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Synthesis Novel Compounds Include Diazo and Tetramine Groups and Investigated Dyeing Properties on Polyester Fabrics

Diazo ve Tetraamin Grubu İçeren Yeni Bileşiklerin Sentezi ve Boyama Özelliklerinin Poliester Kumaşlar Üzerinde İncelenmesi

Research Article

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ABSTRACT

In this study, we have synthesized eight novel compounds used as dyes for polyester fabrics. Benzene-1,4-diamine, 4-(4-aminophenoxy)benzenamine, 4-(4-aminophenylthio)benzenamine and 4-(4-aminophenylsulfonyl)benzenamine were diazotized and coupled with malononitrile to give phenylazo malononitriles (1a-d). Then, including tetraminopyrazoles compounds (2a-d) were synthesized by heating phenylazo malononitriles and hydrazine monohydrate in ethanol. The compounds were characterized by FT-IR, NMR spectroscopic techniques (^{1}H NMR, ^{13}C NMR) and elementel analyses. UV-visible absorption spectra of the compounds are discussed (2a-d). The synthesized 1a-d and 2a-d were applied on polyester fabrics to investigated dyeing properties.

Key Words
Diazo dyes, polyester fabrics, malononitrile, dyeing properties.

ÖZET

Bu çalışmada, polyester yapılar için kullanılabilecek 8 yeni bileşik sentezlendi. Benzene-1,4-diamine, 4-(4-aminofenoksi)benzamine, 4-(4-aminofenoltiyo)benzamine ve 4-(4-aminofenilsülfonil)benzamine malononitril ile kenetlenip fenilazomalononitriller elde edildi. Etil alkol içerisinde fenilazo malononitriller bileşikleri ile hidrazinmonohidrat etkileştirilmesi ile tetraamino pirazol içeren bileşikler sentezlendi. Bileşiklerin yapıları elemental analiz, FT-IR, NMR gibi spektroskopik teknikler kullanılarak karakterize edildi. Bileşiklerin UVvis. absorpsiyon spektrumları alındı ve sonuçlar tartışıldı. Sentezlenen bileşikler 1a-d ve 2a-d boyama özelliklerinin araştırılması için polyester kumaşa uygulandı.

Anahtar Kelimeler
Diazo boyaları, poliester yapılar, malononitril, boyama özellikleri.

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INTRODUCTION

It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibers, the coloring of different materials, colored plastics, biological-medical studies an advanced applications in organic synthesis. Many patents and papers describe the synthesis and dyeing properties of azo compounds [1–6]. Especially, azo dyes based on heterocyclic amines have been developed, and the resultant dyes have been higher tinctorial strength and give brighter dyeing than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afford very electronegative diazo components and consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [7–10]. Aminopyrazoles are very important class of heterocyclic due to their biological and pharmacological activities [11,12]. These compounds often exhibit anti-inflammatory, herbicidal, fungicidal, bactericidal, and antipyretic activities, and also can be used as plat growth regulating agents as well as protein kinase inhibitors [13–17]. Polyfunctionally substituted heteroaromatics are biologically interesting molecules and their synthesis has recently received considerable attention [18–20]. Recently, some pyrazoles were reported to have non-nucleoside HIV-1 reverse transcriptase inhibitory activity [21–25]. Some azopyrazole derivatives also find application in dyes, biological and pharmacological studies and complexes [26– 30].

EXPERIMENTAL

General

All melting points reported are uncorrected ATR-FTIR measurements were made with a Nicolet 6700 FTIR (USA) spectrometer equipped with a smart orbit accessory in the range of 4000-500 cm^{-1}. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Schimadzu 160A spectrophotometer in various solvents. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer in DMSO-d_6 as a solvent and TMS as an internal reference. Elementel analyses were performed on a LECO CHNS-932 analyzer. The chemicals used for the synthesis of the compounds were obtained from Aldrich-Sigma Chemical Co. without further purification. The solvents used were of spectroscopic grade. Synthesized dyes, dispersant agent (Setalan DFT, Setas Chem.), and water purified ion exchange, were used for the dyeing tests. Scoured knitted polyester fabric (180 g/m^2) was obtained from Setas Chem. Reflectance spectrum were recorded on a Konica & Minolta spectrophometer model 3600d at (D65/10°). Dyeing tests were carried out on a Termal Laboratory Dyeing Machine. Fastness results obtained from rubbing fastness apparatus (Termal), washing fastness machine (Thermal) and Xenotest 150s+ (Atlas) respectively.

General procedure for synthesis of compounds (1a-d).

