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# Quantum chemical studies and dyeing performance of some novel benzoquinoline based heterocyclic monoazo dyes on polyester fiber

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# ABSTRACT

Some novel benzoquinoline based heterocyclic monoazo dyes have been derived by the diazotization of 1H-benzo[g]pyrazolo[3,4-b]quinoline-3-ylamine with various phenyl pyrazolone as coupling components. All the heterocyclic monoazo dyes have been characterized by elemental analyses and various spectral data (FT-IR, UV–Vis, <sup>1</sup>H NMR and <sup>13</sup>C NMR), and their 3D model structures were predicted through B3LYP/6-31G(d,p) method. The dyeing performance on polyester fibers inferred that all the dyes gave moderate to excellent fastness properties on fiber. In addition, colorimetric studies of synthesized dyes have also been discussed.

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PIĞMĔNTS

# 1. Introduction

It has been recognized for several years that azo compounds are the most widely used compounds in various fields such as the dyeing of textile fiber, the coloring of different materials, colored plastic and polymer, biological-medical studies and advanced applications in organic synthesis. A number of azo dyes have been prepared from amino heterocycles by using selected quinolines, benzoquinoline, thiazole and quinazoline derivatives as coupling components [1–20]. Quinolines and benzoquinolines combined with five or six member rings in linear approach is known to possess good pharmacological activities and are also used as intermediates in dyestuff industry [21–24]. Therefore, keeping the above facts in view, we have concentrated our research work on developing quinoline/benzoquinoline containing heterocyclic azo compounds. Due to the significant dyeing applications of quinoline, benzoquinoline and quinazoline containing heterocyclic azo compounds, it appeared expedient to synthesize a series of heterocyclic monoazo compounds derived from diazotization of 1H-benzo[g]pyrazolo[3,4-b]quinoline-3-ylamine and coupled with

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phenyl pyrazolone based coupling components that give good dyeing properties.

The present paper deals with the facile and convenient synthesis of novel benzoquinolines based heterocyclic monoazo dyes and study of their dyeing properties and fastness properties are reported. The spectral properties and colorimetric data (L\*, a\*, b\*, C\*, H\*, K/S) have also been discussed. Further, we have performed DFT calculations at B3LYP/6-31G (d,p) method to get the theoretical optimized structural parameters, HOMO and LUMO of the dyes.

# 2. Experimental

#### 2.1. Materials and methods

All chemicals were of analytical grade and used directly. All melting points were determined in PMP-DM scientific melting point apparatus and are uncorrected. The purity of all dyes were determined by thin-layer chromatography (TLC) [25] using silica gel-G coated Al-plates (0.5 mm thickness, Merck). Infrared spectra were recorded on a Shimadzu FT-IR 8400S model using KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired on a Varian 400 MHz model spectrophotometer using DMSO-*d*<sub>6</sub> as solvent and TMS as internal reference (chemical shifts in  $\delta$ , ppm). Elemental analysis of C, H and



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N were carried on Carlo Erba 1108 instrument. The light fastness was assessed in accordance with BS: 1006–1978 (Standard test method, 1978, 1994). The rubbing fastness test was carried out with a Crock meter (Atlas) in accordance with AATCC-1961 (AATCC test method, 1961) and the wash fastness test in accordance with IS: 765–1979 (Indian standard ISO, 1979). Colorimetric data (L\*, a\*, b\*, C\*, H\*, K/S) were recorded on Reflectance Spectrophotometer Gretag Macbeth CE: 7000.

#### 2.2. Synthesis of N-naphthalen-2-yl-acetamide (1)

A mixture of 1-naphthylamine (1.0 mmol) and catalytic amount of triethylamine (1.2 mmol) was stirred in acetone at room temperature for an hour. Thereafter, acetyl chloride (1.2 mmol) was added dropwise during a period of an hour. During addition of acetyl chloride white precipitate was formed. The mixture was further stirred for another 1 h. The completion of reaction was monitored by TLC. The solution was then poured directly onto crushed ice. The resulting white precipitate was filtered, washed with water, and dried in air. The product was recrystallized from ethanol to give the title compound **1** as white needles. Yield 75%, mp: 159–160 °C; IR (KBr disk, cm<sup>-1</sup>): 3270 (NH), 1656 (CO), 1548, 1398 cm<sup>-1</sup> (C=N, C–N); <sup>1</sup>H NMR (DMSO-  $d_{6}$ ,  $\delta$  ppm): 2.17(3H, s, COCH<sub>3</sub>), 7.46–8.42 (7H, m Ar–H).

