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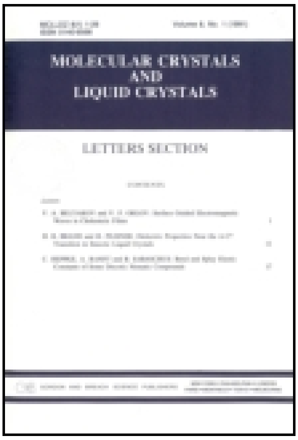

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Synthesis and Spectral Characteristics of Disazo Dyes Containing Heterocyclic Diazo Components

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Disazo dyes were derived from heterocyclic amines by diazotizing 2-Amino-6-nitrobenzothiazole, 2-Amino-5-nitrothiazole, and 2-Amino-3,5-dinitrothiophene and coupling with Aniline as middle components, and 1-Naphthylamine, N,N-Dimethyl-1-naphthylamine, N,N-Dibutylaniline and N,N-Diethylaniline, Aniline as final components. Disazo red, violet, blue dyes were synthesized and the absorption bands of these compounds were observed in the range of 512–668 nm. The effects of diazo components and final coupling components on the visible absorption maxima of the dyes were also discussed.

Keywords Absorption maximum; benzothiazole; disazo dyes; solvatochromism; thiazole; thiophene

Introduction

Azo compounds are very important in the fields of dyes, pigments and advanced materials. It has been known for many years that azo compounds are the most widely used class of dyes because of their versatile application in various fields, such as the dyeing of textile fibres and the coloring materials in the food colorants, cosmetic, printing, pharmaceuticals, plastics, biological-medical studies as well as for advanced applications in organic synthesis [1, 2].

There are monoazo dyes derived from heterocycles, such as pyridine, pyrazolone, indoles, quinoline and thiophene derivatives. The use of heterocyclic coupling components and diazo components in the synthesis of disperse dyes is well established, and the dyes exhibit good tinctorial strength and brighter dyeing than those derived from aniline-based components [2–4]. Although, many researchers have described the synthesis and dyeing properties of monoazo dyes, only a few disazo dyes have been synthesized and their properties investigated in recent years [2, 5, 6].

In this study, the synthesis of seven disazo dyes derived from various electron donating coupling components and the heterocyclic diazo components, such as 2-amino-6-nitrobenzothiazole, 2-amino-5-nitrothiazole, and 2-amino-3,5-dinitrothiophene is reported. The visible absorption spectra in various solvents of these dyes were also discussed. The

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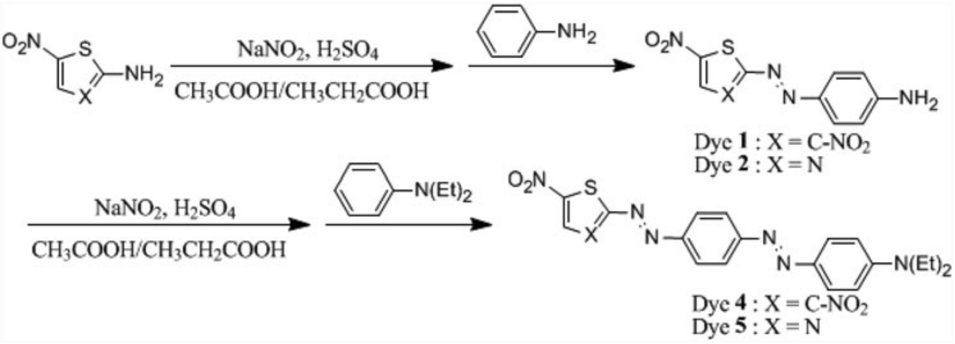
*Address correspondence to Prof. Jae-Hong Choi, Department of Textile Engineering, Kyungpook National University, 1370 Sangyuk-dong, Buk-gu, Daegu 702-701, Korea (ROK). Tel.: (+82)53-950-5644; Fax: (+82)53-950-6617. E-mail: jaehong@knu.ac.kr synthetic method involved in the preparation of monoazo dyes **1–3** by coupling of diazotized heterocyclic amines with coupler (aniline) containing diazotizable amino groups, as well as the subsequent synthesis of final disazo dyes **4–10**.

