Synthesis, Spectroscopic Studies and Technical Evaluation of Novel Disazo Disperse Dyes Derived from 3-(2-hydroxyphenyl)-2-pyrazolin-5-ones for Dyeing Polyester Fabrics

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Abstract In one of our projects, on disperse dye, we were interested in the synthesis, tautomeric structures and evaluation of pyrazolin-5-one azodyes with better dyeing properties. In this regard novel bisazo-pyrazolin-5-one dyes 3a-f were synthesized via coupling of the select diazotized p-nitroaniline with 4-arylhydrazono-3-(2’-hydroxyphenyl)-2-pyrazolin-5-ones 2a-f. On further treatment of these products 3a-f with acetic anhydride in the presence of p-toluenesulfonic acid furnished the corresponding diacetylpyrazolone derivatives 4a-f. A combination of spectral evidence and acetylation reaction provided a coherent picture of compounds under scrutiny is best described as the azo-hydrazone tautomeric form (A24) as the Z,E-configuration. Finally, two series of the synthesized dyes 3a-f and 4a-f were applied as disperse dyes for dyeing polyester fabrics and their fastness properties were evaluated. Also, the position of color in CIELAB coordinates (L*, a*, b*, H*, C* and K/S) estimated and discussed.

Keywords Bisazo dye, Pyrazolin-5-ones, Azo-hydrazone Tautomerism, Acetylation, Disperse Dyes, Polyester Fabrics, Dyeing Characteristics

1. Introduction

Azo dyes are a versatile class of coloured organic dyes and receive a large amount of attention in the literature, as a consequence of their exciting biological properties and their applications in various fields, such as textiles, papers, leathers, additives, cosmetics and organic synthesis[1–5]. A typical example in this respect are those containing azopyrazolone moieties that deserve special attention due to their applications as disperses dyes[6-8], as well as their widely important applications in biological activities and in analytical chemistry[9-12]. These compounds are potentially tautomeric entities and much attempts[13-18] have subjected to their molecular structure. It has now been conclusively established that they almost exist as the hydrazone tautomer with intramolecular hydrogen bonding between the CO and NH groups.

On the other hand, among the known azo dyes, azophenolic compounds have an elegance role in dyes chemistry due to their auxochromic nature. These properties have made them useful in dyeing of almost all kind of fabrics, whether natural or synthetic. Also, the intriguing properties of these class of compounds in relation to its tautomeric behavior can be ascribed to the existence of azophenol or hydrazoquinone tautomer[19-25]. Therefore, we expect that, the obtained bisazo dyes of two of the above-mentioned azo dye together in a single entity possess interesting tautomeric structure and dyeing characteristics, mainly strong ability of these dyes on fabrics. We have previously reported the synthesis and elucidation of the tautomeric structures of mono and bis-azodyes containing 4-arylhydrazono-3-(2’-hydroxyphenyl)-2-pyrazolin-5-ones, which were able to dye polyester[26-28]. Based on these result, it was thought judicious to study the synthesis of novel bisazo compounds 3a-f and 4a-f in order to obtain information for an inclusive study of their tautomeric structure and exploring their application in dyeing polyester fabrics.

2. Experimental Section

2.1. Materials and Instrumentation

All reagents and solvents were used as obtained from the supplier or recrystallized/redistilled as necessary.
2.2.1.4-(2-Phenyldrazonylo)-3-(5’-(4-nitrophenylazo)-2’-hydroxyphenyl)-2-pyrazolin-5-one (3a)

Yield: 70%; UV-Vis (λ<sub>max</sub> in dioxane): 265, 362, 400, 440 nm. IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3400 (OH), 3315, 3200 (NH), 3022, 2986 (CH, Ar.), 1658 (C=O, Pyrazolinone), 1612 (>C=N), 1545 (C=C-NH-N=), 1520, 1360, 1330 (NO<sub>2</sub> and C<sub> arom</sub>-N), 1464 (N=N), 1250 (C=O), 1HNMR (300 MHz, DMSO-d<sub>6</sub>, δ/ppm): 7.10-8.29 (m, 12H, Ar-H), 10.11 (s, 1H, OH, D<sub>2</sub>O exch.), 12.22 (s, 1H, NH (pyrazoline), D<sub>2</sub>O exch.), 14.13 (s, H, NH<sub>hydrogen</sub>, D<sub>2</sub>O exch.). Anal. Calcd. for C<sub>32</sub>H<sub>22</sub>N<sub>7</sub>O<sub>4</sub>: C, 59.71; H, 3.62; N, 22.91.

