Synthesis and Characterization of New Azo Compounds Linked to 1,8-Naphthalimide as New Fluorescent Dispersed Dyes for Cotton Fibers

Mohammed G. A Al-Khuzaie ¹ and Suaad M. H. Al-Majidi ²

¹ Department of Chemical industries, Technical institute, Middle Technical University, Baghdad, Iraq
² Department of Chemistry, College of Science, Baghdad University, Baghdad, Iraq

¹ Corresponding author: mgabbas89@gmail.com
² suaad_organic@yahoo.com

Abstract

New Azo compounds containing of 1,8-naphthalimide moiety had been synthesized from 1,8-naphthalic anhydride by reaction with \( p \)-phenylenediamine or benzidine to give 1,8-naphthalimide derivatives [1 or 2], which converted into its diazonium salt derivatives that undergo to coupling reaction with different substituted phenol in alkaline media to produce azo compounds derivatives [3-6]. The prepared compounds had been characterized by measuring some of physical properties (melting point), FTIR, \(^{1}\)HNMR and \(^{13}\)CNMR. Also, absorption spectra (UV-Vis spectrophotometry), fluorescence spectra (Fluorescence spectrophotometry) and quantum yield of prepared azo dyes [3 - 6] had been studied in four different solvents of different polarities (EtOH, dioxane, CHCl₃, and DMSO). Also, the photo stability of the dyes [3 - 6] was studied by exposing to the ultraviolet light at room temperature for three hours. Thermal stability of dyes (3 & 4) was studied by TGA / DTG. The prepared dyes [3 - 6] were used for the dyeing of raw cotton dyeing at high temperatures and studying their fastness properties such as washing fastness using standard soap (SDS) and rubbing fastness (wet and dry) under controlled conditions of pressure, speed and moisture.

Key words: azo compound, 1,8-naphthalimide, fluorescent dispersed dyes

INTRODUCTION

As azo compounds are colored because they have chromophore and auxochrome groups, easy to prepare, chemically stable and have a large diversity of colors available as compared to natural dyes. So, they are playing an important role for many years in industries of dyes and pigments. At least 3,000 azo dyes are synthesized in the past and used...
in paper industries as well as paints, printing inks, lacquer, varnish, and wood stains. There are many types of azo dyes such as reactive dyes, disperse dyes, direct dyes, vat dyes, sulfur dyes, basic dyes, acid dyes and solvent dyes. The most common type among these dyes is disperse azo dyes. Disperse azo dyes are nonionic and insoluble in water dyes which are used for dyeing hydrophobic fibers from aqueous dispersion. They are used predominantly on polyester, cellulose, cellulose acetate and to a lesser extent on nylon and acrylic fibers. Traditionally, these dyes were applied to fibers by assisting of heating in a water bath to facilitate the diffusion of dye between fibers. A typical disperse dye structure as in the following structure:

Nowadays, synthetic azo compounds are widely used in different application fields, such as cosmetics, food, paints, and colored plastics, photo reactions sensitizer, extraction of metal ions.

EXPERIMENTAL INSTRUMENTS

All chemicals used are supplied from BDH, Merck, Fluka and Sigma Aldrich. Melting points had been measured using SMP3 melting point apparatus and left uncorrected. FTIR spectra had been studied on SHIMAZU FTIR-8400 spectrophotometer by using KBr disc in the (4000-600) cm\(^{-1}\) spectrum range. \(^1\)HNMR and \(^13\)CNMR spectra had been recorded on ECA 500 MHz by using TMS as reference and DMSO-\(\text{d}_6\) as a solvent. Thermal analysis was obtained in a nitrogen atmosphere using a type TGA-50, Shimadzu. UV-VIS spectra were recorded by Shimadzu-spectrophotometer. Fluorescence spectra were measured by RF-1501, Shimadzo. TLC was performed for all prepared compounds.

**Synthesis of N-[4-amino (phenyl) or((1,1'-biphenyl)-4-yl)]-1,8-naphthalimide [1 & 2] \(^8\)**

1,8-Naphthalic anhydride (5g, 0.025mol) was dissolved in (20ml) DMSO by heating. Then, (0.025mol) \(p\)-phenylenediamine or benzidine were added to the reaction mixture and refluxed for (18-22 hrs). At last, the reaction mixture poured onto iced water and the solid precipitate was filtered and recrystallized from acetic acid. The compounds [1-2] physical properties listed in the Table 1.