Preparation of 2-[4-(Dicyanomethyl-azo)-phenylazo]-malononitrile (1a). Benzene-1,4-diamine (1.08 g, 0.010 mole) and conc. H_2SO_4 (3.13 mL, 0.060 mole) were mixed slowly. The salt of benzene-1,4-diamine sulphuric acid was dissolved in 25 mL distilled water. This solution was stirred and cooled to -5 to 0°C and diazotized by the careful drop wise addition (over a period of 30 minutes) of sodium nitrite in cooled water (1.38 g, 0.020 mole). The solution must be cold (-5 to 0 °C) during the addition. Ten minutes later the solution of malononitrile (1.32 g, 0.020 moles) in ethanol was added drop by drop in this temperature. In this mixture was added sodium acetate (1.64 g, 0.020 mole) to adjust pH. The mixture was stirred at this temperature 2h. The precipitate obtained and filtered then recrystallized in ethanol. Yield: 68 %; brown microcrystals (from ethanol); m.p 248-9 °C; IR (ATR, cm^{-1}) ν 3180 (NH), 3040 (Aro.-H), 2226 (-CN) ^{1}H-NMR (DMSO-d$_6$, ppm) ν 12.05 (s, 1H); 7.29 (s, Ar-H, 2H), 13.06 (b, NH). ^{13}C-NMR (DMSO-d$_6$, ppm) ν 118, 125, 129, 172. Anal. Calcd for $C_{12}H_6N_8$: C, 54.96; H, 2.31; N, 42.73. Found : C, 54.68; H, 2.13; N, 43.07.

Preparation of 2-[4-[4-(Dicyanomethyl-azo)-phenoxy]-phenylazo]-malononitrile (1b). Yield: 68 %; Primrose yellow (from ethanol); m.p 261-263 °C; IR (ATR, cm^{-1}) ν 3132 (NH), 3072 (Aro.-H), 2221 (-CN). ^{1}H-NMR (DMSO-d$_6$, ppm) ν 7.07(d, Ar-H, 2H), 7.49 (d, Ar-H, 2H), 13.02 (b, NH). ^{13}C-NMR (DMSO-d$_6$, ppm) ν 86, 110, 115, 118, 125, 132, 142.

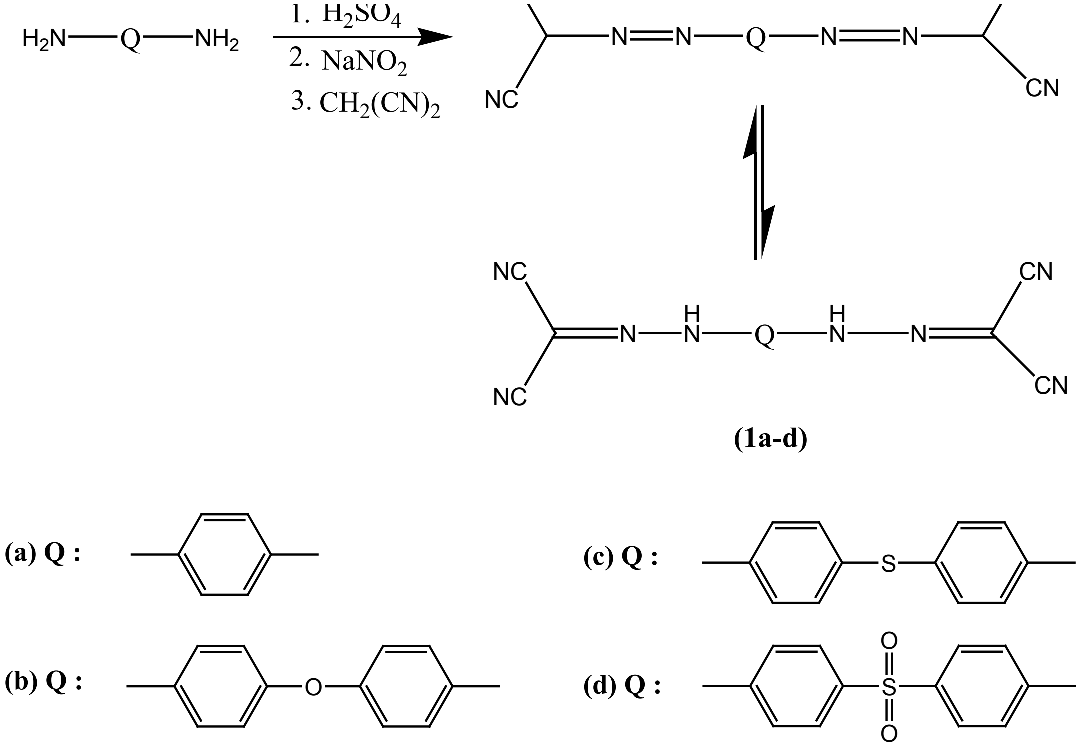
Anal. Calcd for $C_{18}H_{10}N_8O$: C, 61.02; H, 2.84; N, 31.62. Found : C, 60.64; H, 2.41; N, 32.00.