Experimental

Synthesis of Dyes

Synthesis of monoazo dye 2. As presented in Scheme 1, sodium nitrite (97%, 0.46 g, 0.34 mmol) was added to 95% sulfuric acid (5ml) to make a nitrosylsulfuric acid and the mixture was heated to 60–70°C for 1 hr and then cooled to 5°C. 2-Amino-5-nitrothiazole (1g, 0.34 mmol) was portionwised to an acetic acid and propionic acid mixture (1:1, 20 ml) under 10°C, and then the mixture was cooled below 5°C while a nitrosylsulfuric acid was being dropped. Diazotization was checked by TLC. The resulting diazonium solution was added slowly to a vigorously stirred solution of aniline (0.64 ml, 0.34 mmol) dissolved in 99% acetic acid with crushed ice and then the mixture was stirred for 1 hr at 5°C. After the reaction was completed, the mixture was neutralized by using aqueous sodium hydroxide solution (25%). The crude monoazo dye was filtered, and washed with water several times, then dried and re-crystallized by ethanol [2].



Scheme 1. Synthetic scheme for the preparation of monoazo dye precursors and disazo dyes derived from thiophene and thiazole diazo components.

This procedure was also used for the synthesis of monoazo dye **1** and **3**.

Dye 1 Yield: 45%. $C_{10}H_7N_5O_4S$ ^1H NMR($CDCl_3$), δ: 8.39 (s, 1H, 2-thiophene), 6.63–7.40 (m, 4H, Ar-***H***), 5.33 (s, 2H, N***H***$_2$). Found C: 40.65; H: 2.48; N: 23.95; S: 10.86 Calculated C: 40.96; H: 2.41; N: 23.88; S: 10.93, MS 293.26(M+)

Dye 2 Yield: 57%. $C_9H_7N_5O_2S$ ^1H NMR($CDCl_3$), δ: 9.03 (s, 1H, thiazole) 7.34 (m, 4H, Ar-***H***), 3.45 (m, 2H, N***H***$_2$-). Found C: 43.01; H: 2.86; N: 28.31; S: 12.54 Calculated C: 43.37; H: 2.83; N: 28.10; S: 12.86, MS 249.25(M+)

Dye 3 Yield: 63%. ^1H NMR($CDCl_3$), δ: 8.05–8.64 (m, 3H, benzothiazole), 6.65–7.25 (m, 4H, Ar-***H***), 5.35 (s, 2H, -N***H***$_2$). $C_{13}H_9N_5O_2S$ Found C: 52.45; H: 3.12; N: 23.12; S: 10.41 Calculated C: 52.17; H: 3.03; N: 23.40; S: 10.71, MS 229.31(M+)

Synthesis of disazo dye 5. As presented in Scheme 1, sodium nitrite (97%, 0.28 g, 0.40 mmol) was added to 95% sulfuric acid (3 ml) and the mixture was heated to 60–70°C for 1 hr and then cooled to 5°C. Monoazo dye (1 g, 0.40 mmol) prepared in advance was portionwised to an acetic acid-propionic acid mixed solution (1:1, 20 ml) under 10°C, and then the mixture was cooled less than 5°C while a nitrosylsulfuric acid was being dropped. Diazotization was checked by TLC. The resulting diazonium solution was added slowly to a vigorously stirred solution of *N*,*N*-diethylaniline (0.60ml, 0.40mmol) dissolved in 99% acetic acid with crushed ice, and then the mixture was stirred for 1hr at 5°C. After the reaction was completed, the mixture was neutralized by using aqueous sodium hydroxide solution (25%) [2]. The resulting disazo dye was filtered, and washed with water several times, then dried and purified by column chromatography with n-hexane (95%) : ethyl acetate (99.5%) (SiO_2, n-hexane:ethyl acetate = 5:1).

All other disazo dyes were prepared in a similar procedure.

Dye 4 Yield: 41%. $C_{20}H_{19}N_7O_4S$ ^1H NMR($CDCl_3$), δ: 6.93–8.37 (m, 8H, Ar-***H***), 8.38 (s, 1H, 2-thiophene), 3.35 (m, 4H, N-C***H***$_2$-), 1.12 (t, 6H, -C***H***$_3$). Found C: 52.69; H: 4.25; N: 21.78; S: 7.25 Calculated C: 52.97; H: 4.22; N: 21.62; S: 7.07, MS 453.47(M+)

Dye 5 Yield: 56%. $C_{19}H_{19}N_7O_2S$ ^1H NMR($CDCl_3$), δ: 9.05 (s, 1H, thiazole) 6.99–8.44 (m, 8H, Ar-***H***), 3.45 (m, 4H, N-C***H***$_2$-), 1.19 (t, 6H, -C***H***$_3$). Found C: 55.62; H: 4.59; N: 23.65; S: 7.98 Calculated C: 55.73; H: 4.68; N: 23.95; S: 7.83, MS 409.96(M+)