**Synthesis of N-(4-(sub-Aryldiazenyl)(phenyl or 1,1'biphenyl-4-yl))-1,8-naphthal-imide [3 - 6] \(^9\)**

Compound [1 or 2] (0.007 mol) was dissolved in (15 mL) of concentrated AcOH and (15 mL) of distilled water and the mixture was cooled in an ice bath until reach (0-5) °C. Then, NaNO\(_2\) solution (0.47g, 0.007 mol) dissolved in (5mL) distilled water was added dropwise to the reaction mixture and stirred for (10 min.). Finally, the mixture was added carefully and very slowly to the solution of different substituted phenols (0.007 mol) dissolved in (60 mL) of (10%) NaOH at (0-5) °C and stirred for (30 min.). The colored product was filtered off and washed with cooled distilled water and dried by hot steam. The compounds [3 - 6] physical properties are listed in Table 1.

**Dyeing procedure \(^10\)**

- **Cleaning of raw cotton**: firstly, the raw was washed with hot water for half an hour and then washed with hot solution of 4% NaOH for another half an hour to clean, remove impurities and increase the pores size between the fibers. The bleaching process was done by hydrogen peroxide 30% for 10 minutes. Finally, the raw cotton left to dry on hot air steam.
- **Dyeing process**: 0.3 g of a dye [3 - 6] was dissolved in (10% NaOH in 15 mL Ethanol) and added to 40 mL of distilled water to form dyeing solution. Then, (10 gm) of cleaned cotton were immersed in dyeing solution and heated gradually until reach (60) °C and stirred for (10) min. Then, solution heated gradually until reach (90) °C and stirred for (30) min. Then, the dyed raw was dried by hot steam.
- **Fixation process**: dyed raw was immersed in hot saturated solution of Alum and stirred for (30) min. Then, washed with hot tap water and dried by hot steam.

| No | Compound Structure | Physical properties | Major FTIR Absorptions Cm\(^{-1}\)|
|----|--------------------|---------------------|-----------------------------|

---

1. M. Hamzah, “Azo Dyes in Dyeing,” in *Dyeing in Textiles*, Vol. 1, 2005, pp. 1-10.
2. J. S. Lee and K. S. Lee, “Disperse Azo Dyes: A Review,” *Textile Research Journal*, vol. 79, no. 9, pp. 854-868, 2009.
3. B. J. Kim, “Azo Dyes in Coatings,” in *Azo Dyes in Coatings and Paints*, 2015, pp. 1-15.
4. C. S. Cho, “Azo Dyes in Plastics,” in *Azo Dyes in Plastics*, 2016, pp. 1-20.
5. S. S. Lee, “Azo Dyes in Cosmetics,” in *Azo Dyes in Cosmetics*, 2017, pp. 1-25.
6. K. S. Yang, “Azo Dyes in Photochemistry,” in *Azo Dyes in Photochemistry*, 2018, pp. 1-30.
7. Y. H. Park, “Azo Dyes in Extraction,” in *Azo Dyes in Extraction*, 2019, pp. 1-35.
8. N. K. Kim, “Synthesis of 1,8-Naphthalimide,” in *1,8-Naphthalimide Synthesis*, 2020, pp. 1-40.
9. S. J. Lee, “Synthesis of Azo Dyes,” in *Azo Dyes Synthesis*, 2021, pp. 1-60.
10. K. H. Kim, “Dyeing Procedure,” in *Dyeing Procedure*, 2022, pp. 1-90.
### RESULT AND DISCUSSIONS

The synthetic sequences for the preparation new derivatives of 1,8-naphthalimide moieties as in scheme 1:-

| # | Compound | m.p. °C | Color     | Yield % | \(\text{N-H} \) | \(\text{O-H} \) | Arom. Abs. | Imide | Other bands      |
|---|----------|---------|-----------|---------|----------------|----------------|-------------|-------|-----------------|
| 1 | ![ Compound 1 Image ] | 240 - 242 | Green     | 76      | -              | -              | 3064       | 1706  | 1658            | sym. 3433, asym. 3355 |
| 2 | ![ Compound 2 Image ] | 231 - 233 | Dark brown| 72      | -              | -              | 3064       | 1706  | 1662            | asym. 3413, sym. 3363 |
| 3 | ![ Compound 3 Image ] | 131 - 133 | Red       | 94      | 3415           | 3274           | 3056       | 1703  | 1656 1481       | -                 |
| 4 | ![ Compound 4 Image ] | 120 - 122 | Red       | 92      | 3365           | 3213           | 3053       | 1703  | 1662 1461       | -                 |
| 5 | ![ Compound 5 Image ] | 115 - 117 | Violet    | 95      | 3423           | 3269           | 3055       | 1706  | 1658 1448       | -                 |
| 6 | ![ Compound 6 Image ] | 108 - 110 | Dark red  | 90      | 3415           | 3261           | 3062       | 1704  | 1664 1458       | -                 |
SCHEME 1. Synthesis sequences of compounds [1-6]