Preparation of 2-[4-[4-(Dicyanomethyl-azo)-phenylsulfanyl]-phenylazo]-malononitrile (1c).
Yield: 86 %; Orange solid (from ethanol) m.p. 262-265; IR (ATR, cm^{-1}); ν 3182 (NH), 3065 (Aro.-H), 2217 (-CN). ^{1}H-NMR (DMSO-d$_6$, ppm) 7.35(d, Ar-H, 2H), 7.46 (d, Ar-H, 2H), 13.13 (b, NH). ^{13}C-NMR (DMSO-d$_{6,}$ ppm) 85, 110, 114, 118, 125, 132, 141. Anal. Calcd for $C_{18}H_{10}N_8S$: C, 58.37; H, 2.72; N, 30.25; S, 8.66. Found : C, 58.12; H, 2.51; N, 30.52; S, 8.85.

Preparation of 2-[4-[4-(Dicyanomethyl-azo)-benzenesulfonyl]-phenylazo]-malononitrile (1d).
Yield: 79 %; Primrose yellow (from ethanol). m.p. 263-265; IR (ATR, cm^{-1}); 3190 (NH), 3086 (Aro.-H), 2230 (-CN) ^{1}H-NMR (DMSO-d$_6$, ppm) 7.64(d, Ar-H, 2H), 7.96 (d, Ar-H, 2H), 13.21 (b, NH). ^{13}C-NMR (DMSO-d$_6$, ppm) 88, 109, 114, 117, 129, 137, 145. Anal. Calcd for $C_{18}H_{10}N_8O_2S$: C, 53.73; H, 2.50; N, 27.85; S, 7,97. Found : C, 53.39; H, 2.13; N, 28.19; S, 8.45.

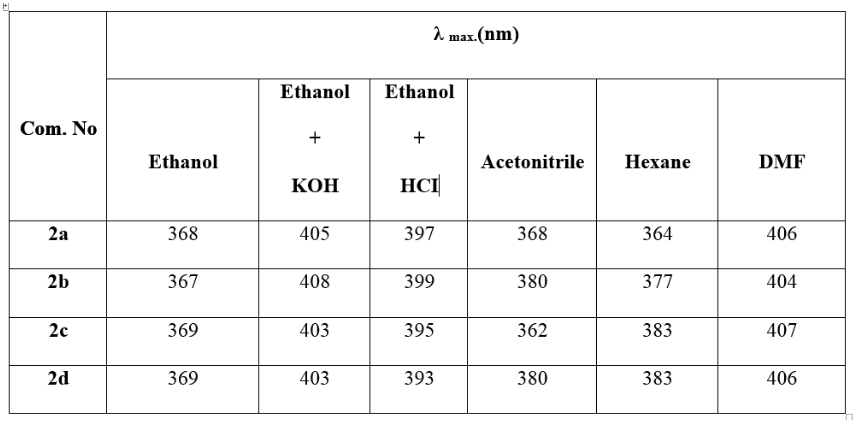
Synthesis of heterocyclic tetraazo dyes 2a-d
1,4-Phenylenebis(diazene-2,1-diyl)bis-4,4′-(1H-pyrazole-3,5-diamine) (2a). Hydrazine monohydrate (0.62 mL, 0.020 mol) was added to a solution of **1a** (2.62 g, 0.010 mol) in 30 mL ethanol. The reaction mixture was heated under reflux for 4 h. The reaction mixture was concentrated in vacuo and then triturated with water whereby the resulting solid product was collected by filtration and crystallized from ethanol [31], give brown solid 3,5-diamine-4-phenylazo-1*H*-pyrazole (*2a*). mp: 310-313 °C. IR (ATR, cm^{-1}); ν 3393, 3307 (NH$_2$), 3187 (NH), 3048 (Aro.-H). ^{1}H-NMR (DMSO-d$_6$, ppm) 6.10 (m, NH$_2$, 4H), 7.04(d, Ar-H, 2H), 7.69 (d, Ar-H, 2H), 10.23 (b, NH). ^{13}C-NMR (DMSO-d$_6$, ppm)ν 112, 121, 122, 150, 154. Anal. Calcd for $C_{12}H_{14}N_{12}$: C, 44.17; H, 4.32; N, 51.51. Found : C, 43.74; H, 3.92; N, 52.34.

4,4′-Oxybis(4,1-phenylene)bis(diazene-2,1-diyl)bis-4,4′- (1H-pyrazole-3,5-diamine) (2b). mp: 319-321°C. Gren solid. IR (ATR, cm^{-1}); 3393, 3307 (NH$_2$), 3187 (NH), 3087 (Aro.-H). ^{1}H-NMR



Scheme 1

Table 1. Influence of solvent on λ $_{max}$(nm) of dyes 2a-d.



Com. No	λ max.(nm)					
	Ethanol	Ethanol + KOH	Ethanol + HCl	Acetonitrile	Hexane	DMF
2a	368	405	397	368	364	406
2b	367	408	399	380	377	404
2c	369	403	395	362	383	407
2d	369	403	393	380	383	406

(DMSO-d_6, ppm) 6.20 (m, NH_2, 4H), 7.04(d, Ar-H, 2H), 7.71 (d, Ar-H, 2H), 10.02 (b, NH). ^{13}C-NMR (DMSO-d_6, ppm) 114, 119, 121, 122, 150, 155. Anal. Calcd for $C_{18}H_{18}N_{12}O$: C, 51.67; H, 4.34; N, 40.17. Found : C, 51.52; H, 4.19; N, 40.39.