#### 2.3. Synthesis of 2-Chlorobenzo[h]quinoline-3-carbaldehyde (2)

To a solution of *N*-naphthalen-2-yl-acetamide (5.4 mmol) in dry DMF (14 mmol) was added POCl<sub>3</sub> (102 mmol) and the mixture stirred at 75 °C for 6 h. The mixture was poured onto crushed ice and the resulting solid filtered, washed with water and dried in an oven. The sample was recrystallized from ethyl acetate—petroleum ether at 60–80 °C to give the title compound as yellow needles. Yield 72%, mp: 210–212 °C; IR (KBr disk, cm<sup>-1</sup>): 1685 (CO), 1579, 1365 cm<sup>-1</sup> (C=N, C–N); <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.47–8.48 (7H, m, Ar–H), 10.58 (1H, s, CHO).

# 2.4. Synthesis of 2-chloro-benzo[g]quinoline-3-carbaldehyde oxime (3)

To a solution of 2-chlorobenzo[g]quinoline-3-carbaldehyde (1.0 mmol) in ethanol, hydroxyl amine hydrochloride (1.2 mmol) and sodium acetate (1.2 mmol) was added at room temperature and the mixture was stirred for an hour. While stirring, white precipitate was formed. The completion of the reaction was monitored by TLC. The reaction mixture was poured onto ice cold water, filtered, dried and used for further reaction. Yield 80%, mp 172–176 °C, IR(KBr disk, cm<sup>-1</sup>) 3335 (O–H), 1548, 1398 (C=N, C–N), 758 cm<sup>-1</sup> (C–Cl). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 2.55(1H, s, OH), 7.48–8.54 (7H, m Ar–H).

# 2.5. Synthesis of 2-chloro-benzo[g]quinoline-3-carbonitrile (4)

2-Chloro-benzo[g]quinoline-3-carbaldehyde oxime (1.0 mmol) was stirred in benzene. Then SOCl<sub>2</sub> (3.0 mmol) was added dropwise at room temperature. After the addition of SOCl<sub>2</sub>, the reaction mixture was refluxed for an hour. The completion of reaction was monitored by TLC. The solvent was removed by vacuum distillation. A brown yellow needle crystal formed which was used for further reaction. Yield 82%, mp 184–189 °C, IR(KBr disk, cm<sup>-1</sup>) 2221 (C–N), 1548, 1398 (C=N, C–N), 754 cm<sup>-1</sup> (C–Cl). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 7.48–8.41 (7H, m Ar–H).

#### 2.6. Synthesis of 1H-benzo[g]pyrazolo[3,4-b]quinoline-3-ylamine(5)

2-chloro-benzo[g]quinoline-3-carbonitrile (1.0 mmol) on reaction with hydrazine hydrate (1.2 mmol) in ethanol gave 1H-benzo [g]pyrazolo[3,4-b]quinoline-3-ylamine. The reaction mixture was reflux for 24 h. The reaction mixture was poured onto ice cold water. The yellow color precipitate was filtered and dried. Yield 78%, mp 286–290 °C, IR(KBr disk, cm<sup>-1</sup>) 3200–3289 (–NH), 1548, 1398 (C=N, C–N), 758 cm<sup>-1</sup> (C–Cl). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  ppm: 7.48–8.79 (7H, m Ar–H), 7.85 (2H, s, NH<sub>2</sub>), 12.56 (1H, s, NH).