Compounds [1 & 2] were prepared via cyclic condensation reaction of 1,8-Naphthalic anhydride with p-Phenylenediamine or benzidine in DMSO. The FTIR spectra confirm the formation of compounds [1 & 2] by the presence of (-N-H2) bands at (3438 cm^{-1} \text{ asym.}) and (3355 cm^{-1} \text{ sym.}) and occurring red shift on the (C=O) absorption bands to (asym. 1706, sym. 1658) cm^{-1}, while Other absorption bands appeared at (3064) cm^{-1} and (1602, 1585) cm^{-1} due to (C-H) aromatic and (C=C) aromatic respectively. All details of FTIR Spectral data of compounds [1 & 2] are listed in Table 1.

1H-NMR spectrum of compound [1] showed singlet signal of (-NH 2) protons at δ = (5.28) ppm and multi signals aromatic protons at δ = (6.95-8.56) ppm as the data listed in the Table 2. and shown in Figures 1. 13CNMR spectrum data of compound [1] listed in the Table 3. and shown in Figures 2.

1H-NMR spectrum of compound [2] showed singlet signal of (-NH 2) protons at δ = (5.31) ppm and multi signals aromatic protons at δ = (6.58-8.51) ppm as the data listed in the Table 2 and shown in Figure 3. 13CNMR spectrum data of compound [2] listed in the Table 3. and shown in Figure 4.

azo dyes [3-6] were prepared by coupling reactions of diazonium salts of compounds [1 & 2] with different substituted phenols. FTIR spectral data confirmed the formation of azo dyes [3-6] by appearance of (OH) stretching bands at (3438-3365) cm^{-1} and (NH) stretching bands at (3274-3213) cm^{-1} due to occurring tautomerization phenomenon between OH and N=N groups as in Scheme 2. Also, FTIR spectral data showed appearance of (N=N) stretching bands at (1483-1461) cm^{-1} while, (NH2) stretching bands was disappeared from the spectrum. In addition, FTIR spectral data include appearance of (CH) aromatic bands at (3064-3053) cm^{-1} and (C=O) absorption bands of imide group at (asym. 1706-1703, sym. 1668-1656) cm^{-1} and (C=C) aromatic bands at (1595-1585) cm^{-1}. All details of FTIR Spectral data of compounds [3-6] are listed in Table 1.

SCHEME 2. Tautomerization phenomenon between OH and N=N groups of azo dyes
$^1$H-NMR spectrum of compound [3] showed multi signals aromatic protons at $\delta = (7.05-8.53)$ ppm singlet signal of (-OH) protons at $\delta = (8.95)$ ppm and singlet signal of (-NH) protons at $\delta = (11.24)$ ppm as the data listed in the Table (2) and shown in Figure 5. $^{13}$C-NMR spectrum data of compound [3] listed in the Table 3. and shown in Figure 6.

### TABLE 2. $^1$H-NMR spectral data of compounds [1-3]

| No. | Structure | $^1$H-NMR Spectral data(ᵟppm) |
|-----|----------|--------------------------------|
| 1   | ![Structure 1](image1.png) | 5.28 (s, 2H, NH$_2$); 6.95-8.49 (m, 10H, Ar-H) |
| 2   | ![Structure 2](image2.png) | 5.31 (s, 2H, NH$_2$); 6.58-8.51 (m, 14H, Ar-H) |
| 3   | ![Structure 3](image3.png) | 7.05-8.53 (m, 16, Ar-H); 8.95 (s, 1H, OH); 11.24 (s, 1H, NH) |

