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Dyeing Properties of Some New Disperse Dyes Containing Piperazine Moiety

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ABSTRACT

Four novel azo disperse dyes based on 1-(4-bromobenzyl)-4-phenylpiperazine were synthesized in two steps, using alkylation and azo coupling reactions. Chemical structure of the dyes was characterized and confirmed by the Ultraviolet Visible, Fourrier Transform Infrared, Proton Nuclear Magnetic Resonance and Carbon Nuclear Magnetic Resonance analyses. The solvatochromic behavior of the dyes was studied in a set of 10 solvents with different polarity and considerable results were obtained. The prepared dyes were applied as disperse dyes for dyeing polyester fibers and their dyeing properties were evaluated. The fastness properties of the dyed fabrics such as wash, light and rubbing fastness degrees were measured by standard methods. Investigation of antioxidant activity of compounds was carried out by ferric reducing antioxidant power (FRAP) method. The activity data show that the synthesized dyes B1-B4 have promising antioxidant activity. Prog. Color Colorants Coat. 8 (2015), 197-206 © Institute for Color Science and Technology.

1. Introduction

Azo dyes are the most attractive known classes of organic dyes due to their various applications in food industry, textile dying, cosmetics, pigments and paints, high technology materials, biological-medical studies, optical storage capacity, optical switching and holography. Since their discovery in the 19th century, azo compounds have been extensively used as colorants and account for over 50% of all commercial dyes. In addition, a vast majority of azo dyes are mono azo chromophores linking two aromatic systems [1-4]. Azo dyes as disperse colorants have been intensively investigated to produce bright and strong color shades on synthetic textile fibers. On the other hand, the scale and growth of the dye industry is completely linked to that of the textile industry. Consequently, dye manufacturers tend to concentrate their efforts on producing dyes particularly disperse dyes for two most important cotton and polyester textile fibers [5-9].

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From a medical point of view, many azo colorants are non-toxic, although some, such as dinitroaniline orange, ortho-nitroaniline orange, or Pigment Orange 1, 2 and 5 have been found to be mutagenic [10].

In recent years, there has been an increased interest in the application of antioxidants to medical sciences. Free radicals may oxidize nucleic acids, proteins, lipids or DNA and can initiate degenerative disease, including cancer, arthritis, inflammatory, cardiovascular and neurodegenerative diseases. Owing to these facts, synthetic compounds with potential antioxidant activity are receiving increased attention in medicine and biological research [11, 12]. In addition, it is necessary that the range of novel antimicrobial dyes would be increased for the textile industry.

On the other hand, synthesis and characterization of azo dyes containing bioactive piperazine moiety have been reported [13, 14], however, there is little or no published information regarding dyeing polyester fiber with piperazine-based dyes. These compounds also reported to have good biological properties. The piperazine scaffold is an important pharmacophore found in a large number of biologically active compounds. In addition, piperazines are core fragments in a variety of natural products such as the antibiotic bicyclomycin, cytotoxic chetracin A and ergotamine [15-18]. In our previous study of novel piperazine derivatives (triazene and azo dyes) [13], we have found that the synthesized azo dyes in contrast to the triazenes show good biological activity and strong color shades. The encouraging results prompted us to extend the study on piperazine derivatives. In this paper we report the synthesis of four novel azo dyes bearing a piperazine nucleus in order to evaluate their spectral, dyeing and antioxidant properties.

2. Experimental

2.1. Material and apparatus

All compounds used in this study were obtained from Merck Chemical Company and were used without further purification. All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer (Japan). The Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a FT-NMR (400 MHz) Brucker apparatus spectrometer (Germany), and the chemical shifts are expressed in δ ppm using TMS as an internal standard and *J* values are given in Hz. The visible spectra were measured using a Pharmacia Biotech Spectrophotometer (United States). The light, wash and rubbing fastness of all prepared dyes were measured according to BS 1006-1990 UK-TN, ISO105-A02:1993 and ISO 105-X12:1993(E) standards, respectively. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates (Merck Chemical Company, Germany).