2.2.1.2.4-[(4-Methylphenyl)hydrazonylo]-3-(5’-(4-nitrophenylazo)-2’-hydroxyphenyl)-2-pyrazolin-5-one (3b)

Yield: 79%; UV-Vis (λ<sub>max</sub> in dioxane): 265, 362, 400, 440 nm. IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3412 (OH), 3250, 3190 (NH), 3041, 1364, 1322 (NO<sub>2</sub> and Carboxyl-N), 1469 (-N=N-), 1255 (C–O). 1HNMR (300 MHz, DMSO-d<sub>6</sub>, δ/ppm): 2.49 (s, 3H, CH<sub>3</sub>), 7.08-8.28 (m, 11H, Ar-H), 10.22 (s, 1H, OH, D<sub>2</sub>O exch.), 12.20 (s, 1H, NH (pyrazoline), D<sub>2</sub>O exch.), 14.21 (s, H, NH<sub>hydrogen</sub>, D<sub>2</sub>O exch.). Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>7</sub>O<sub>4</sub>: C, 57.69; H, 3.73; N, 21.34. Found: C, 57.52; H, 3.69; N, 21.43.

2.2.1.3.4-[(4-Methoxyphenyl)hydrazonylo]-2’-hydroxyphenyl)-2-pyrazolin-5-one (3c)

Yield: 81%; UV-Vis (λ<sub>max</sub> in dioxane): 276, 362, 412, 446 nm. IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3396 (OH), 3240, 3188 (NH), 3048, 3022 (CH, Ar.), 1658 (C=O, Pyrazolinone), 1619 (>C=N), 1545 (C=C-NH-N=), 1518, 1362, 1340 (NO<sub>2</sub> and C<sub> arom</sub>-N), 1458 (N=N), 1255 (C=O). 1HNMR (300 MHz, DMSO-d<sub>6</sub>, δ/ppm): 3.99 (s, 3H, OCH<sub>3</sub>), 7.19-8.17 (m, 11H, Ar-H), 10.27 (s, 1H, OH, D<sub>2</sub>O exch.), 12.31 (s, 1H, NH (pyrazoline), D<sub>2</sub>O exch.), 14.09 (s, H, NH<sub>hydrogen</sub>, D<sub>2</sub>O exch.). Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>7</sub>O<sub>4</sub>: C, 59.59; H, 3.86; N, 22.11. Found: C, 58.67; H, 3.62; N, 22.91.

2.2.1.4-(4-Chlorophenyl)hydrazonylo)-3-(5’-(4-nitrophenylazo)-2’-hydroxyphenyl)-2-pyrazolin-5-one (3d)

Yield: 68%; UV-Vis (λ<sub>max</sub> in dioxane): 266, 356, 401, 440 nm. IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3436 (OH), 3261, 2193 (NH), 3054 cm<sup>-1</sup>.

2.2.2. Synthesis and Spectroscopic Characterization

2.2.2.1. General Procedure for the Synthesis of

4-arylhydrazono-3-(5’-(4-nitrophenylazo)-2’-hydroxyphenyl)-2-pyrazolin-5-ones 3a-f