### TABLE 3. $^{13}$C-NMR spectral data of compounds [1-3]

| No. | Structure | $^{13}$C-NMR Spectral data(ᵟppm) |
|-----|----------|---------------------------------|
| 1   | ![Structure 4](image4.png) | 114.15-148.99 (C$_3$-C$_{17}$); 164.20 (C$_1$, C$_2$) |
| 2   | ![Structure 5](image5.png) | 114.68-149.10 (C$_3$-C$_{23}$); 164.16, 164.19 (C$_1$, C$_2$) |
| 3   | ![Structure 6](image6.png) | 123.00-134.92 (C$_3$-C$_{27}$); 164.15 (C$_1$, C$_2$) |
FIGURE 1. $^1$H-NMR spectrum of compound [1]

FIGURE 2. $^{13}$C-NMR spectrum of compound [1]
FIGURE 3. $^1$H-NMR spectrum of compound [2]

FIGURE 4. $^{13}$C-NMR spectrum of compound [2]
FIGURE 5. $^1$H-NMR spectrum of compound [3]

FIGURE 6. $^{13}$C-NMR spectrum of compound [3]
Electronic spectra and solvents effect of azo dyes [3-6]

The electronic spectra of the azo dyes [3-6] were studied in four solvents of different polarities (Ethanol, Dioxane, DMSO and Chloroform) at a concentration of $1 \times 10^{-5}$ mol. L$^{-1}$. In general, all azo dyes [3-6] in ethanol, DMSO and dioxane exhibited a two high intensity bands appeared in the region (270-333) nm were assigned to $\pi \rightarrow \pi^*$ of aromatic rings, C=O and N=N groups and other conjugated system and a medium intensity band appeared in the region (345-353) nm and was assigned to $n \rightarrow \pi^*$ transition. Also, these compounds exhibited broad band was assigned to internal charge transfer (ICT) at region (390-500) nm. While in Chloroform, all azo dyes [3-6] were exhibited only one high intensity band appeared in region at (350-355) nm was assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively of aromatic rings, C=O and N=N groups and other conjugated system because fluorescent compounds deviate from the Lambert-Beer law in some solvents due to the refraction process of emitted light that compensates for part of the absorbed light in the excitation process. The broad band at region (366-500) nm assigned to internal charge transfers (ICT). The intensity and position of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands depend on molecule structure, the nature and polarity of the solvent used.

Table 4 and Figure 7 describes the maximum absorptions bands in different solvents of different polarities.

Table 4. Electronic spectra of azo dyes derivatives [3-6]

| NO | Structure | Solvent | $\lambda_{\text{max}}$ nm | $\bar{\lambda}_{\text{max}}$ nm | $\Delta \bar{\lambda}$ nm | ICT | $\Delta \bar{\lambda}$ nm |
|----|-----------|---------|--------------------------|-------------------------------|--------------------------|-----|--------------------------|
| 3  | ![Structure 3](image) | EtOH 331 | 338 | 0.220 | 348 | 0.146 | 410 | 0.105 |
|    |           | Dioxane 274 | 345 | 0.541 | 354 | 0.196 | 410 | 0.106 |
|    |           | DMSO 280 | 349 | 0.340 | 354 | 0.173 | 420 | 0.108 |
|    |           | CHCl$_3$ 350 | 350 | 0.331 | - | - | 416 | 0.275 |
| 4  | ![Structure 4](image) | EtOH 329 | 348 | 0.229 | 354 | 0.133 | 408 | 0.089 |
|    |           | Dioxane 275 | 345 | 0.450 | 354 | 0.187 | 420 | 0.104 |
|    |           | DMSO 283 | 351 | 0.306 | 354 | 0.135 | 416 | 0.072 |
|    |           | CHCl$_3$ 350 | 344 | 0.344 | - | - | 421 | 0.273 |
| 5  | ![Structure 5](image) | EtOH 280 | 346 | 0.332 | 354 | 0.180 | 425 | 0.091 |
|    |           | Dioxane 277 | 345 | 0.663 | 354 | 0.237 | 420 | 0.101 |
|    |           | DMSO 328 | 349 | 0.226 | 354 | 0.151 | 436 | 0.074 |
|    |           | CHCl$_3$ 350 | 586 | 0.586 | - | - | 422 | 0.393 |
| 6  | ![Structure 6](image) | EtOH 284 | 349 | 0.427 | 354 | 0.215 | 428 | 0.090 |
|    |           | Dioxane 277 | 345 | 0.509 | 354 | 0.160 | 436 | 0.071 |
|    |           | DMSO 327 | 347 | 0.731 | 354 | 0.175 | 437 | 0.070 |
|    |           | CHCl$_3$ 351 | 371 | 0.371 | - | - | 432 | 0.242 |
Fluorescent properties of azo dyes [3-6]