4,4′-Thiobis(4,1-phenylene)bis(diazene-2,1-diyl)bis-4,4′- (1H-pyrazole-3,5-diamine) (2c). mp: 318-320 °C. Orange solid. IR (ATR, cm^{-1}); 3409, 3382 (NH_2), 3117 (NH), 3066 (Aro.-H). ^{1}H-NMR (DMSO-d_6, ppm) 6.10 (dm, NH_2, 4H), 7.33(d, Ar-H, 2H), 7.67 (d, Ar-H, 2H), 10.80 (b, NH). ^{13}C-NMR (DMSO-d_6, ppm) 115, 121, 127, 131, 132, 136, 153. Anal. Calcd for $C_{18}H_{18}N_{12}S$: C, 49.76; H, 4.18; N, 38.68; S, 7.38. Found : C, 49.41; H, 3.93; N, 39.02; S, 7.64.

4,4′-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)bis-4,4′-(1H-pyrazole-3,5-diamine) (2d). mp: 343-346 °C. Orange solid. IR (ATR,cm^{-1}); 3399, 3298 (NH_2), 3202 (NH), 3096 (Aro.-H). ^{1}H-NMR (DMSO-d_6, ppm) ν 6.38 (dm, NH_2, 4H), 7.79(d, Ar-H, 2H), 7.91 (d, Ar-H, 2H), 10.92 (b, NH). ^{13}C-NMR (DMSO-d_6, ppm) ν 116, 121, 126, 131, 133, 137, 154. Anal. Calcd for $C_{18}H_{18}N_{12}O_2S$: C, 46.35; H, 3.89; N, 36.03; S, 6.87. Found : C, 45.81; H, 3.17; N, 36.92; S, 7.19.

Dyeing

The synthesized dyes **1a-d** and **2a-d** were applied on polyester fabrics. Their dyeing properties are given Table 2, Table 3, Table 4, and Table 5. Each solution (100 mL) was prepared at 25°C with dye, dispersant agent (1 mL/l) and water, in which the dye concentrations were 0.1, 0.5, 1 and 2 respectively. Polyester fabric (5 g) at a liquor ratio of 20:1 immersed in the dyebath from the beginning. Dyeing was continued for a further 60 min at 130 °C to permit exhaustion. After dyeing,

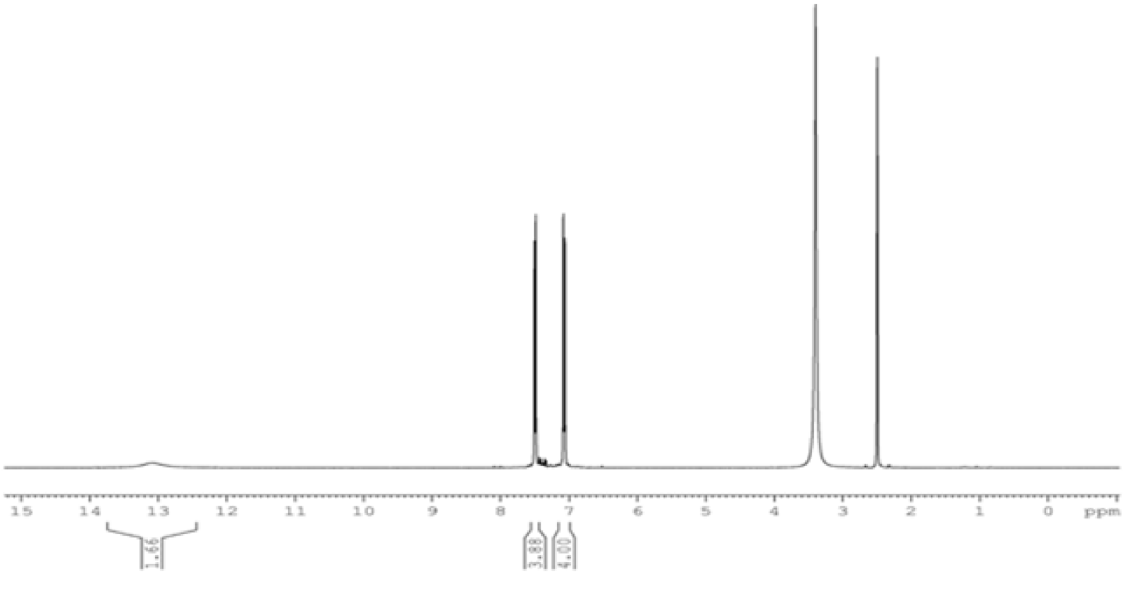


Figure 1. ^{1}H NMR Spectra of compound 1b.