2.2. Synthesis of 1-(4-bromobenzyl)-4-phenyl-piperazine (B)

A mixture of *N*-phenylpiperazine (0.486 g, 3 mmol) and 1-bromo-4-(bromomethyl)benzene (0.747 g, 3 mmol) with catalytic quantity of potassium carbonate was refluxed in DMF for 2-3 h and then cooled to 0-1 °C in an ice bath (Step 1, Scheme 1). After that HCl (0.5 M) and water are added and the precipitate is filtered and washed with cold water. The solid product was purified by recrystallization from EtOH/ H_2O.

White solid; yield 96%; m.p. 102-104 °C; FT-IR (KBr) ν cm^{-1}: 3036, 2825, 1591, 1127, 996. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 2.62 (t, 4H, *J* = 5.2 Hz, N-CH_2), 3.22 (t, 4H, *J* = 5.2 Hz, N-CH_2), 3.54 (s, 2H, -CH_2), 6.88 (t, 1H, *J* = 7.2 Hz, Ar-H), 6.95 (dd, 2H, *J* = 0.8 Hz, Ar-H), 7.25-7.31 (m, 4H, Ar-H), 7.48 (d, 2H, *J* = 8.4 Hz, Ar-H).

2.3. Synthesis of azo disperse dyes (B1-B4)

The diazonium salts were prepared in good yield from equimolar mixture of corresponding aromatic amines and nitrous acid according to the previously described methods [19]. After completion of diazotization, the azo liquor was slowly added to a stirred solution of 1-(4-bromobenzyl)-4-phenylpiperazine (1) dissolved in 10 mL of glacial acetic acid and 2–3 mL of DMF in acidic medium by adjusting the pH at 5.5-6.0 and the temperature was maintained at 0-4 °C. The resulting mixture was stirred for 2.5-3 h in an ice bath then allowed to reach room temperature. After completion of the reaction, the pH of the solution was maintained at 6.5–7.5 by addition of sodium acetate (Step 2, Figure 1).

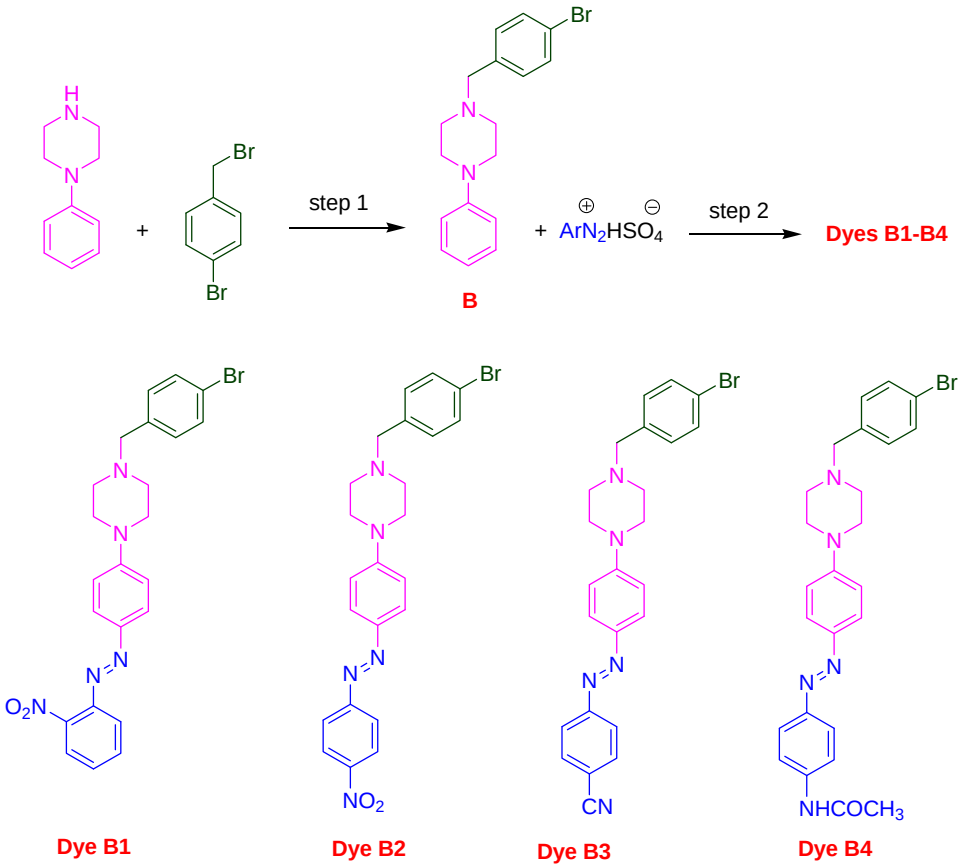

Figure 1: General synthetic route for synthesis of dyes **B1-B4**.