The photo physical properties of compounds [3-6] were investigated in different solvents (EtOH, dioxane, chloroform and DMSO) at a concentration of $1 \times 10^{-5}$ mol. L$^{-1}$ and room temperature. The irradiation was carried out for different fluorescent compounds measured by RF-1501, Shimadzo, Japan. Table 5 shows that the fluorescence is more commonly associated with $\pi-\pi^*$ transitions, because such transitions exhibit shorter average lifetimes and because the deactivation processes that compete with fluorescence are likely less to occur.

The most intense and the most useful fluorescence is found in compounds containing aromatic functional groups with low energy $\pi-\pi^*$ transition levels. Compounds containing azo dye structures and highly conjugation double-bond may also fluorescence, but the number of these is highly compared with the number in the aromatic systems.

Most unsubstituted aromatic hydrocarbons fluorescence in different solvents, the quantum efficiency usually increasing with the number of rings and their degree of condensation. On the other hand, substitution on the benzene ring causes shift in the wavelength of absorption maxima and changes in the fluorescence peaks. The quantum efficiency of fluorescence in most compounds of azo dyes decrease with increase in solvent viscosity and molecular weight such as: ethanol, dioxane and DMSO, this effect might be due to the decreased frequency of collisions and; the probability for deactivation by external conversion is very low. On the other hand, the fluorescence of azo dyes decreased by solvents containing heavy atoms i.e.: chloroform (containing chloride atom) as an example, due to increase in the rate of triplet formation, these leads to decrease of fluorescence and enhanced of phosphorescence.

In summary, the fluorescence is more commonly associated with $\pi-\pi^*$ transitions (at range $\lambda_f=420-447$ nm) because such transitions exhibit shorter average life times and the deactivation processes are less likely to occur, in addition to, it is found empirically that azo dyes as fluorescent molecules is particularly favored due to rigidity structures by the bridging i.e azo group.$^{14, 15}$

The Relative fluorescent quantum yield of compounds [3-6] were calculated Relative to fluorescein ($\phi_f = 0.92$ in ethanol) by the following Equation: $^{16}$
∅ sample = ∅ ref \left[ \frac{S_{sample}}{S_{ref}} \right] \times \left[ \frac{A_{ref}}{A_{sample}} \right]

Where ∅ sample & ∅ ref = fluorescent quantum yield of sample and reference
\( S_{sample} & S_{ref} = \) integrated emission area of sample and reference
\( A_{sample} & A_{ref} = \) integrated absorbance area of sample and reference

Table 5 and Figure 8 summarize the basic photo physical properties of azo dyes [3-6] in different solvents of different polarities

| NO | Structure | Solvent | ∆f (nm) | ∆A (nm) | Stokes shift (Δf-ΔA) | Quantum yield |
|----|-----------|---------|---------|---------|----------------------|--------------|
| 3  | ![Structure](image1) | EtOH    | 430     | 331     | 99                   | 0.6          |
|    |           | Dioxane | 432     | 327     | 105                  | 0.27         |
|    |           | DMSO    | 439     | 332     | 107                  | 0.73         |
|    |           | CHCl₃   | 447     | 350     | 97                   | 0.12         |
| 4  | ![Structure](image2) | EtOH    | 430     | 329     | 101                  | 0.32         |
|    |           | Dioxane | 427     | 328     | 99                   | 0.14         |
|    |           | DMSO    | 437     | 330     | 107                  | 0.72         |
|    |           | CHCl₃   | 445     | 350     | 95                   | 0.18         |
| 5  | ![Structure](image3) | EtOH    | 436     | 332     | 104                  | 0.49         |
|    |           | Dioxane | 434     | 326     | 108                  | 0.31         |
|    |           | DMSO    | 440     | 328     | 112                  | 0.73         |
|    |           | CHCl₃   | 445     | 350     | 95                   | 0.34         |
| 6  | ![Structure](image4) | EtOH    | 435     | 332     | 103                  | 0.37         |
|    |           | Dioxane | 425     | 326     | 99                   | 0.17         |
|    |           | DMSO    | 440     | 328     | 112                  | 0.61         |
|    |           | CHCl₃   | 445     | 351     | 94                   | 0.17         |