# 2.7. Diazotization and coupling (6)

Concentrated HCl was added to a well stirred suspension of 1Hbenzo[g]pyrazolo[3,4-b]quinoline-3-ylamine (0.0048 mol) in water and the mixture was heated up to 70 °C and maintained at that temperature till the clear solution is obtained. After cooling the solution to 0-5 °C in an ice-bath, an aqueous solution of sodium nitrite 0.66 g in water was added dropwise over a period of 30 min with continuous stirring. The reaction was stirred at a temperature below 5 °C for about an hour. The excess of nitrous acid is tested using starch iodide paper and was removed by adding required amount of sulfamic acid solution (10%). The clear diazonium salt solution thus obtained was used immediately in the coupling reaction.

Coupling component (**6a-e**) was dissolved in sodium hydroxide solution. The solution was cooled to 0-5 °C in an ice-bath. To this well stirred solution, the above diazonium solution was added dropwise keeping temperature below 5 °C. The reaction mass was further stirred for 2 h at 0-5 °C maintaining the pH 8.0 by adding required amount of 10% sodium carbonate solution. The reaction mass was then heated up to 60 °C and diluted with water. The dye was filtered off, washed with hot water until the washings were neutral, dried, and powdered. The product was purified by dissolving it in DMF and pouring in water. The similar coupling procedure and conditions were followed for all the dyes.

#### 2.7.1. Dye **6a** (p-toluene phenyl methyl pyrazolone)

Yield: 78%; **Mp** gt; 300 °C; **IR (KBr)** v cm<sup>-1</sup>: 3250 (NH), 1552 (N=N), 1330 & 1564 (C–N & C=N), 2900–3100 (–CH stretching), 1478 (CH bending); <sup>1</sup>H NMR (400 MHz, DMSO-*d*6)  $\delta$  ppm: 2.10 (s, 3H, –CH<sub>3</sub> of pyraozlone ring; 2.42 (s, 3H, CH<sub>3</sub> of benzene ring), 7.68–9.07 (m, 11H, Ar–H), 12.08 (s, 1H, –NH, benzoquinoline ring); <sup>13</sup>C NMR (400 MHz, DMSO-*d*6)  $\delta$  ppm: 13.42 (C-32, CH<sub>3</sub> group of pyrazolone ring), 21.15 (C-31,CH<sub>3</sub> group of benzene ring), 118–152.12 (21C, Ar–C), 152.61 (C-17, of pyrazole ring carbon atoms), 158, 160 (C-28, 30 of pyrazolone ring carbon atoms); C<sub>25</sub>H<sub>19</sub>N<sub>7</sub>O (433.67): Calc. C, 69.27; H, 4.42; N, 22.62, found: C, 69.24; H, 4.38; N, 22.57.

# 2.7.2. Dye **6b** (2,5-dichloro phenyl methyl pyrazolone)

Yield: 78%; **Mp** gt; 300 °C; **IR (KBr)** ν cm<sup>-1</sup>: 3252 (NH), 1548 (N=N), 1333 & 1558 (C–N & C=N), 2982–3100 (CH stretching), 1475 (CH bending), 752–754 (Ar–Cl); <sup>1</sup>H NMR (400 MHz, DMSOd6) δ ppm: 2.04 (s, 3H, CH<sub>3</sub> of pyrazolone ring); 7.44–8.97 (m, 10H, Ar–H), 12.10 (s, 1H, –NH, benzoquinoline ring); <sup>13</sup>C NMR (400 MHz, DMSO-d6) δ ppm: 13.46 (C-31, CH<sub>3</sub> group of pyrazolone ring), 111.24–150.12 (19C, Ar–C), 152.58 (C-17, of pyrazolone ring carbon atoms), 158.14, 160.12, (C-30, C-28, of pyrazolone ring carbon atoms; C<sub>24</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>7</sub>O (487.07): Calc. C, 59.03; H, 3.10; N, 20.08; found: C, 59.00; H, 3.12; N, 20.12.