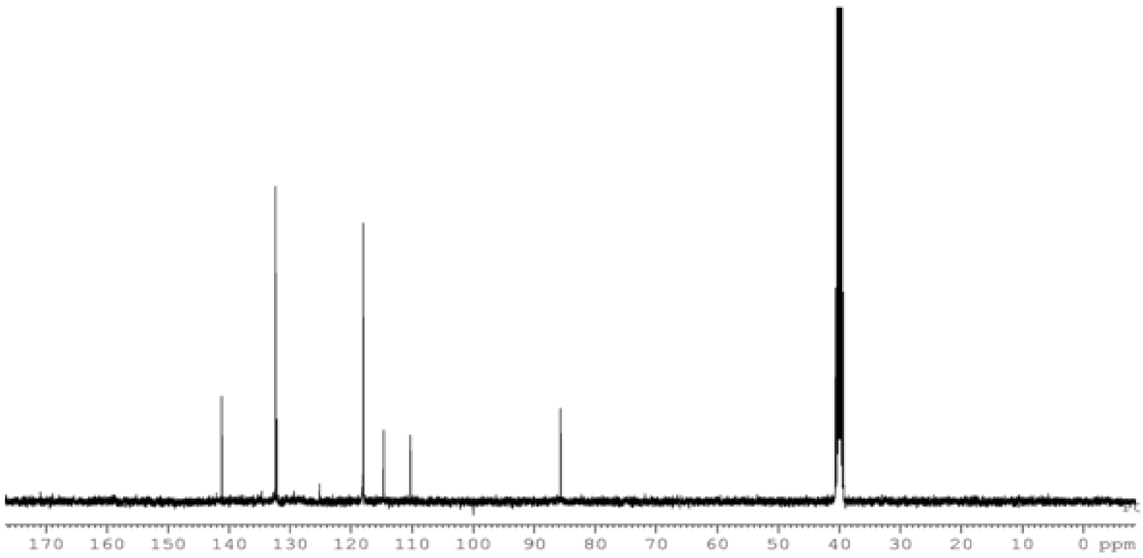


Figure 2. ^{13}C NMR Spectra of compounds 1b.

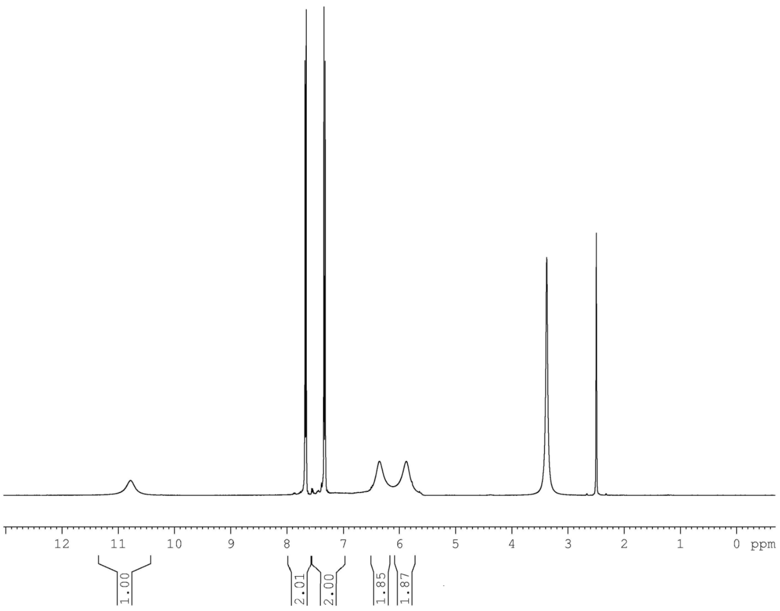


Figure 3. ^{13}C NMR Spectra of compounds 2d.

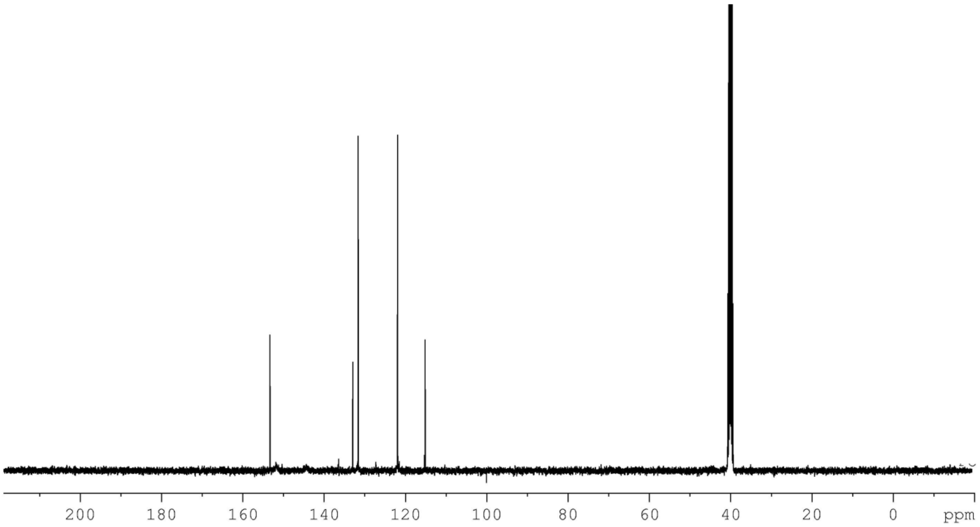


Figure 4. ^{13}C NMR Spectra of compounds 2d.