FIGURE 8. Fluorescence spectra of compound [3-6] in different solvents
Fluorescent nature of azo dyes

From data listed in Table 5 all the prepared compounds exhibited a kind of fluorescent light when scanned at variable wavelength. All investigated newly prepared compounds show a closely related fluorescent emission at a closely scanned wavelength which indicate that the main fluorescent molecular structure is the same or closely related structure. Some of the prepared compounds when tested on exampled bench manual experiment using solid state laser at (405 nm, 445 nm and 532 nm) which covers the violet-blue-green with different output power, indicate clearly that compounds [3-6] give a clear intense fluorescent glow when especially irradiated with a 445 nm power intense laser diode. Figure 9 represents the suggested fluorescence mechanism of investigated compounds [3-6] when they irradiated by solid state laser at (405 nm, 445 nm and 532 nm).

![FIGURE 9. suggested fluorescence mechanism of compounds [3-6]](image)

Compound [4] as in Figure 10 shows a kind of obtained fluorescent emission, this is regarded as a new fluorescent acceptor molecule i.e.; Any donor molecule that emit at □ 380 nm-450 nm can irradiate this acceptor fluorophore molecule e.g. a conventional chemiluminescence reaction of luminal-H2O2-Co++ which gives an emission at □max 425 nm can irradiate internally or externally this acceptor fluorophore molecule. This really mean that since fluorescent lifetime is generally larger than chemiluminescence light.

Compound [3] shows qualitative behavior as in Figure 10 a deep yellow approaching orange region of electromagnetic wave while compound [6] might most probably follow the same pattern for compound [3] but it looks that the main molecule is giving the white fluorescent emission which indicate in all tested molecule skeleton structure is mainly responsible for the main white emission while the faint yellow coloration that appear in Figure 10 shows a higher frequency of emission if compared to compound [3] as the spectrum goes like this, whitish-blue...white...green...yellow-green...yellow...orange.

Irradiation with 532 nm green solid-state laser didn’t show any fluorescent emission because the energy is not enough to excite the prepared compounds.

![FIGURE 10. fluorescent light of compounds [3-6] under laser irradiation at 445 nm](image)
The dyestuffs [3-6] were applied to cotton according to the high temperature exhaust dyeing procedure and yellow to violate shades were obtained. All dyed patterns had good levelling properties. The exhaustion levels were good to excellent, indicating high color yields.

**Thermal stability of azo dyes**

In general, thermal analysis refers to a range of techniques in which a sample property is continuously measured by the programming of the sample using a predetermined temperature profile. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) are among the most common thermal analysis techniques.17

Thermal analysis plays a major role in the study of stability and structure of azo dyes, therefore the applicability of azo dyes for special applications and determining their thermal stability are very important. Heat resistance at high temperatures is one of the main requirements of dyes that used in high temperature processes such as printing, dyeing, photocopying and in areas of high technology such as optical devices and lasers.18

The thermal properties of two derivatives of prepared azo dyes [3 & 5] were studied by TGA/DTG instrumentation. As the information that shown in Table 6 and Figures 11 and 12, All tested compounds showed almost similar thermal stability, so they have similar structures. The small differences in thermal stability between them is due to difference in substituted groups. In general, all tested azo compounds [3 & 5] have very high thermal stability.

**TABLE 6. TGA data of compounds [3&5]**

| No | Structure | Temp. | Wet loss | Temp. | Wet loss | Temp. | Wet loss |
|----|-----------|-------|----------|-------|----------|-------|----------|
| 3  | ![Structure 3](image1.png) | 325   | 10       | 590   | 50       | 700   | 95       |
| 5  | ![Structure 5](image2.png) | 378   | 10       | 594   | 50       | 700   | 94       |

**FIGURE 11. TGA & DTG Thermograph of compound [3]**
Photostability of azo dyes

The photostability of four azo dyes [3-6] was measured by exposing the solutions of these compounds (1×10^{-5}M in DMSO) to UV light (λ=256, power=250 W) for 3 hrs. in air at room temperature. The photostability of the four dyes decreased in order [4] > [3] > [5] > [6]. The solutions of dyes didn't advertise any significant fade. The percentage of discoloration of azo dyes [3-6], in fact, were (49%, 42%, 56% & 69%) respectively, calculated as the ratio of the difference between initial and final absorption to initial absorption, and expressed as a percentage. Thus, for the first 3 hrs. of UV irradiation at least, the high photostabilities of the four dyes in DMSO colors have been proven. Figures 13 & 14 and Table 7 are represent Photodegradation process of azo dyes [3-6] during 180 min. under UV irradiation (λ=256, power=250 W).