#### *2.7.3. Dye* **6c** (*m*-chloro phenyl methyl pyrazolone)

Yield: 82%; **Mp** gt; 300 °C; **IR (KBr)** v cm<sup>-1</sup>: 3242 (NH), 1556 (N=N), 1328 & 1545 (C−N & C=N), 2900-3100 (CH stretching),

1478 (CH<sub>3</sub> bending), 758 (Ar–Cl); <sup>1</sup>H NMR (400 MHz, DMSO-d6) δ **ppm**: 2.00 (s, 3H, CH<sub>3</sub> of pyraozlone ring:, 12.10 (s, 1H, NH, benzoquinoline ring), 7.29–8.95 (m, 11H, Ar–H); <sup>13</sup>C NMR (400 MHz, DMSO-d6) δ **ppm**: 13.40 (C-31, –CH<sub>3</sub> group of pyrazolone ring), 112.24–150.12 (22C, Ar–C), 152.58 (C-17, of pyrazole ring carbon atoms), 157.14, 162.14, (C-30, C-28 of pyrazolone ring carbon atoms); C<sub>24</sub>H<sub>16</sub>ClN<sub>7</sub>O (453.11): Calc. C, 63.51; H, 3.55; N, 21.60; found: C, 63.55; H, 3.52; N, 21.64.

# 2.7.4. Dye 6d (o-chloro phenyl methyl pyrazolone)

Yield: 76%; **Mp** gt; 300 °C; **IR** (**KBr**) v cm<sup>-1</sup>: 3252 (NH), 1560 (N=N), 1330 & 1548 (C–N & C=N), 2900–3100 (CH stretching), 1490 (CH bending), 760 (Ar–Cl); <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$  ppm: 2.06 (s, 3H, CH<sub>3</sub> of pyraozlone ring;, 7.40-8.95 (m, 11H, Ar–H), 12.02 (s, 1H, NH, benzoquinoline ring); <sup>13</sup>C NMR (400 MHz, DMSO-d6)  $\delta$  ppm:13.38 (C-31, –CH<sub>3</sub> group of pyrazolone ring), 111.24–152.12 (22C, Ar–C), 152.60 (C-17, of pyrazole ring carbon atoms), 156.11, 160.16 (C-30, C-28 of pyrazolone ring carbon atoms); C<sub>24</sub>H<sub>16</sub>ClN<sub>7</sub>O (453.11): Calc. C, 63.51; H, 3.55; N, 21.60; found: C, 63.52; H, 3.52; N, 21.65.

#### 2.7.5. Dye **6e** (3,4-dichloro phenyl methyl pyrazolone)

Yield: 84%; **Mp** gt; 300 °C. **IR** (**KBr**) v cm<sup>-1</sup>: 3242 (NH), 1556 (N=N), 1329 & 1552 (C–N & C=N), 2900–3100 (CH stretching), 1474 (CH bending), 760–774 (Ar–Cl); <sup>1</sup>H NMR (400 MHz, DMSO-*d*6)  $\delta$  ppm: 2.04 (s, 3H, CH<sub>3</sub> of pyraozlone ring:, 7.32-8.97 (m, 10H, Ar–H), 12.04 (s, 1H, NH, benzoquinoline ring); <sup>13</sup>C NMR (400 MHz, DMSO-*d*6)  $\delta$  ppm: 13.32 (C-31, CH<sub>3</sub> group of pyrazolone ring), 110.16–150.10 (20C, Ar–C), 152.42 (C-17, of pyrazole ring carbon atoms), 158.11, 164.76, (C-30, C-28 of pyrazolone ring carbon atoms); C<sub>24</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>7</sub>O (487.07): Calc. C, 59.03; H, 3.10; N, 20.08; found: C, 59.12; H, 3.16; N, 20.12.

#### 2.8. Computational methodology

The Gaussian 09W [26] computer program has been used for all quantum chemical calculations. The quantum-chemical calculations of compound have been performed using Becke's three parameter exchange function (B3) with Lee-Yang-Parr correlation function (LYP), with basis-set 6-31G(d,p). Geometry optimizations of heterocyclic monoazo dyes and their model compounds in gas

phase were carried out at DFT level of theory using B3LYP without any symmetry restrictions. All optimized geometries have been confirmed by frequency analyses at the same level of theory.