The solid product was collected by filtration and washed two times with water. The crud products were purified by recrystallization from DMF/H_2O. The physical and spectral data of prepared dyes are given below.

2.3.1. 1- (4-bromobenzyl) -4- (4- (2-nitro-phenylazo) phenyl) piperazine (B1)

Yellow Solid; yield: 92%; m.p. 118-120 °C; FT-IR (KBr) ν cm^{-1}: 1590 (C=C), 1510 (N=N). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 3.21 (t, 4H, *J* = 9.6 Hz, N-CH_2), 3.36 (t, 4H, *J* = 10.0 Hz, N-CH_2), 3.47 (s, 2H, -CH_2), 6.91 (d, 2H, *J* = 9.2 Hz, Ar-H), 7.28-7.33 (m, 3H, Ar-H), 7.47 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.62 (m, 3H, Ar–H), 7.87 (d, 1H, *J* = 8.1 Hz, Ar–H) 7.98 (d, 1H, *J* = 8.0 Hz, Ar–H). ^{13}C NMR ($CDCl_3$), δ (ppm): 47.0, 52.2, 61.0, 113.6, 120.2, 122.9, 125.2, 127.4, 131.5, 131.6, 132.8, 137.9, 143.6, 143.9, 153.2, 155.8, 157.3.

2.3.2. 1- (4-bromobenzyl) -4- (4- (4-nitro-phenylazo) phenyl) piperazine (B2)

Red Solid; yield: 90%; m.p. 181-183 °C; FT-IR (KBr) ν cm^{-1}: 1596 (C=C), 1509 (N=N). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm): 3.37 (s, br, 4H, N-CH_2), 3.44 (t, 4H, *J* = 10.0 Hz, N-CH_2), 3.51 (s, 2H, -CH_2), 7.10 (d, 2H, *J* = 9.2 Hz, Ar-H), 7.31 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.54 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.85 (d, 2H, *J* = 9.2 Hz, Ar-H), 7.96 (d, 2H, *J* = 8.8 Hz, Ar-H), 8.37 (d, 2H, *J* = 8.8 Hz, Ar-H). ^{13}C NMR ($CDCl_3$), δ (ppm): 47.0, 52.6, 61.4, 114.2, 120.5, 123.1, 125.4, 126.0, 131.53, 131.59, 137.9, 143.6, 144.3, 154.2, 156.4.

2.3.3. 1- (4-bromobenzyl) -4- (4- (4-cyano-phenylazo) phenyl) piperazine (B3)

Orange Solid; yield: 95%; m.p. 175-177 °C; FT-IR (KBr) ν cm-1: 2220 (C≡N), 1580 (C=C), 1500 (N=N). 1H NMR (400 MHz, CDCl3, 298 K), δ (ppm): 3.25 (t, J = 10.0 Hz, 4H, N-CH2), 3.36 (t, 4H, J = 10.0 Hz, N-CH2), 3.50 (s, 2H, -CH2), 6.90 (d, 2H, J = 8.8 Hz, Ar-H), 7.24 (d, 2H, J = 8.4 Hz, Ar-H), 7.48 (d, 2H, J = 8.4

Hz, Ar-H), 7.80 (d, 2H, J = 8.8 Hz, Ar-H), 7.87 (d, 2H, J = 8.4 Hz, Ar-H), 8.12 (d, 2H, J = 8.4 Hz, Ar-H). 13C NMR (CDCl3), δ (ppm): 47.0, 52.4, 61.2, 113.5, 115.1, 120.1, 122.9, 124.8, 125.5, 131.2, 131.4, 137.2, 142.3, 143.8, 152.6, 155.2.

