cm^{-1} was attributed to the nitro and azo group respectively. The ^1H NMR spectra of (**6c**) revealed the broad band at δ : 15.56 ppm for the hydroxy protons^[17] and δ : 14.00 ppm for the carboxylic proton, at 11.06 ppm for amide proton. Peaks obtained in the range of δ : 7.07 to 8.89 ppm was assigned to aromatic protons

(Ar-H). The ^{13}C NMR spectrum of compound **6c** showed 3 peaks at δ : 178.44, 168.86 and 165.50 due to carbon of carbamide and carboxylic acid groups respectively. Moreover the peaks appeared at δ : 150.74 (C-NO₂), 146.7 (C-OH) ppm due to the carbon attached to the nitro and hydroxyl groups respectively. The peak at δ : 115.07 ppm can be assigned to carbon, which is attached to nitrogen of the azo linkage (ArC-N=N). The aromatic carbon peaks, which appeared in the range of δ : 121-148 ppm.

Spectral data of dyes (**6a-c**)

Compound	Spectral data
6a	IR (KBr): 3500-2800 cm^{-1} (OH, COOH), 1697 cm^{-1} (C=O), 1506 cm^{-1} (N=N), 1524 cm^{-1} , (NO ₂). ^1H NMR (DMSO- <i>d</i> ₆ , ppm): 8.65 (s, ArH, 1H), 8.56 (s, ArH, 1H), 8.51 (s, ArH, 1H), 8.38-8.40 (d, ArH, 1H, <i>J</i> = 8.09), 7.92-7.88 (d, ArH, 1H, <i>J</i> = 7.58), 7.74-7.70 (t, ArH, 1H, <i>J</i> = 14.61, 7.39), 7.52-7.49 (t, ArH, 1H, <i>J</i> = 14.61, 7.29). ^{13}C NMR (DMSO- <i>d</i> ₆ , ppm): 174.92 (COOH), 165.49 (COOH), 147.4 (C-OH), 146.5, (C-NO ₂), 133.72, 133.16, 131.83, 131.12, 130.70, 127.45, 126.94, 126.56, 126.56, 126.24, 122.70 (ArC), 115.49 (C-N=N). LCMS <i>m/z</i> : 426.2(<i>M</i> +1, 100)
6b	IR(KBr): 3648-3613 cm^{-1} (OH), 3487-3445 cm^{-1} (NH), 1697 cm^{-1} (C=O), 1501 cm^{-1} (N=N), 1549 cm^{-1} (NO ₂). ^1H NMR (DMSO- <i>d</i> ₆ , ppm): 15.86 (br, s, OH 1H), 13.87 (s, COOH, 2H), 11.01 (s, 1H, NH), 8.82 (s, ArH, 1H), 8.69 (s, ArH, 1H), 8.53 (s, ArH, 1H), 8.40-8.38 (d, ArH, 1H, <i>J</i> = 7.89), 8.12-8.10 (d, ArH, 1H, <i>J</i> = 7.71), 8.02-8.00 (d, ArH, 1H, <i>J</i> = 7.42), 7.78-7.74 (t, 1H, ArH, <i>J</i> = 15.13, 7.47), 7.56-7.51 (t, ArH, 1H, <i>J</i> = 14.42, 7.51), 7.31-7.22 (m, ArH, 3H), 7.10-7.07 (t, ArH, 1H, <i>J</i> = 14.57, 7.29). ^{13}C NMR ((DMSO- <i>d</i> ₆ , ppm): 177.44 (C=O), 165.41 (COOH), 163.83 (COOH), 149.84 (C-NO ₂), 146.89 (C-OH), 148.65, 143.45, 135.46, 134.28, 133.84, 132.65, 131.46, 131.12, 130.46, 128.63, 127.89, 127.54, 126.85, 126.29, 126.28, 123.28, 122.86, 122.34, 121.26 (ArC), 115.07 (C-N=N)
6c	IR (KBr): 3500-3200 cm^{-1} (OH, NH), 1624 cm^{-1} (C=O), 1490 cm^{-1} (N=N), 1544 cm^{-1} , (NO ₂). ^1H NMR (DMSO- <i>d</i> ₆ , ppm): 15.56 (br, s, OH 1H), 14.00 (s, COOH, 2H), 11.06 (s, 1H, NH), 8.89 (s, ArH, 1H), 8.71 (s, ArH, 1H), 8.56 (s, ArH, 1H), 8.42-8.40 (d, ArH, 1H, <i>J</i> = 7.92), 8.15-8.13 (d, ArH, 1H, <i>J</i> = 7.88), 8.00-7.98 (d, ArH, 1H, <i>J</i> = 7.45), 7.79-7.75 (t, 1H, ArH, <i>J</i> = 15.11, 7.48), 7.59-7.55 (t, ArH, 1H, <i>J</i> = 14.35, 7.39), 7.31-7.22 (m, ArH, 2H), 7.10-7.07 (t, ArH, 1H, <i>J</i> = 14.57, 7.29) 2.66 (3H, CH ₃). ^{13}C NMR ((DMSO- <i>d</i> ₆ , ppm): 178.44 (C=O), 168.86 (COOH), 165.50 (COOH), 150.74 (C-NO ₂), 148.73 (C-OH), 148.45, 143.12, 136.46, 134.14, 133.48, 132.81, 131.56, 131.07, 130.69, 128.16, 127.89, 127.54, 126.85, 126.29, 126.28, 123.28, 122.34, 121.26 (ArC), 115.07 (C-N=N), 17.99 (CH ₃).