A mixture of p-nitroaniline (5 mmol), water (4 ml) and conc. HCl (2 ml) was heated with stirring until a clear solution was obtained. This solution was cooled to 0–5°C and a solution of NaNO<sub>2</sub> (5 mmol, 0.35 g) in 3 ml H<sub>2</sub>O was added dropwise while the temperature was maintained below 5°C. The resulting mixture was stirred for 30 min in an ice bath. Then, it has been added to a well-stirred solution of 4-arylhydrazono-3-(2’-hydroxyphenyl)-2-pyrazolin-5-ones 2a-f (5 mmol) and sodium hydroxide (5 mmol, 0.2 g) in ethanol (20 ml). The reaction mixture was allowed to stir at (0–5°C) for 2 hrs, and then the solid was collected by filtration. The crude products thus obtained, were dried and recrystallized from the appropriate solvent to give the corresponding compounds 3a-f.
(CH, Ar.), 1662 (C=O, Pyrazoline), 1631 (>C=N), 1548 (C=C-NH=N=), 1527, 1369, 1341 (NO2 and C arom-N), 1466 (-N=N-), 1276 (C=O), 770 (C=C). 1H NMR (300 MHz, DMSO-d6, δ/ppm): 7.22-8.29 (m, 11H, Ar-H), 14.22 (s, H, NH (hydrazone), D2O exch.). Anal. Calcd. for C25H18BrN7O6 (591.05): C, 50.69; H, 3.06; N, 16.68. Found: C, 50.88; H, 3.25; N, 16.68.

2.2.2.4.4-(Methylphenyl)hydrazono)-3-(5'- (4-nitropheny lazo)-2'-acetox yphenyl)-1-acetyl-2-pyrazolin-5-one (4b)

Yield: 79%; IR (KBr, νmax/cm–1): 3212 (NH), 3054 (CH, Ar.), 2931 (CH, Aliph.), 1732 (C=O, ester), 1690 (C=O, N-acetyl), 1662 (C=O, Pyrazoline), 1623 (>C=N), 1539 (C=C-NH=N=), 1527, 1373, 1349 (NO2 and C arom-N), 1426 (-N=N-), 1268 (C=O). 1H NMR (300 MHz, DMSO-d6, δ/ppm): 2.48 (s, 3H, CH3), 3.02 (s, 3H, NCOCH3), 3.37 (s, 3H, OCOCH3), 7.24-8.11 (m, 11H, Ar-H), 14.23 (s, H, NH (hydrazone), D2O exch.). Anal. Calcd. for C26H21N7O7 (547.15): C, 57.46; H, 3.89; N, 18.04. Found: C, 57.34; H, 4.08; N, 18.20.

2.2.2.4.4-(Chlorophenyl)hydrazono)-3-(5'- (4-nitropheny lazo)-2'-acetox yphenyl)-1-acetyl-2-pyrazolin-5-one (4d)

Yield: 84%; IR (KBr, νmax/cm–1): 3253 (NH), 3046, 3011 (CH, Ar.), 1730 (C=O, ester), 1679 (C=O, N-acetyl), 1648 (C=O, Pyrazoline), 1610 (>C=N), 1549 (C=C-NH=N=), 1526, 1373, 1342 (NO2 and C arom-N), 1428 (-N=N-), 1259 (C=O), 771 (C=C). 1H NMR (300 MHz, DMSO-d6, δ/ppm): 3.02 (s, 3H, NCOCH3), 3.61 (s, 3H, OCOCH3), 7.11-8.40 (m, 11H, Ar-H), 14.22 (s, H, NH (hydrazone), D2O exch.). Anal. Calcd. for C26H18ClN7O6 (543.15): C, 57.46; H, 3.89; N, 18.04. Found: C, 57.34; H, 4.08; N, 17.77.

2.2.2.5.4-(Bromo mophenyl)hydrazono)-3-(5'- (4-nitrophenylazo)-2'-acetox yphenyl)-1-acetyl-2-pyrazolin-5-one (4e)