2.3.4. 1- (4-bromobenzyl) -4- (4- (4-acetamido-phenylazo) phenyl) piperazine (B4)

Brown Solid; yield: 62%; m.p. 144-146 °C; FT-IR (KBr) ν cm^{-1}: 3341 (N-H), 1680 (C=O), 1590 (C=C), 1515 (N=N). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 2.13 (s, 3H, CH_3), 3.17 (t, 4H, *J* = 10.0 Hz, N-CH_2), 3.31 (t, 4H, *J* = 10.4 Hz, N-CH_2), 3.46 (s, 2H, -CH_2), 6.88 (d, 2H, *J* = 9.0 Hz, Ar-H), 7.25 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.42 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.67 (d, 2H, *J* = 9.0 Hz, Ar-H), 7.75-7.81 (m, 4H, Ar-H), 10.23 (s, 1H, N-H). ^{13}C NMR ($CDCl_3$), δ (ppm): 31.3, 47.4, 52.3, 61.1, 111.9, 118.2, 121.1, 123.2, 126.0, 130.2, 131.5, 136.0, 141.1, 141.4, 143.3, 143.7, 178.6.

2.4. Dyeing procedure and Determination of fastness properties

Dyeing was carried out in an Infra Color apparatus using liquor ratio (L:G) of 30:1 and pH was adjusted to 5–6 using acetic acid. The concentrations of the dye dispersions were 0.1, 0.4, 0.8, 1.2, 2 and 4% owf. The owf indicates wt% of a dye relative to fiber weight of a dried fiber. The dyeing was carried out by raising the dye bath temperature from 40 to 100 °C at a rate of 2 °C/min and the bath temperature was maintained at 100ºC for 60 min. After that, the bath was rapidly cooled down to 70 at a rate of 3 ºC/min. Finally, the fabrics were washed off with cold water and dried.

The light fastness was done under irradiation in a commercial xenon arc weather meter until the change in shade of blue-standard fibers using the grey scale. The black panel temperature was 50 °C and the power of light was 1500 W. The changes in color were evaluated based on the blue scale 1-8 where one is poor and eight is excellent. For wash fastness evaluation, dyed fibers were attached to the same size undyed polyester fibers and immersed in a bath of 0.5% detergent at 35 °C and at a liquor ratio of 50:1. After 30 min, the samples were removed, washed twice with deionized water, washed with tap water, and air-dried. Changes in shade and staining of adjacent fabrics were evaluated with the aid of grey-scale 1-5 for color change and transfer. Rubbing fastness was measured using a Crockmeter in accordance with ISO 105-X12:1993(E). This property was also determined according to the grey scale.

2.5. FRAP assay

FRAP was performed according to Benzie and Strain (1996) with minor modifications [20]. The principle of this method is based on the reduction of a ferric 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (Fe^{3+}-TPTZ) to ferrous, in the presence of synthetic compounds. FRAP reagent was prepared from 0.3 M acetate buffer (pH = 3.6), 10 mmol TPTZ solution in 40 mmol HCl and 20 mmol iron (III) chloride solution in proportions of 10:1:1 (v/v), respectively. The FRAP reagent was freshly prepared before analysis and warmed to 37 °C prior to use. 100 µl of diluted compound (20-200 µM) was added to 1.4 mL of the FRAP reagent. The absorbance of the reaction mixture was measured after 5 min against blank at 593 nm. Increased absorbance of the reaction mixture indicated increased reducing power. A standard curve was prepared using different concentrations (0.5-10 mM) of ferrous sulfate. All determinations were carried out in triplicate.

3. Results and discussion

3.1. Chemistry

All the investigated dyes were synthesized by treating the corresponding aryl diazonium salts with 1-(4-bromobenzyl)-4-phenylpiperazine (B) in acetic acid using diazotization-coupling reactions. Alkylation reaction of commercially available *N*-phenylpiperazine with 1-bromo-4-(bromomethyl) benzene in refluxing DMF in the presence of the K_2CO_3 catalyst affords excellent yields of the 1-(4-bromobenzyl)-4-phenylpiperazine (Scheme 1). The structure of prepared dyes was confirmed by analyzing their spectral characteristics.