the polyester fabric was washed cool and boiled water, to detergent Setawash BNH (Setas Chem) had been added to give a concentration 1 g/L, to remove unfixed dye, and dried [32].

The resulting color yield (K/S) is increases when dye molecules grow. The highest color yield is achieved at compound **2d**, while the lowest one is at the compound **2a**. In general, the synthesized dyes are yellow. The larger the molecule size of the compound, the higher the saturation (b) of the yellow color is [33].

As a result of the dyestuff application on different fastness trials, the light, rubbing and washing fastnesses are at adequate level. The fastnesses at pale shades are better than dark shades.

RESULTS AND DISCUSSION

Structures of synthesized compounds were characterized spectroscopically by IR, ^{1}H NMR, ^{13}C NMR and elementel analysis. Same characteristic peaks indicating the presence of particular functional groups. The absorption at 3180, 3132, 3182, 3190 cm^{-1} are characteristic of ν(NH), 2226, 2221, 2217, 2230 (CN), respectively for compounds **1a-d.**

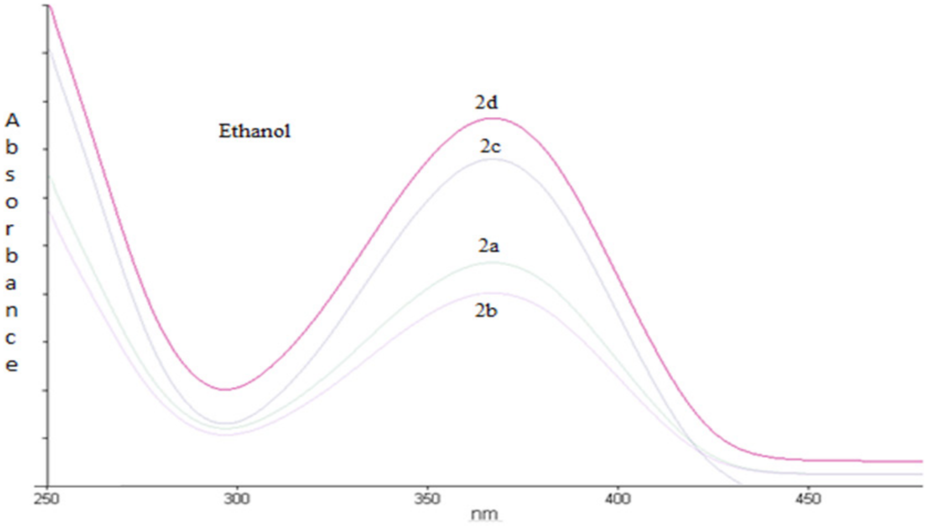


Figure 5. Solvent effect of compounds 2a-d in ethanol.

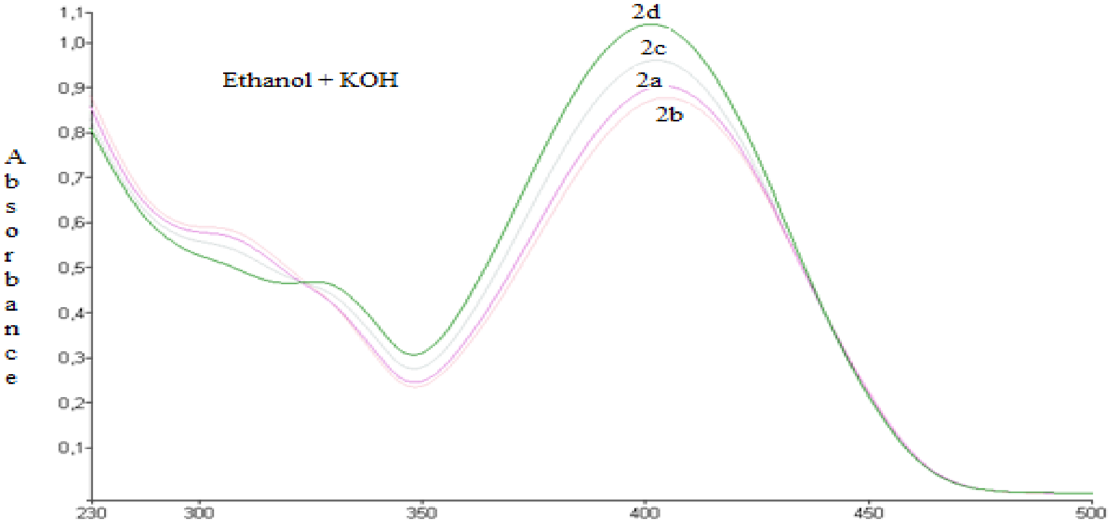


Figure 6. Base effect on compounds 2a-d in ethanol.