Yield: 69%; IR (KBr, νmax/cm–1): 3233 (NH), 3034, 3002 (CH, Ar.), 1741 (C=O, ester), 1684 (C=O, N-acetyl), 1659 (C=O, Pyrazoline), 1617 (>C=N), 1549 (C=C-NH-N=), 1514, 1361, 1336 (NO2 and C arom-N), 1411 (-N=N-), 1266 (C=O), 578 (C=C). 1H NMR (300 MHz, DMSO-d6, δ/ppm): 3.03 (s, 3H, NCOCH3), 3.38 (s, 3H, OCOCH3), 7.13-8.37 (m, 11H, Ar-H), 14.12 (s, H, NH (hydrazone), D2O exch.). Anal. Calcd. for C26H18BrN7O6 (591.05): C, 50.69; H, 3.30; N, 16.55. Found: C, 50.88; H, 3.25; N, 16.68.
2.2.2.6.4-(4-Nitrophenyl)hydrazono)-3-(5`-(4-nitrophenylazo)-2`-acetox yphenyl)-1-acetyl-2-pyrazolin-5-one (4f)

Yield: 60%; IR (KBr, νmax/cm–1): 3212 (NH), 3091, 3060 (CH, Ar.), 1734 (C=O, ester), 1687 (C=O, N-acetyl), 1662 (C=O, Pyrazolinone), 1519, 1374, 1339 (NO2 and Caro m.-N), 1551 (C=C-NH-N=), 1423 (-N=N-), 1272 (C–O). 1HNM R (300 M Hz, DM SO-d6, δ/ppm): 3.22 (s, 3H, NCOCH3), 3.50 (s, 3H, OCOCH3), 7.13 -8.30 (m, 11H, Ar-H), 14.31 (s, H, NH(hydrazone), D2O exc h.). Anal. Calcd. for C25H18N8O8 (558.12): C, 53.77; H, 3.25; N, 20.06. Found: C, 53.97; H, 3.14; N, 20.19.

2.3. Dyeing and Fastness Determinations

2.3.1. Preparation of Dye Dispersion

The required amount of the dye (2% shade) was dissolved in 1 ml acetone and then added dropwise with stirring to a solution of Setamol WS (sodium salt of a condensation product of naphthalene sulfonic acid and formaldehyde) as anionic dispersing agent of BASF. The dye was precipitated in a fine dispersion ready for use in dyeing after evaporation of the solvent by warming.

2.3.2. Dyeing of Polyester Fabrics

The dye bath (1:20, good to dye liquor ratio) in a sealed stainless steel dye pots of 250 ml capacity in “Galvanin-Marino VI-Italy” dyeing machine. Additional dispersing agent (0.5 -1.0 g/l) was added and the pH of the bath adjusted to 5.5 using glacial acetic acid. Dyeing carried out by raising the dye bath temperature from 20 to 130 ºC at a rate of 3 ºC/min and holding at this temperature for 60 min before rapidly cooling to 50ºC at 9.9 ºC/min. The dyed fabrics were then rinsed with cold water, reduction -cleared using sodium hydroxide (2 g/l) and sodium hydrosulphite (1 g/l) and soaped with 2% nonionic detergent and ammonia (pH 8.5) at 50 ºC for 30 min to improve washing fastness.

2.3.3. Color Fastness Tests

The color fastness of dyeing was evaluated using the standard method[31] and given in Table 1. The fastness to light, sublimation and perspiration was assessed in accordance with AATCC-15 (1985). The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-88 (1988) and the wash fastness test in accordance with IS: 765-1979.

2.3.4. Color Assessment

The colorimetric parameters (Table 2) of the dyed polyester fabrics were determined on a reflectance spectrophotometer (GretagMacbeth CE 7000a), equipped with a D65/108 source and barium sulfate as standard blank, UV excluded ,specular component included and three repeated measurements average settings.

3. Results and Discussions

3.1. Synthesis and Tautomeric Structure

The basic synthetic route employed for the construction of the target compounds 4a-f is outlined in Scheme 1. The 4-arylhydrazono-3-(2`-hydroxyphenyl)-2-pyrazolin-5-ones 2a-f required for the construction of the target molecules were synthesized by reaction of 2,3,4-chromantrione-3-aryl hydrazones 1a-f with hydrazine hydrate in boiling ethanol as we have recently reported[27]. Coupling of compounds 2a-f in an alkaline solution at 0 -5 ºC with diazotized p-nitroaniline afforded the corresponding bis-arylazo derivatives 3a-f. Treatment of these products, 3a-f, with acetic anhydride in the presence of p-toluenesulfonic acid gave the corresponding diacetyl derivatives 4a-f (Scheme 1).