The FT-IR spectra of all synthesized dyes showed azo bands (N=N) at about 1500 cm^{-1}. The ^{1}H NMR spectra of all synthesized disperse dyes showed two triplet signals at about 3.0 and 3.4 ppm, which was attributed to methylene protons (CH_2) of piperazine ring. The ^{1}H NMR spectra of the dyes also showed a singlet signal at about 3.5 ppm. This signal corresponds to benzylic protons (CH_2) resonance of the dyes. Aromatic protons appeared as d (doublet), t (triplet)

and m (multiplet) forms at 6.90–8.37 ppm according to the different H-H couplings. In addition, the number of carbon signals and their chemical shifts correspond to the structure of synthesized dyes. The UV-vis absorption spectra of all the synthesized dyes showed a strong band at about 406-486 nm, which attributed to $n\rightarrow\pi^*$ and/or $\pi\rightarrow\pi^*$ electronic transitions of unsaturated azo group. These results prove the structure of the prepared disperse dyes **B1**-**B4**.

3.2. The solvatochromic studies of disperse dyes B1-B4

In order to study of solvent effects on the absorption spectra of the dyes **B1**-**B4**, we recorded their absorption spectra in solvents with different polarity at a concentration of 10^{-4}-10^{-5} M at room temperature (Table 1). The λ_{max} values of the synthesized dyes in DMF varied within the range of 438-482 nm due to the $n\rightarrow\pi^*$ and/or $\pi\rightarrow\pi^*$ electronic transitions of azo chromophore. Comparing the λ_{max} values of the dyes in all studied solvents shows that they follow the order of **B2** > **B3** > **B4** > **B1** (Figure 2). Predictably, the introduction of an electron-accepting substituent into the diazo component ring (particularly para position) of an azobenzene dye containing a donor group (NR_2) in the coupling component ring produced a bathochromic shift, as shown in Table 1. On the other hand, dye **B2** has the highest maximum absorption value and dye **B1** the lowest ($\Delta\lambda_{max}$ = 48 nm in DMF). The hypsochromic shift of dye **B1** relative to **B2** is due to the steric prevention found in ortho substituted azo dye (Figure 3). On the basis of electronic effects, delocalization of charge on to the oxygen atom of the o-nitro group, similar to that given by a p-nitro group. The reason for the differences arises from the fact that while dye **B2** is a planar molecule, steric congestion forces compound **B1** to adopt a non-planar conformation. This happens because the o-nitro group clashes sterically with the lone pair of electrons on one of the azo nitrogen atoms and is thus forced to rotate out of a planar conformation [3]. Since rotation about a double bond requires more energy than rotation about a single bond, the first excited state of compound **B1** is destabilized relative to its ground state, with a consequent reduction in the maximum wavelength.

Table 1: Spectral data of the synthesized dyes in various solutions [21].

Solvents	π*	Dyes			
		B1	**B2**	**B3**	**B4**
Cyclohexane	0.00	416	430	411	406
Butanol	0.47	422	448	424	415
Ethyl acetate	0.54	422	450	422	415
Ethanol	0.54	423	448	425	416
Ethanol + HCl	_	400	538, 498, 429	512, 404, 340	393
Ethanol + KOH	_	424	453	430	419
THF	0.55	425	454	425	416
Chloroform	0.58	424	452	426	422
Methanol	0.60	423	450	448	416
Dichloromethane	0.82	426	456	428	430
DMF	0.87	438	486	452	442
DMSO	1.00	440	484	449	444