Absorption spectra

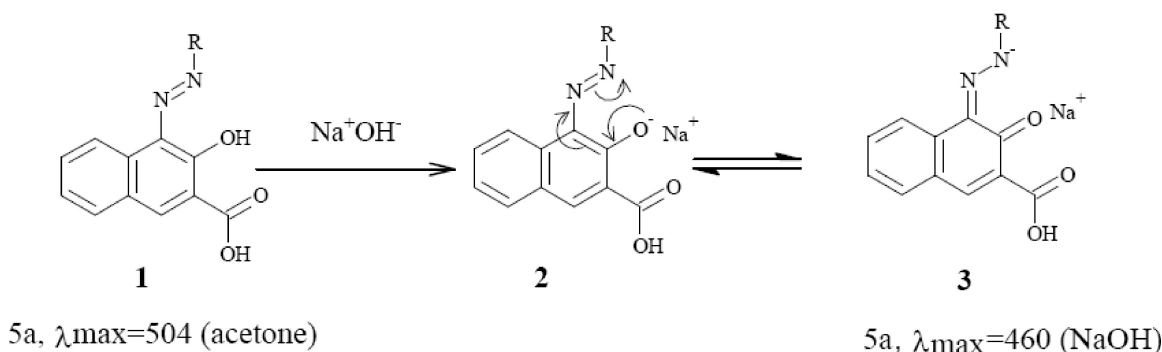
Solvent effect

Absorption spectra of the dyes (**6a-6c**) were recorded in various solvents at a concentration of 10⁻⁴ to 10⁻⁵ M and results are summarized in TABLE 2. Two typical spectra are shown in Figure 1a and 1b. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence, which did not show a regular variation with the polarity of the solvents. It is believed that although DMF, DMSO, MeOH, THF, and acetone the absorption spectra did not change significantly, λ_{max} of the dyes shifted considerably in NaOH (e.g. dye **6c**, the λ_{max} : 494 nm in DMSO, 496 nm in DMF, 495 nm in MeOH, 497 nm

in THF, and 485 nm acetone). λ_{max} of the (**6a-6c**) in NaOH showed considerable change shift in λ_{max} towards the red shift and one more appeared at the 350 nm (e.g. for the dye **6c**, λ_{max} : 353 nm in NaOH.). But in case of proton abstracting solvents this equilibrium depends on the acidity of solvents used such as DMF, DMSO. The dyes give blue shift of λ_{max} exists mainly in the anion form^[18-24].