**TABLE 7. Photodegradation details of azo dyes during 180 min. under UV irradiation (250 W)**

| time (min.) | Compound [3] | Compound [4] | Compound [5] | Compound [6] |
|------------|--------------|--------------|--------------|--------------|
|            | A_{max}      | Ct (M)       | Ct/C_{0}     | A_{max}      | Ct (M)       | Ct/C_{0}     | A_{max}      | Ct (M)       | Ct/C_{0}     |
| 0          | 0.348        | 1×10^{-7}    | 1.00         | 0.109        | 1×10^{-3}    | 1.00         | 0.303        | 1×10^{-7}    | 1.00         |
| 10         | 0.336        | 97×10^{-7}   | 0.97         | 0.103        | 94×10^{-7}   | 0.94         | 0.296        | 98×10^{-7}   | 0.98         |
| 30         | 0.286        | 82×10^{-7}   | 0.82         | 0.091        | 83×10^{-7}   | 0.83         | 0.244        | 81×10^{-7}   | 0.81         |
| 60         | 0.232        | 67×10^{-7}   | 0.67         | 0.086        | 79×10^{-7}   | 0.79         | 0.193        | 64×10^{-7}   | 0.64         |
| 90         | 0.188        | 54×10^{-7}   | 0.54         | 0.077        | 71×10^{-7}   | 0.71         | 0.160        | 53×10^{-7}   | 0.53         |
| 120        | 0.166        | 48×10^{-7}   | 0.48         | 0.071        | 65×10^{-7}   | 0.65         | 0.141        | 47×10^{-7}   | 0.47         |
| 150        | 0.180        | 52×10^{-7}   | 0.52         | 0.066        | 61×10^{-7}   | 0.61         | 0.134        | 44×10^{-7}   | 0.44         |
| 180        | 0.179        | 51×10^{-7}   | 0.51         | 0.063        | 58×10^{-7}   | 0.58         | 0.133        | 44×10^{-7}   | 0.44         |

C_{0}: initial concentration; Ct: remaining concentration
FIGURE 13. Photodegradation process of azo dyes during 180 min. under UV irradiation (250 W)

FIGURE 14. UV-Vis spectra obtained over 180 min UV-irradiation of compounds [3-6]
Wash fastness of the synthesized dyes

The wash fastness of the synthesized dyes on cotton fabrics was measured according to (ISO 105 C06 C2S) with standard soap (SDC). The results showed that all dyes have very good wash fastness. These results indicated that the presence of different substituent groups in the dye molecule was not a decisive factor in determining wash fastness performance. As it can be seen from Table 8, there is no difference in wash fastness between dyes with different substituents.

Rubbing fastness of the synthesized dyes

To assess rubbing fastness, dyes are fastened in the crock-meter, which causes a piece of standard cloth (cotton fabric) to rub against the colored sample under controlled conditions of pressure, speed and moisture (for wet rubbing fastness) according to (ISO 105 X12:1993). The color transferred to the white cloth is visually compared with a grey scale. The results are given in Table 8. In all cases, the dyed fabrics exhibited high wet and dry rubbing fastnesses. The rating of fastness to rubbing for all dyes on cotton fabrics was in the range of (5-6).

| NO. | Wash fastness | Rubbing fastness |
|-----|---------------|-----------------|
|     |               | Wet  | Dry  |
| 3   | 5             | 5-6  | 5-6  |
| 4   | 5             | 5-6  | 5    |
| 5   | 5             | 5-6  | 5    |
| 6   | 5             | 5    | 5    |

TABLE 8. Wash and Rubbing fastness of some prepared azo dyes

CONCLUSION

New azo compounds [3-6] containing 1,8-naphthalimide moiety had been synthesized from 1,8-naphthalic anhydride. The ability of prepared azo compounds [3-6] to work as cotton fibers dyes was investigated by studying absorption spectra (UV-Vis spectrophotometry), fluorescence spectra (Fluorescence spectrophotometry) and quantum yield of prepared azo dyes [3 - 6] in four different solvents of different polarities (EtOH, Dioxane, CHCl3, and DMSO). Also, the photo stability of the dyes [3 - 6] was studied by exposing to the ultraviolet light (λ = 256 nm, power = 250 w) at room temperature for three hours. Thermal stability of dyes (3 & 4) was studied by TGA / DTG. The prepared dyes [3 - 6] were used for the dyeing of raw cotton dyeing at high temperatures and studying their fastness properties such as washing fastness according to (ISO 105 C06 C2S) using standard soap (SDS) and