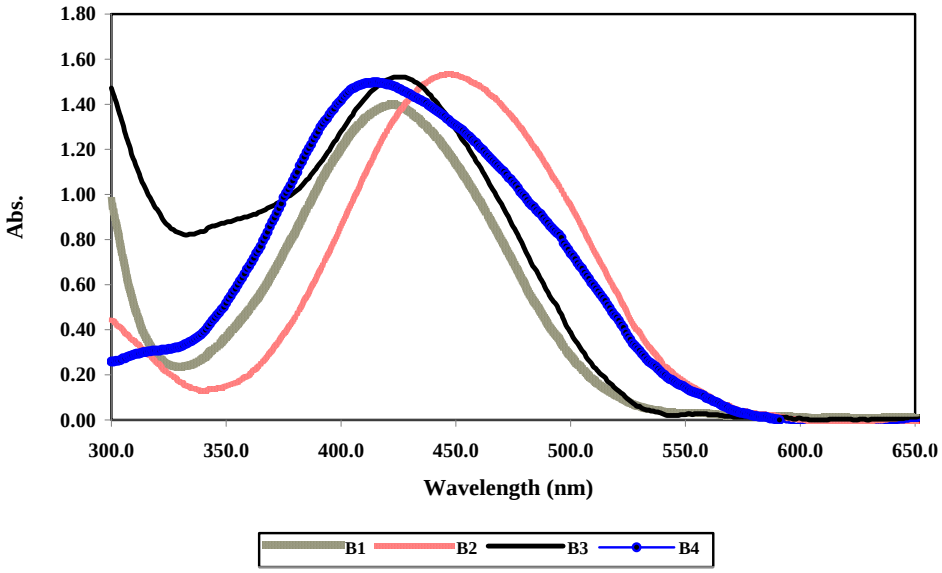

Figure 2: Absorption spectra of dyes **B1**-**B4** in Ethanol.

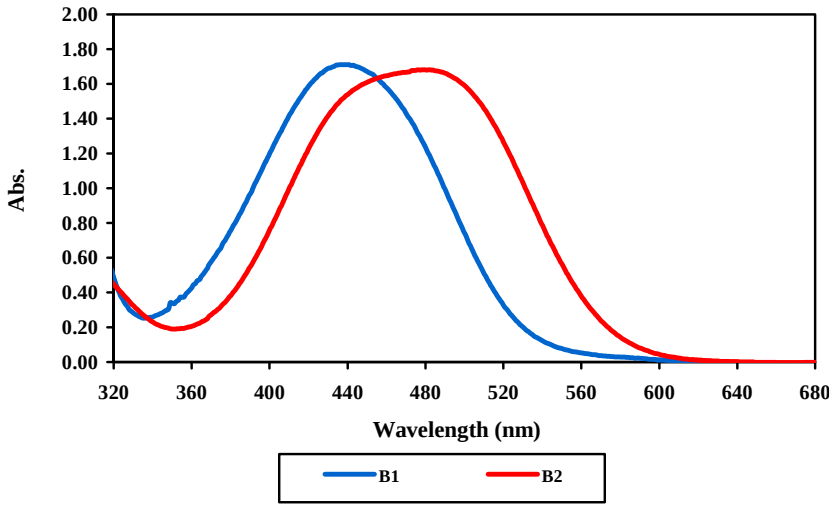

Figure 3: Absorption spectra of dyes **B1** and **B2** in DMF.

Furthermore, as can be seen from the Table 1, there is a strong solvent dependency for dyes **B1-B4** with solvent polarity parameter (π*), indicating bathochromic effect (positive solvatochromism) in more polar solvents. These effects are provided when the ground state of dyes is destabilized relative to its first excited state in polar aprotic solvents such as DMF and DMSO. Furthermore, as shown in Table 1, the effects of the acid and base on the absorption spectra of dyes were investigated in ethanol. It was observed that the absorption spectra of all dyes (except for dye B1) were sensitive for the addition of HCl solution (0.5 M) in Ethanol. As shown in Table 1, in acid solution dyes **B2** and **B3** show three absorption peak, which are probably related to the tautomeric azo-hydrazone forms in acidic medium (Figure 4 and Figure 5). It was also

observed that the absorption spectra of the synthesized dyes were not significantly sensitive to base solutions. Nevertheless, the λ_{max} of dyes showed a slightly bathochromic shift when a small amount of 0.5 M KOH was added to their alcoholic solutions. However, we believe that solvatochromic behavior should be evaluated using Kamlet–Taft equation.