^{1}H NMR spectra of **1a-d** showed broad peak at 13.06, 13.02, 13.13, 13.21 ppm (NH), respectively. Aromatic proton signals showed ν 7.07 - 7.96 ppm. The ^{13}C NMR spectral data on synthesized compounds are also in accordance with the proposed structures.

Compounds **2a-d** were shown two peaks for (NH_2), and one peak for (NH). ^{1}H NMR spectra of **2a-d** showed broad peak at 10.23, 10.02, 10.80, 10.92 ppm (NH), 6.10 , 6.20, 6.10, 6.38 ppm (NH_2) respectively. Aromatic proton signals showed 7.04-7.91 ppm. The ^{13}C NMR spectral data on synthesized compounds are also in accordance with the proposed structures.

Solvent effects on UV-vis spectra

Absorption spectra of tetra-amino dyes **2a-d** were recorded in various solvents at a concentration of 10^{-6}–10^{-8} M and these are all run at same concentrations. The results are summarized in *Table 1*.

The visible absorption spectra of the dyes did not correlate with the polarity of solvent. Dyes

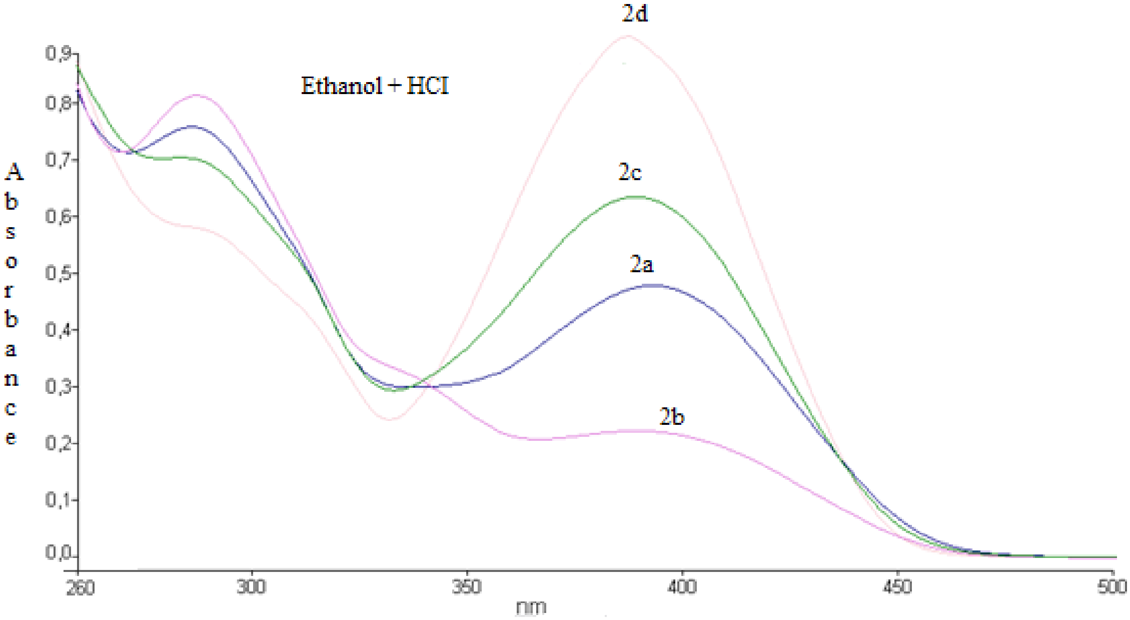
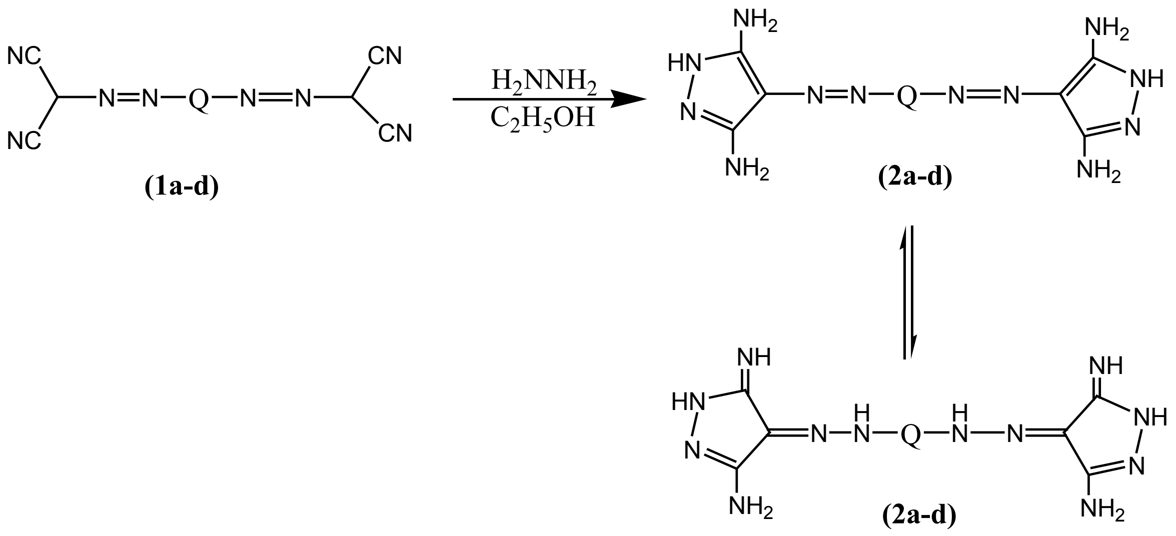