# 3. Results and discussion

#### 3.1. Chemistry

Various routes have been developed for functionalization of quinolines/benzoquinolines. Among them, the Vilsmeier approach [27] is found to be the most efficient for achieving useful transformations and heteroannulations. Therefore, we have performed the synthesis of 2-chlorobenzo[h]quinoline-3-carbaldehyde 2 from the reaction of N-naphthalen-2-yl-acetamide 1 with Vilsmeier reagent, and then the transformation of the 2-chloro and 3carbaldehyde groups into different functionalities (Scheme 1). The required *N*-naphthalen-2-yl-acetamide **1** intermediate was obtained in very good yield by the reaction between 1naphthylamine and acetyl chloride in presence of catalytically amount of TEA at room temperature, which was characterized by the disappearance of -NH<sub>2</sub> group and appearance of -NH and -C=0 groups in IR spectrum which showed bands at 3345 cm<sup>-1</sup> and 1710 cm<sup>-1</sup> respectively. The Vilsmeier cyclisation of acetanilide **1** was carried out by adding POCl<sub>3</sub> to the substrate in DMF at 0-5 °C followed by heating to 90 °C to afford 2-chlorobenzo[h] quinoline-3-carbaldehyde 2 in moderate yield. The IR spectrum of compound **2** showed a sharp and strong stretching absorption band in the range of 1680-1700 cm<sup>-1</sup> for the aldehyde group, and absorption at around 2720 and 2830  $\text{cm}^{-1}$  for aldehyde proton. The bands for -C-N and -C=N of benzoquinoline ring was identified at 1342 and 1562 cm<sup>-1</sup> respectively. The carbaldehyde group in quinolines 2 was also transformed into other functionalities to afford new quinolines which are equally important synthons for the synthesis of fused quinoline systems. Compound 2 condensed with hydroxyl amine hydrochloride in presence of sodium acetate at room temperature to give 2-chloro-benzo[g] quinoline-3-carbaldehyde oxime 3, which was confirmed by the appearance of a broad –OH stretching band at 3400–3500 cm<sup>-1</sup> in IR spectrum. Compound 3 on reflux with SOCl<sub>2</sub> gave 2chloro-benzo[g]quinoline-3-carbonitrile 4 in good yield, which was confirmed by the presence of -CN stretching band at



R = Various phenyl pyrazolone derivatives as coupling components

Scheme 1. Schematic diagram for the synthesis of heterocyclic monoazo dyes (Table 2).



Fig. 1. B3LYP/6-31G(d,p) optimized structure of **6a** and **6b** along with their HOMO and LUMO diagrams.

2221 cm<sup>-1</sup>. Compound **4** on further cyclization with hydrazine hvdrate gave 1H-benzo[g]pvrazolo[3.4-b]guinoline-3-vlamine 5 which showed two characteristic band in the region of 3200-3400 cm<sup>-1</sup> confirm the presence of  $-NH_2$  group. Compound 5 on diazotization and followed by coupling with various phenyl pyrazolones yielded benzoquinoline based azo compounds **6a-e** in high yield. The <sup>1</sup>H NMR spectra of **6a-e** showed signal at 2.10 and 2.42 ppm due to -CH<sub>3</sub> group attached to pyraozlone ring and benzene ring respectively. Compounds 6ae showed singlet at 12.08 ppm due to the presence of --NH in benzoquinoline ring and the remaining aromatic protons are resonated at 7.48–9.67 ppm as multiplet. In <sup>13</sup>C NMR spectra, the signals in the range between 13.22 and 13.70 were assigned to -CH<sub>3</sub> group of pyrazolone ring. Whereas the signals in between 18.00 and 21.15 were attributed to the presence of -CH<sub>3</sub> group of benzene ring. The peaks at 160 and 158 ppm were attributed to the carbon atoms of pyrazolone heteroatom ring while peak at 152.61 was attributed to the carbon atom of the pyrazole heteroatom ring. Remaining all aromatic carbons was resonated in the range of 118-152.12. The principle benefit for using benzoquinoline based moiety is high percentage yield and simple workup procedure, which facilitates easy preparation of starting material.