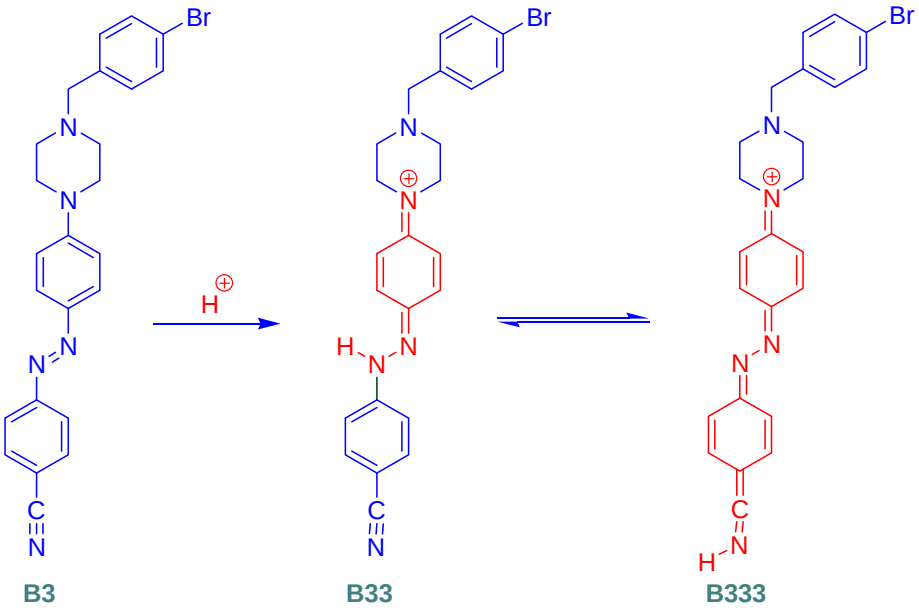

Figure 4: Possible tautomeric forms of dye **B3** in acid solution.

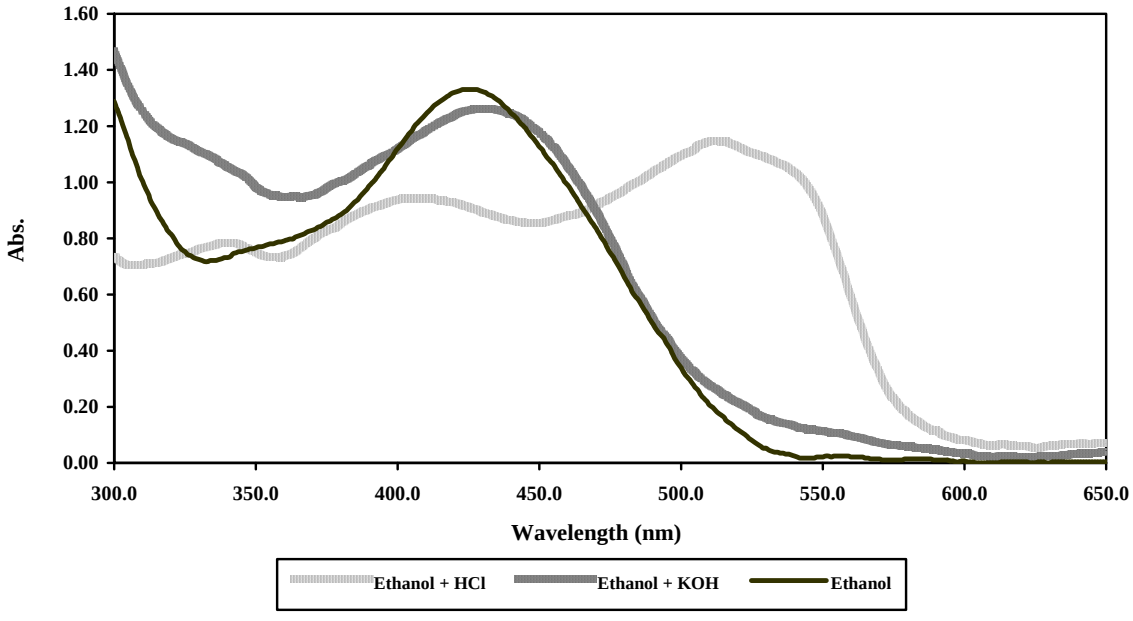

Figure 5: Absorption spectra of dye **B3** in acidic and basic solutions.