Figure 7. Acid effect of compounds 2a-d in ethanol.



Scheme 2

Table 2. K/S values and CIE Lab colour coordinates of dyed fabrics (1a-d).

Dye no.	Applied depth	K/S	L	a	b
1a	0.1	0.22	81.43	-0.4	11.11
	0.5	0.64	77.76	3.12	18.36
	1	0.88	78.10	2.38	22.45
	2	1.64	73.11	4.88	21.54
1b	0.1	1.17	76.48	-2.15	24.98
	0.5	2.33	74.47	-3.92	32.25
	1	3.39	75.49	-4.90	39.89
	2	3.89	74.62	-1.44	39.15
1c	0.1	1.02	74.60	-1.59	28.68
	0.5	2.77	72.26	4.08	54.76
	1	5.11	72.26	3.44	51.76
	2	5.23	72.22	5.32	53.59
1d	0.1	1.71	68.03	3.30	30.48
	0.5	7.52	64.82	8.23	53.89
	1	11.13	60.85	12.58	58.37
	2	17.65	67.14	11.66	67.69

Table 3. Colour fastness properties of synthesized dyes on polyester fabric (1a-d).

Dye no.	Applied depth	light	rubbing (dry/wet)	washing (change/staining)
1a	0.1	3-4	4-5/5	5/5
	0.5	4	5/4-5	5/4-5
	1	4	4-5/4	5/4
	2	3-4	4/4	4-5/4
1b	0.1	4-5	4-5/4	5/4-5
	0.5	3-4	5/4	5/4
	1	3	4-5/4	5/4
	2	3	4-5/5	4-5/3-4
1c	0.1	4	5/4-5	5/5
	0.5	3	4-5/4	5/4-5
	1	3-4	4/4	5/4-5
	2	3	4-5/4	5/4
1d	0.1	5	4-5/5	5/5
	0.5	41	3-4/4	4-5/4-5
	1	4	4/3-4	4-5/4
	2	4	4/3-4	4-5/3-4

Table 4. K/S values and CIE Lab colour coordinates of dyed fabrics (2a-d)

Dye no.	Applied depth	K/S	L	a	b
2a	0.1	0.24	87.37	-0.6	12.77
	0.5	0.71	80.44	2.44	21.86
	1	0.92	80.60	2.70	26.76
	2	1.65	73.99	4.70	29.49
2b	0.1	1.14	80.58	-3.87	23.83
	0.5	2.64	79.17	-2.90	36.17
	1	3.56	80.46	-5.03	42.80
	2	4.11	78.07	-1.20	42.01
2c	0.1	1.28	78.69	-1.21	30.60
	0.5	2.92	75.73	3.20	44.77
	1	5.17	74.59	4.36	55.40
	2	6.96	75.52	7.59	58.11
2d	0.1	1.82	74.13	3.36	33.75
	0.5	7.15	68.36	10.74	56.51
	1	13.94	63.41	12.34	61.23
	2	15.96	65.72	12.78	65.92

2a-d gave a maximum absorption peak in all used solvents. This result suggests that dyes **2a-d** are present in a single toutomeric form in all used solvent.

Acid and base effects on UV-vis spectra

The effects of acid and base on the absorption of dye solutions were investigated in ethanol. When hydrochloric acid (0.10 M) and potassium hydroxide (0.10 M) were added to dye solutions in ethanol, λ_{max} of dyes **2a-d** showed little bathochromic shifts with respect to the λ_{max} in ethanol. This result suggests that these compounds, **2a-d**, are present in a different tautomeric form in ethanol + HCl (or KOH) than that in ethanol and this tautomeric form resembled in DMF.

CONCLUSION

We synthesized eight novel compounds and characterized by spectroscopic techniques. These compounds were applied on polyester fabrics to investigated dyeing properties.

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