Florescence studies

Fluorescence properties of the prepared dyes were investigated. For this, the dye solution is excited at the respective λ_{max} and recorded the emission spectrum. The excitation wavelengths were found to 255 and 258 nm, while the emission wavelengths were noticed to be 522



Scheme 2

TABLE 2 : Absorption maxima (nm) of dyes (6a-c) in various solvents

Dye	DMF	DMSO	THF	Acetone	Pyridine	Aceoto nitrile	Acetic acid	MeOH	NaOH	MeOH+ NaOH	MeOH+ HCl
6a	498	489, 319	494,323	495, 317	496, 320	499	493, 402	495, 326	509, 350	481, 353	494, 303
6b	496	493, 308	487,373	486, 364	511, 320	484	486, 364	490	511, 466 ^s	515 ^s , 470	508, 312
6c	496	494, 303	497,316	485, 317	495, 301	486	486, 290	500, 485	509, 472 ^s	515 ^s , 475	511, 319

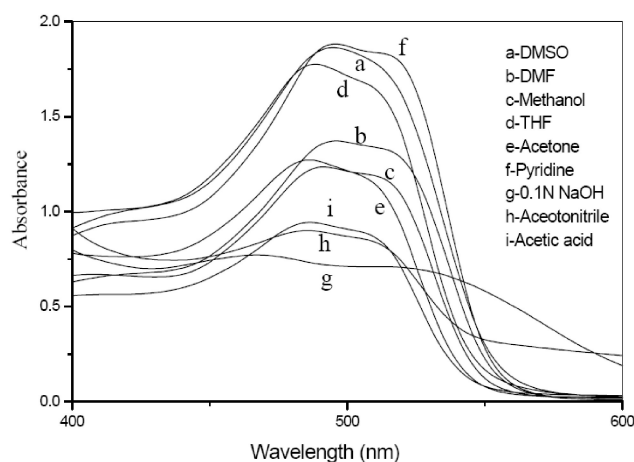


Figure 1a : Absorption spectra of (6b) in various solvents

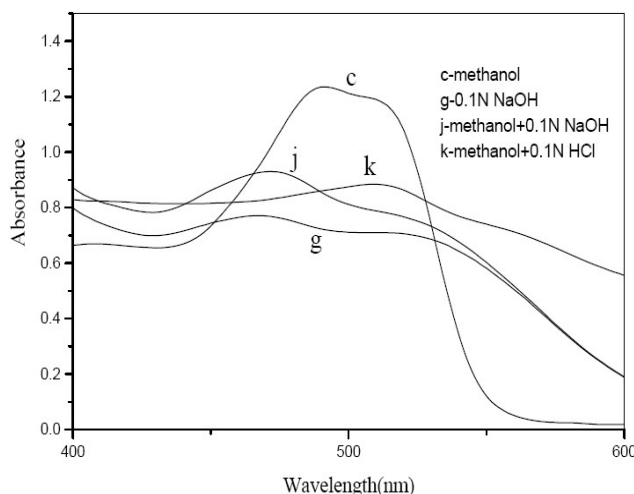


Figure 1b : Absorption spectra of (6b) in acidic and basic conditions

TABLE 3 : Florescent data of dyes (6b) & (6c)

Dye No.	Wavelength of excitation (nm)	Wavelength of emission (nm)	Relative Fluorescence intensity	Stoke's shift
6b	255	522	440	20058
6c	258	514	20	19304

and 514 nm, respectively^[25]. It was observed that the dye 6b were more fluorescent while 6c was weakly fluorescent. 1 mg of each dye is dissolved in a drop of dilute NaOH and diluted to 25 ml with distilled water in a 25 ml volumetric flask so as to obtain 40 ppm. Further, 0.5 ml of 40 ppm solution is diluted to 3 ml and used this solution for recording fluorescence measurements. The dyes 6b was found to be more fluorescent while others were weakly fluorescent. The excitation and emission wavelengths and Stoke's shift are given in the TABLE 3.

Thermal properties and kinetic parameters

The thermo analytical data and kinetic parameters are of all the compounds are summarized in TABLE 4. The typical TGA curve of the compounds (6a-6c) are illustrated in Figure 2. Kinetic and thermodynamic parameters of all the compounds have been evaluated by Broido's method^[26]. Plots of $\ln(-\ln Y)$ versus $1/T$ (where Y is the fraction of the compound undecomposed) were developed for the decomposition segment where loss of functional group occurs. The

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TABLE 4 : Thermodynamic and kinetic parameters of the dyes (6a-6c)

Dye	Decomposition range ($^{\circ}\text{C}$)	DTA _{max} ($^{\circ}\text{C}$)	E_a (kJ mol^{-1})	$\ln A$ (s^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})	ΔG (kJ mol^{-1})
6a	155-280	210	3.5027	5.4403	-0.5128	-149.99	72.445
	460-575	521	57.914	16.428	51.313	-143.79	114.22
6b	230-300	262	3.6011	5.3816	-0.8468	-149.27	79.860
	500-585	553	64.544	17.104	57.676	-143.83	118.86
6c	225-330	269	2.6373	4.8540	-1.8688	-149.12	80.824
	475-580	529	36.574	12.577	29.906	-144.52	115.93