3.3. Dyeing properties of synthesized dyes on polyester fiber

Colorants are applied to fiber by different methods of dyeing for different types of fibers. However, interest in eco-friendly textile wet processing techniques has been increasing in recent years due to the increased awareness of environmental issues [22-24]. Disperse dyes are traditionally non-ionic chemicals with low solubility in water which, consequently, are able to retain comparatively better substantively for hydrophobic fibers, such as polyester, nylon and acetate. The measurement of fastness properties of novel dyes on fibers is important to determine that they are good colorants. In this part, dyes **B1**-**B4** were applied to polyester fibers by high-temperature pressure method. Table 2 shows the results of wash, light and rubbing fastness of the prepared dyes on polyester fibers. The results indicate that the dying on polyester fibers show excellent fastness to washing and rubbing tests. This may be attributed to the good penetration and hard removal of synthesized dyes on polyester fibers. According to the Table 2, the light fastness of the dyes is moderate. The light fastness of the prepared dyes depended on nature of the diazo components which change the electron density around azo group. In fact, all dyeing show good light fastness except for dye **B4** with electron-donating group.

3.4. Antioxidant activity

Several assays have been used to estimate antioxidant capacities in organic compounds including 2,2-azinobis (3-ethyl-benzothiazoline-6-sulfonic acid) (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH), and the ferric reducing antioxidant power (FRAP) and etc. [25-26]. In this research, FRAP method was used for assaying the antioxidant activity of synthesized azo disperse dyes **B1**-**B4**. The results obtained from the FRAP assay are presented in Table 3. In the FRAP assay, antioxidant activity of the compounds is related with their electron releasing ability to the reduction of Fe^{3+} ions. Compounds having electron-donating groups such as amino ($-NR_2$) and hydroxy (-OH) are found relatively more active. All studied compounds showed significance antioxidant activity due to bearing two amino groups on the piperazine ring. In other words, all synthesized compounds reduce Fe^{3+} ions to Fe^{2+} ions which are complex with TPTZ. Antioxidant activity of studied compounds decreased in the order **B4** > **B2** > **B3** > **B1** > **B**. It seems clear that compounds containing azo group showed strong antioxidant activity in contrast to precursor **B**. Additionally, amide group bonded to the aromatic ring, such as dye **B4** slightly increases this activity. From the above discussion, it is concluded that the antioxidant activity depends on the position and the type of substituent. In general, this notable antioxidant activity may be rationalized on the basis that the prepared compounds possess piperazine bioactive component that act as potential antioxidants [27].

Table 2: Fastness properties of the dyes **3a-d** on polyester fibers

Dyes	Color	Washing		Rubbing		Light
		Change in shade	Staining on polyester	Dry	Wet	
B1	Yellow	4	4	4-5	4-5	4
B2	Red	4	4-5	4-5	4-5	6-7
B3	Orange	4-5	5	4-5	4-5	5
B4	Brown	5	4-5	4-5	4-5	2

Table 3: Antioxidant Activity of compound **1** and dyes **B1-B4** assayed by FRAP method.

Entry	Compound	FRAP (μM), Fe^{2+} (Con.)
1	1	94 ± 1.5
2	B1	118 ± 1.1
3	B2	135 ± 2.0
4	B3	124 ± 0.5
5	B4	155 ± 2.5

4. Conclusions

This paper suggests a convenient and useful method for the synthesis of four azo disperse dyes with piperazine bioactive moiety using azo coupling reactions. The structures of prepared dyes were confirmed by ^{1}H NMR, ^{13}C NMR, FTIR and UV-Vis spectroscopies. The absorption spectra of the synthesized dyes in solvents with different polarity were evaluated. The solvatochromic behavior of prepared dyes revealed that there is a large bathochromic shift upon increasing the solvent polarity. In addition, the prepared disperse dyes were investigated for their dyeing characteristic on polyester fibers and showed moderate to excellent light, washing and rubbing fastness. Finally, the results of antioxidant properties indicated that these dyes were effectively show antioxidant capacity as confirmed by the ferric reducing antioxidant power method.

Acknowledgements

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