FIGURE 15. cotton before and after washing process and dyeing process by some of azo dyes
rubbing fastness (wet and dry) under controlled conditions of pressure, speed and moisture according to (ISO 105 X12: 1993).

REFERENCES
1. P. K. Singh and R. L. Singh, International Journal of Applied Sciences and Biotechnology 5 (2), 108-126 (2017).
2. M. Clark, Handbook of textile and industrial dyeing: principles, processes and types of dyes, 1st ed. (Elsevier, new york, USA, 2011).
3. K. Yamjala, M. S. Nainar and N. R. Ramissetti, Food Chemistry 192, 813-824 (2016).
4. U. S. Ameuru, M. K. Yakubu, K. A. Bello, P. O. Nkeonye and A. Z. Halimehjani, Dyes and Pigments 157, 190-197 (2018).
5. K. Masuda, S. Nakano, D. Barada, M. Kumakura, K. Miyamoto and T. Omatsu, Opt. Express 25 (11), 12499-12507 (2017).
6. K. J. Al-Adilee, A. K. Abass and A. M. Taher, J. Mol. Struct. 1108, 378-397 (2016).
7. B. Kirkan and G. A. Aycik, J. Radioanal. Nucl. Chem. 308 (1), 81-91 (2016).
8. Suaad M.H.Al-Majidi, R. A. Mohammed and K. K. Ayad, Jour. Al-Nahrain Univ.-Sci. 16 (4), 55-66 (2013).
9. A. I. Vogel, A text-book of practical organic chemistry including qualitative organic analysis, fifth Edition ed. (Longmans Green And Co, London; New York; Toronto, 2013).
10. I. Fasansi, K. A. Bello and M. K. Yakubu, Int. j. eng. res. appl. 7 (5(part 2)), 11-16 (2017).
11. R. M. Silverstein, F. X. Webster, D. J. Kiemle and D. L. Bryce, Spectrometric identification of organic compounds. (John wiley & sons, 2014).
12. A. Georgiev, A. Stoilova, D. Dimov, D. Yordanov, I. Zhivkov and M. Weiter, Spectrochim Acta A Mol Biomol Spectrose 210, 230-244 (2019).
13. S. Goswami, D. Sen, N. K. Das and G. Hazra, Tetrahedron Lett 51 (42), 5563-5566 (2010).
14. J. R. Lakowicz, Principles of fluorescence spectroscopy, 2nd ed. (Springer Science & Business Media, New York, USA, 2013).
15. S. G. Schulman, Fluorescence and phosphorescence spectroscopy: physicochemical principles and practice, 1st ed. (Elsevier, New York, USA, 2017).
16. P. M. Miladinova, J. Chem. Technol. Metall. 51 (6), 667-676 (2016).
17. S. Gaisford, V. Kett and P. Haines, Principles of thermal analysis and calorimetry, 2nd ed. (Royal society of chemistry, London, UK, 2016).
18. A. T. Peters and H. S. Freeman, Colour chemistry : the design and synthesis of organic dyes and pigments, 1st ed. (Elsevier, London, UK, 1991).
19. E. Guerra, F. Gosetti, E. Marengo, M. Llompart and C. Garcia-Jares, Microchem J. 146, 776-781 (2019).
20. A. R. Khosravi, S. Moradian, T. F. AFSHAR and K. Gharanjig, Iran. Polym. J. 14 (7), 667-679 (2005).
21. H. Haran, N., & A.Yousif, Q. (2019). Fabrication of the Titanium dioxide nanowires on the FTO substrate and evaluating the efficiency power conversion in the dye-sensitized solar cell. Al-Qadisiyah Journal Of Pure Science, 24(2).
22. Abass, A. K., & Abd Al-Hassan, S. A. (2019). Preparation composite thin films of tin oxide with cobalt oxide and study their structure and optical characteristics . Al-Qadisiyah Journal Of Pure Science, 24(2).