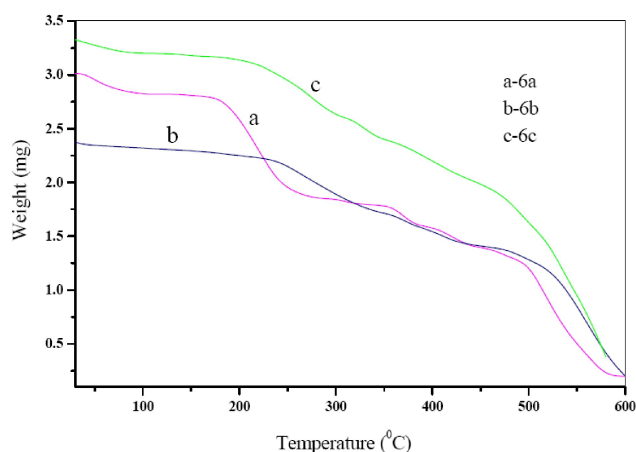
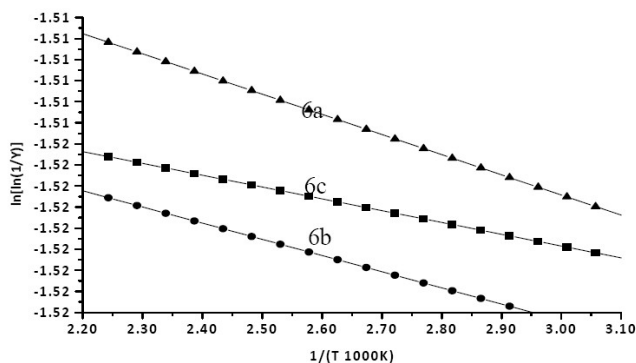
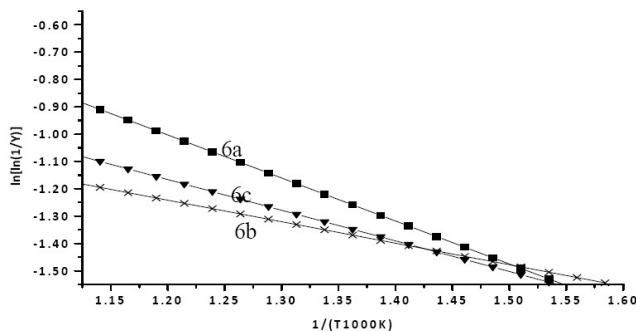


Figure 2 : TGA curves of (6a-c)

thermoanalytical studies of (6a-6c) in air revealed that these compounds degrade in two steps. The first and

Figure 3a : Plots of $\ln(\ln(1/Y))$ versus $1/T$ thermal degradation of (6a-6c)Figure 3b : Plots of $\ln(\ln(1/Y))$ versus $1/T$ thermal degradation of (6a-6c)

second degradation steps seem to be gradual, and may be attributed to the rapture of whole molecule and all steps are endothermic in nature. The compound (6a) shows that all the peaks are endothermic and the decomposition occurs in two steps, first step in the range of 155-280 $^{\circ}\text{C}$ with decomposition temperature of 210 $^{\circ}\text{C}$ with endothermic peak, second step occurred in the range of 460-575 $^{\circ}\text{C}$ with decomposition temperature (T_d) was 421 $^{\circ}\text{C}$. From the plots Figure 3a and 3b the energy of activation (E_a), frequency factor ($\ln A$), and various thermodynamic parameters like Enthalpy (ΔH), Entropy (ΔS) and free energy (ΔG) were calculated using standard equations. It is understood from the TGA of dyes, that high activation energy causes rapid degradation around their decomposition temperatures, where activation energies low represents the gradual degradation.