It is noteworthy to point out that several tautomeric structures may be postulated for bisazo dyes 3a-f. The following are theoretically possible A1–A24 owing to tautomeric displacement (Fig. 1). It is possible to disqualify the most of these structures by examining the spectral data and chemical properties of the compounds actually obtained.

![Scheme 1. Synthesis of the studied compounds 3a-f and 4a-f](image-url)
In an attempt to shed light on the actual tautomeric structure(s) of these compounds 3a-f, we studied their $^1$H NMR spectra. The latter spectra revealed that absence of a proton at C-4 signal at about 6.4 ppm[32] excludes the possibility of the CH-azo structures A$_{1-6}$. The fact that the coupling products 3a-f showed a set of three deuterium exchangeable protons confirming the presence of three different (N-H) groups and/or (O-H) groups (see the experimental part). On the basis of this fact, it is reasonable to rule out the possibility of structures A$_{7-12}$ since these structures would not possess this property.

Moreover, the deconvolution of the electronic absorption spectral data of that compounds 3a-f revealed that all investigated dyes showed in each case four absorption bands in the regions 265-278, 358-363, 400-424 and 430-450 nm. The first three absorption pattern were observed and these values are practically very close to those reported for the azo-hydrazone tautomeric structure (A$_{24}$) and this evidence is in agreement with those values for 4-arylhydrazono-3-(5-(4-nitrophenylazo)-2'-hydroxyphenyl)-1-phenyl-2-pyrazolin-5-ones[28].

Corroborative evidence that compounds 3a-f exist in the tautomeric form (A$_{24}$) comes from the infrared spectra since the band at 1666-1658 cm$^{-1}$ which is assigned to C=O stretching vibration[32] eliminates the tautomeric structures with no carbonyl group (A$_{1,7,9,17,18,23}$) from consideration. In addition, the structures (A$_{2,3,8,13,14,15}$) were discarded on the basis of this compounds exhibit absorption bands between 3500-3396 cm$^{-1}$ region are attributed to the hydroxyl OH group[26-28]. Further evidence that this compounds gave a deep color with ferric chloride that prove the existence of enolic hydroxyl group[35]. Also, the weak bands assignable to the stretching vibration of azo linkages in compounds 3a-f can be observed at the frequency range of 1474-1458 cm$^{-1}$ as reported in the correlation data for N=N bonds[36]. In addition, the absorption maxima at 3200-3188 and 3315-3200 cm$^{-1}$ which were assigned to NH (hydrazone) and NH (pyrazoline) stretching frequencies respectively[26-28]. The NH frequency assigned to the hydrazone NH group is involved in intramolecular hydrogen bonding (tautomer A$_{24}$[27]. The prominent band occurs around 1550 cm$^{-1}$, on the basis of previous results[37], reasonably be ascribed to the benzene ring C=C skeletal vibration associated with the -NH-N= linkage. In the region

![Figure 1. Possible tautomeric structures of compounds under scrutiny 3a-f](image-url)
1634-1612 cm\(^{-1}\), the hydrazone \(\nu_{C=N}\) stretching vibration is also expected\[38, 39\]. The pyrazolinones investigated possess the hydrazone moiety; therefore, the stretching vibration of the \(C_{arom}-N\) linkage show band around 1350 cm\(^{-1}\) in their spectra\[40\]. These results were compatible with a conclusion of such compounds 4a-f exist as the structure (A\(24\)).

This rationalization is substantiated by that we have previously reported for structurally related compounds [26-28] and also this is rather confirmed from other investigations that were carried out to establish the tautomeric structures of arylazopyrazolone and arylazophenol using a variety of spectroscopic techniques. The spectral data generally led to the conclusion that the tautomeric equilibrium of the arylazopyrazolone dyes is in favor of hydrazone form[7] and the tautomeric equilibrium of arylazophenol dyes is in favour of azo form\[19-25\]. These suggest that these dyes are predominantly in aza-hydrazone form (A\(24\)).