In absence of suitable crystal for X-ray analysis, we performed quantum chemical calculations by applying B3LYP/6-31G (d,p) method to predict the possible molecular structure of the compounds **6a**-e in gas phase. The calculated model structure of the compounds **6a** and **6b** along with their HOMO and LUMO diagrams are shown in Fig. 1 and some physical parameters of the compounds **6a**-e are summarized in Table 1. The results obtained from the DFT calculations inferred that (i) the *m*-chloro substituted compounds **6c** and **6e** are energetically more stable than their corresponding *o*-chloro substituted compounds **6d** and **6b** (Table 1), (ii) except the structure for the *o*-chloro substituted coupling components in compounds **6d** and **6b**, other coupling components are planar in compounds **6a** and **6e**, (iii) all the compounds have almost similar  $\Delta E$  ( $\Delta E = E_{HOMO}-E_{LUMO}$ ) values and (iv) the HOMO and LUMO diagrams (Fig. 1) are lying only on

benzoquinoline ring and azo bond indication for similar energy absorption in all studied dyes.

#### 3.2. Spectral properties of dyes

The visible absorption spectroscopic properties of dyed fabrics were recorded by computer color matching instrument and are presented in Table 2 and Fig. 2. The results summarized in Table 2 inferred that the value of maximum absorbance ( $\lambda_{max}$ ) depends on the nature and position of the coupling component used. The color change observed for each dye is due to the alternation of electrons and the presence of additional substituent.

# 3.3. Dyeing of fibers

Compounds **6a-e** was applied on polyester in 2% shade according to the literature procedure in the dye-bath containing the materials listed in Table 3 [28]. The variation in the hues of the dyed fabric results from the alternation in the coupling components. The remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of these dyes to the fabric.

# 3.4. Exhaustion and fixation study

The percentage dye bath exhaustion and percentage dye bath fixation of the dyed fabric were determined according to the known

Table 1

Quantum chemical parameters of the compounds obtained at  $B3LYP/6\mathchar`-31G(d,p)$  method.

Compounds	Total energy (a.u.)	μ (D)	$E_{HOMO}\left(eV ight)$	$E_{LUMO}\left( eV ight)$	ΔΕ
6a	-1422.55973764	3.3889	-0.20162	-0.09923	0.10239
6b	-2302.41645544	3.9209	-0.20306	-0.10255	0.10051
6c	-1842.83373323	5.5780	-0.20410	-0.10255	0.10155
6d	-1842.82419440	2.5770	-0.20182	-0.09946	0.10236
6e	-2302.42286350	7.3513	-0.20560	-0.10475	0.10085



Table 2

Dye No	Shade of dyed fiber	λ <sub>max</sub> (nm)	Coupling component	Structure of coupling components
6a	Yellow	432	p-toluene phenyl methyl pyrazolone	CH <sub>3</sub> N H <sub>3</sub> C
6b	Yellow	420	2,5-dichlorophenyl methyl pyrazolone	
6c	Yellow	432	m-chloro phenyl methyl pyrazolone	CI N N H <sub>3</sub> C
6d	Yellow	430	o-chloro phenyl methyl pyrazolone	CI N H <sub>3</sub> C
6e	Yellow	440	3,4—dichloro phenyl methyl pyrazolone	CI N H <sub>3</sub> C

method [29] and the results are summarized in Table 4. It is observed that, the percentage dye bath exhaustion of 2% dyeing on polyester ranges from 62% to 69%. The percentage dye bath fixation of 2% dyeing for polyester varied from 85% to 87%. The exhaustion and fixation values of the compounds **6a-e** are very good. This is due to the facts that the diffusion of the dye molecules within the fabric is rapid, so the rate of diffusion is high. The lower exhaustion is caused due to the lower substantivity of the dye molecules



Fig. 2. Visible absorption spectra of reactive dyes 6a-e.

because of their lower hydrophobicity. The introductions of reactive group like s-triazine ring to the dye molecules have improved the exhaustion value.

# 3.5. Fastness properties

The light, wash, and rubbing fastness properties were assessed according to the standard method [30]. As shown in Table 4, the light fastness of all the dyes is rating 3–5 for polyester which indicate that the light fastness is moderate to good. Further, wash fastness and rubbing (dry and wet) fastness of all the dyes rating 3–5 for polyester which showed their fastness is good to excellent.