Cyclic voltammetry studies

Compounds (6a-6c) were carried out in Electroanalyzer-201 cyclic voltammetry using 0.1M H_2SO_4 as supporting electrolyte and DMF (0.5mM) as a solvent. Electrochemical cell consists of a glass container with a cap having holes for introducing elec-

TABLE 5 : Effect of scan rates on the reduction of ring at glassy carbon electrode in DMF contain 0.1M H_2SO_4

Dye	Scan rate (mV/s)	E_{pc} (mV)	I_{pc} (μA)	E_{pa} (mV)	I_{pa} (μA)
		E_{pc1}	I_{pc1}	E_{pa1}	I_{pa1}
6a	25	-173	12.00	412	-8.22
	50	-182	18.15	417	-12.69
	75	-198	21.13	419	-16.65
6b	25	-529	21.03	--	--
	50	-582	27.42	--	--
	75	-592	35.10	--	--
6c	25	-492	15.3	380	-5.12
	50	-500	22.42	389	-10.23
	75	-520	24.19	395	15.40

trodes. The reference electrode used was saturated calomel electrode (SCE), The auxiliary and working electrodes were platinum foil and glassy carbon respectively. The cyclic voltammetric studies of dyes were carried out in the potential range -500mV to $+500\text{mV}$ in three different scan rates 25 mV , 50 mV , and 75 mV .

Reduction of compound (6a-6c)

The results show that the compounds (**6a-6c**) were reduced in a potential range between -592mV to -173mV at pH-2 gave single reduction peak with two electron changes as seen in TABLE 5. The typical cyclic voltammogram curves of the compounds (**6a-6c**) is illustrated in fig 4a and 4b. Whereas the compound (**6a**), (**6b**) and (**6c**) exhibit reduction potential in the range -182mV , -582mV and -500mV at the scan rate of 50 mV .

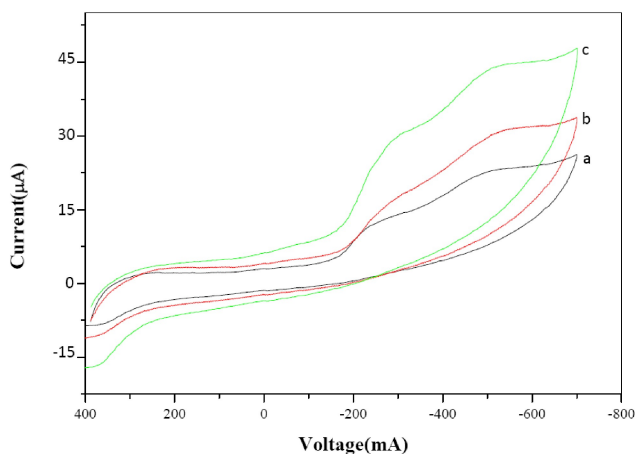


Figure 4a : Cyclic voltammogram of (6a-6c) in different scan rate (25, 50 & 75)

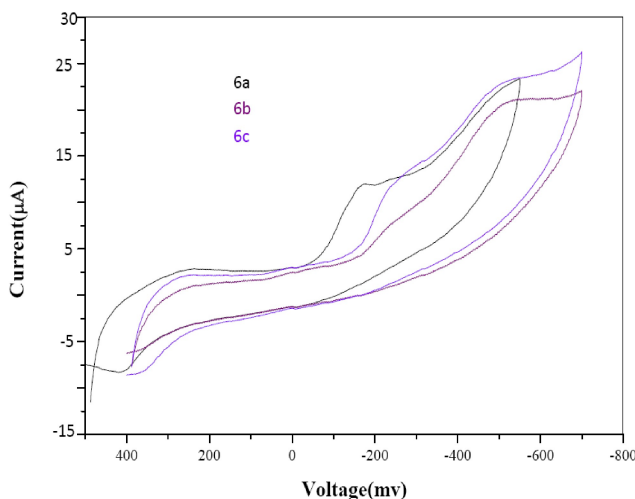


Figure 4b : Cyclic voltammogram of (6a-6c) in 25 scan rate

Oxidation of compound (6a-6c)

The results show that oxidation of compounds (**6a**) and (**6c**) oxidized in a potential range at 417mV and 389mV respectively. However the compound (**6b**) does not show any oxidation potential.

CONCLUSION

We have established an efficient route for the synthesis of novel alkali clearable azo dyes of 3, 5-ANPA. It is certainly interesting to note that the colors of the dyes were intense and λ_{max} of these dyes lie in between $400\text{-}550\text{ nm}$. Moreover these dyes were found to be alkali clearable due to the presence of phenolic and carboxylic acid groups and it may be useful in textile industries.

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