Next to, gain further insight into the structure of tautomerism of the aza-hydrazone form (A\(24\)), we carried out the acetylation reaction of 3a-f. Thus, treatment of 3a-f with acetic anhydride in the presence of p-toluenesulfonic acid afforded the corresponding O- and N-diacetyl derivatives (compounds 4a-f, scheme 1). \(^1\)H NMR spectra of 4a-f emphasis that one deuterium exchangeable proton confirming the presence of hydrazone NH proton, while signal characteristic for OH (phenolic) and NH (pyrazolone) protons are absent (see the experimental part). This is coincident with the outputs of reading their IR spectra revealed three carbonyl absorption bands in regions 1741-1718, 1690-1679 and 1662-1648 cm\(^{-1}\) characteristic for O-acetyl, N-acetyl and pyrazolone carbonyl groups, respectively. The conspicuous absence of absorption bands characteristic for OH (phenolic) and NH (pyrazolone) confirms the assumption for O- and N-acetylation reaction. Further evidence that diacetylation occurred was obtained by elemental analysis. Hence, these results arose the conclusion that compounds 3a-f exist in the tautomeric form (A\(24\)).

Additionally, it is noteworthy to cast some light on the configuration of the double bonds of C=N (hydrazone pyrazolone) and N=N(phenophenol) for the most stable form (A\(24\)) can lead to four possibilities: ZE, ZZ, EE, EZ isomers (Fig. 2). Here, the effect of intramolecular hydrogen bonding and steric factor can heavily tilt the equilibrium toward one of the isomers[41]. Thus, the last two isomers can be rationalized rejection on the basis of steric factor. In agreement of this conclusion, the Z-configuration of hydrazone are expected to be stabilized by intramolecular hydrogen bonding between the C=O and hydrazo NH group. This also based on analog of the our recently reported structure of 4-arylhydrazono-3-(2'-hydroxyphenyl)-2-pyrazolin-5-ones, whose Z-isomer has been confirmed by spectroscopic data and supported by theoretical calculation\[26-28\]. On the other hand, the preferential formation of trans azophenol supports from the identity of the UV characteristics of them with those of trans-azobenzene (\(\lambda_{max}=445\))[42]. This trans configuration can be evident from the diagnostic bands assignable to the stretching-vibration mode of N=N at 1474-1458 cm\(^{-1}\)[43]. The absence of tangible band associated with the bending mode at 927 cm\(^{-1}\) has also ruled out the existence of compounds in mixed conformers of cis and trans[43]. It is therefore realistic to conclude that such compounds 3a-f prefer to stay exclusively in the aza-hydrazone structure (A\(24\)) as the Z,E-configuration.

### 3.2. Dyeing and Fastness Properties

The development of disperse dyes “Dyes insoluble in water and applied from aqueous dispersion rather than from solution” was a revolutionary solution to the problem of coloration of synthetic fibers. The dyes were essentially insoluble in water and were prepared for application by being ground, in the presence of dispersing agents, to microscopically fine particles of the order of a few microns and, then, by pan drying the resultant suspension. The resulting readily dispersible solid could then dye the more hydrophobic acetate fiber by partitioning into the fiber from low dye bath concentrations. The synthesized disperse dyes under investigation 3a-f, 4a-f were applied to polyester fabric at 2% shade by high-temperature pressure technique (130°C). The dyes on polyester fabrics were evaluated in terms of their fastness properties as shown in Table 1.

![Figure 2](image-url)  
**Figure 2.** Possibilities configuration for the compounds 3a-f as they exist in the tautomeric form (A\(24\)).
3.2.1. Fastness to Washing

The dyed polyester fabrics have good fastness to washing according to the international Geometric Grey scale[44] and this may be attributed to inadequate diffusion of dye molecule into the fabrics.

3.2.2. Fastness to Perspiration: (Acid and Alkaline)

The majority of these dyes were found to have good perspiration fastness 3–4. Also, the acetylation of hydroxyl group reduced the fastness to perspiration properties.