#### 3.6. Color measurements

The color of a dyeing on polyester fibers are expressed in terms of CIELAB values (Table 5) and the following CIELAB coordinates were measured, lightness (L\*), chroma (C\*), hue angle form  $0^{\circ}-360^{\circ}$  (H), a\* value represent the degree of redness (positive) and greenness (negative) and b\* represents the degree of yellowness (positive) and blueness (negative). A reflectance spectrophotometer was used for the colorimetric measurements on the dyed samples. K/S values given by the reflectance spectrophotometer are calculated at  $\lambda_{max}$  and are directly correlated with the dye concentration on the substrate according to the Kubelka-Munk equation [31, 32]: K/S =  $(1-R)^{-2}/2R$ , where K, S and R represent absorbance coefficient, scattering coefficient and reflectance ratio, respectively.

Table 3	
Dye-bath containing materials.	

Heterocyclic monoazo dyes	
Weight of polyester fabric	2.0 g
Amount of dye under study	40 mg
Dispersing agent -tamol WS	100 mg
Acetic acid solution (10% w/v)	3.5 mL
Total vol. of the solution in dye-bath	100 mg
pH of dye-bath	5.0
Dyeing temperature	130 °C
Time for dyeing	90 min

Table 4						
%Exhaustion,	%fixation	and	fastness	data	of dyes <b>6</b>	а-е.

Dye No	%Exhaustion	%Fixation	Light fastness	Wash fastness	Rubbing fastness	
					Dry	Wet
	Р	Р	Р	Р	Р	Р
6a	67.00	85.82	4	3	4	5
6b	68.80	85.75	4	4	5	4
6c	63.93	86.04	3-5	4-5	4-5	4
6d	66.12	85.44	4	5	4	3
6e	62.00	85.48	3-5	3-4	3	3-4

Abbreviation: P-Polyester.

Light fastness: (Grading: 1- poor, 2- slight, 3- moderate, 4- fair, 5- good, 6- very good, 7- excellent).

Wash and Rubbing fastness: (Grading: 1- poor, 2- fair, 3- good, 4- very good, 5- excellent).

The color coordinates (Table 5) indicates that the dyes have good affinity to polyester fiber. From the data summarized in Table 5 showed that, for polyester fabric the dyeing obtained using dye **6a** was redder, lighter and brighter than dye **6b**; while dye **6e** was redder, darker and duller than dye **6d**. The K/S value of dyes **6a-e** for polyester fabric was found to be in the following order:

# 6b>6a>6c>6d>6e

Dye **6b** having maximum value of color strength (K/S) while dye **6e** having minimum value of color strength (K/S). From the above data, it is apparent that **6b** having highest K/S value on polyester showed highest affinity for polyester fabric. Further, the graph of K/S value of all the dyes for polyester fiber is shown in Fig. 3.

Table 5Colorimetric data of dyes 6a-e.

Dye No	L*	a*	b*	<b>c</b> *	H*	K/S
	Р	Р	Р	Р	Р	Р
6a	67.38	15.58	63.70	65.58	76.25	11.01
6b	67.36	12.06	63.26	64.39	79.21	12.11
6c	71.26	8.34	62.69	63.24	82.42	10.46
6d	67.72	16.71	61.67	63.89	74.84	10.35
6e	61.87	18.47	54.18	57.24	71.18	8.80



Fig. 3. Graph of K/S value for dyes 6a-e.

#### 4. Conclusions

A series of heterocyclic monoazo dyes containing benzoquinoline moiety were synthesized by conventional method and applied to polyester fabrics. The dyes gave shade like yellow or light yellow color with good fastness properties. The variations in the hues of the dyed fabrics result from both the nature and position of the substituents present on the coupler ring. Fairly good exhaustion and fixation of these dyes indicate that the dyes have good solubility and affinity with the fabric. This type of dye synthesis is generally convenient and economical for use. Another important conclusion that the results obtained from the DFT calculations inferred that the *m*-chloro substituted compounds **6c** and **6e** are energetically more stable than their corresponding *o*-chloro substituted compounds **6d** and **6b** and all the compounds have almost similar  $\Delta E$  ( $\Delta E = E_{HOMO} - E_{LUMO}$ ) values.

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