3.2.3. Fastness to Rubbing

The test is designed to determine the amount of color transferred from the surface of colored fabrics to another surface by rubbing. Most of the dyes have a moderate (3) to good (4) rubbing fastness and this may be attributed to inadequate diffusion of dye molecule into the fabrics.

3.2.4. Fastness to Sublimation

Sublimation fastness properties of synthesized dyes expressed as color staining on the undyed polyester piece ranged from good to very good according to the international Geometric Grey Scale[44]. In most cases, the best sublimation fastness was obtained by unacetylated dyes.

3.2.5. Fastness to Light

It is significantly depended on nature of the substituents which change the electron density around hydrazo group. The high fastness to light may be attributed to electron accepting groups. This agrees with the notion that the azo compounds appended with electron-withdrawing substituents on the diazo components are less prone to photofading[45]. Generally, the prepared dyes showed satisfactory fastness to light ranging 6–7 according to the international Geometric Grey Scale[44].

3.3. Color Assessment

The color parameters (Table 2) of the dyed polyester fabrics were measured using a spectrophotometer (GretaMacbeth Color Eye 7000A, USA) under illuminant D65, with a 10° standard observer. The assessment of color-dyed fabrics was made in terms of tristimulus colorimetry. The following CIELAB coordinates are color-dyed fabrics was made in terms of tristimulus colorimetry. The following CIELAB coordinates are

$$K/S = (1-R)^2 / 2R,$$

where K is the coefficient of absorption; S is the coefficient of scattering; R is the reflectance value of the fabric at peak wavelength. The parent dyestuff in each group is taken as the standard in the color difference calculation ($\Delta L^*$, $\Delta C^*$, and $\Delta H^*$). The results were obtained using CIELAB techniques, and are given in Table 2, where $\Delta L^*$ is the lightness difference, $\Delta C^*$ is the chroma difference, and $\Delta H^*$ is the hue difference. A negative sign of $\Delta L^*$ indicates that the dyed fiber becomes darker than the standard, whereas a positive sign indicates that the dyed fiber becomes lighter than the standard. A negative sign of $\Delta C^*$ indicates that the dyed fiber becomes duller than the standard, whereas a positive sign indicates that the dyed fiber becomes brighter than the standard. A negative sign of $\Delta H^*$ indicates that the color shifted to a red color, while a positive sign indicates that the color shifted to yellowish. The results are shown in Table 2 tend to give the following conclusions:

i. K/S values in the dyes under investigation 3a-f, 4a-f vary from 36.9 to 40.2, which all members of this groups increases strength of the K/S value of the polyester fabric compared with that of the parent 3a. Dyes 4a-f which contain the acetate moiety are characterized by higher K/S values compared with their analogues 3a-f, indicating that the introduction of acetate moiety in dyes 4a-f increases the color strength on polyester fabric.
ii. The color hues of the dyes under investigation on polyester fabric are shifted to the yellowish direction on the yellow-blue axis according to the positive values of b*.

iii. The color hue of the most of the dyes on polyester fabric is shifted to the greenish direction on the red-green axis as indicated from the negative value of a*.

iv. In general, dyeing with the acetylated dyes 4a-f were lighter (as shown by the higher L* values) and duller (as shown by the lower C* values) than the corresponding unacetylated dyes 3a-f.

4. Conclusions

This article describes the synthesis of the hitherto unreported two series of novel bisazo disperse dyes 3a-f and 4a-f having different substituted groups. The influence of the dye structures on the spectroscopic and dyeing properties was investigated. The spectroscopic data of the compounds prepared 3a-f and their acetylation reaction have show the contention that such compounds exist to exist exclusively in the azo-hydrazo structure (A3z) as the E-configuration. Finally, the prepared dyestuffs were dyed on polyester fabrics and subsequently their dyeing properties, light, washing, perspiration, rubbing and sublimation fastnesses and color coordinates were determined. The outstanding characteristics of these properties were proved to be good. Finally, it is worth referring from these investigations, it may be concluded that dyestuffs 3a-f and 4a-f are reasonable bis azo disperse that may be endowed with important dyeing properties on polyester fabrics.

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