Dye 6 Yield: 63%. $C_{19}H_{13}N_7O_2S$ ^1H NMR($CDCl_3$), δ: 8.08–8.64 (m, 3H, benzothiazole), 6.85–8.11 (m, 8H, Ar-***H***), 5.35 (s, 2H, -N***H***$_2$). Found C: 56.35; H: 3.35; N: 24.50; S: 7.54 Calculated C: 56.57; H: 3.25; N: 24.30; S: 7.95, MS 403.42(M+)

Dye 7 Yield: 67%. $C_{23}H_{21}N_7O_2S$ ^1H NMR($CDCl_3$), δ: 8.10–8.67 (m, 3H, benzothiazole), 6.99–8.45 (m, 8H, Ar-***H***), 3.41 (m, 4H, N-C***H***$_2$-), 1.20 (t, 6H, -C***H***$_3$). Found C: 60.01; H: 4.64; N: 21.21; S: 6.98 Calculated C: 60.12; H: 4.61; N: 21.34; S: 6.93, MS 459.52(M+)

Dye 8 Yield: 65%. $C_{27}H_{29}N_7O_2S$ ^1H NMR($CDCl_3$), δ: 8.10–8.69 (m, 3H, benzothiazole), 6.98–8.47 (m, 8H, Ar-***H***), 3.78 (m, 4H, N-C***H***$_2$-), 1.56 (m, 4H, -C***H***$_2$-), 1.38 (m, 4H, -C***H***$_2$-), 0.98 (t, 6H, -C***H***$_3$). Found C: 62.56; H: 5.56; N: 19.31; S: 6.15 Calculated C: 62.89; H: 5.67; N: 19.01; S: 6.22, MS 515.63(M+)

Dye 9 Yield: 60%. $C_{23}H_{15}N_7O_2S$ ^1H NMR($CDCl_3$), δ: 8.08–8.67 (m, 3H, benzothiazole), 7.16–8.19(m, 10H, Ar-***H***), 5.83 (s, 2H, -N***H***$_2$). Found C: 62.56; H: 3.87; N: 10.51; S: 6.45 Calculated C: 62.36; H: 3.98; N: 10.36; S: 6.66, MS 453.48(M+)

Dye 10 Yield: 62%. $C_{25}H_{19}N_7O_2S$ ^1H NMR($CDCl_3$), δ: 7.60–8.26 (m, 3H, benzothiazole), 7.18–8.16(m, 10H, Ar-***H***), 3.08 (s, 4H, -C***H***$_3$). Found C: 40.54; H: 2.48; N: 23.95; S: 10.86 Calculated C: 40.96; H: 2.41; N: 23.88; S: 10.93, MS 481.53(M+)

Structural Analysis and Measurement of Absorption Spectra

Structural analysis of synthesized dyes were measured using an EA 1108 (E.A.) and an HP 6890 & Agilent 5973N MSD (GC-Mass).^{1}H-NMR data were obtained with a Bruker 400 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. UV-visible absorption spectra were obtained from Shimadzu UV-2100.

Results and Discussion

Calculations by the PPP-MO Method

The PPP-MO procedure has been used to calculate the anticipated absorption spectra in the visible range as well as the fluorescence absorption maxima of the dyes [7–11], and PI SYSTEM^{TM} for windows is a commercial program based on a modified PPP SCF-CI-MO method for rapid and convenient calculations. All bonding and nonbonding interactions

Table 1. Calculated and observed absorption maxima of disazo dyes **4–10**

Dye number	$\lambda^{Cal.}{}_{max}$ (nm)	$\lambda^{Obs.}{}_{max}$ (nm)*
4	669	668
5	631	628
6	537	552
7	605	600
8	605	607
9	590	597
10	629	615

*Determined in DMSO.

between the π atoms are calculated by means of Roothaan's formula for *p*-*p* overlap integral [13, 14]. Table 1 shows calculated and observed absorption maxima of the synthesized dyes. The most reliable results were observed with dyes **4**, **5**, **7** and **8** where the difference of absorption maximum between calculated and observed was less than 5 nm. In this case, the calculation of target color would be efficient by eliminating the actual synthetic procedures. For other dyes **6**, **9** and **10**, the gabs in λ_{max} between two methods were found to be smaller than 15 nm which could be also sufficient for the simulation of dye structure to achieve desired colors.

Effects of Heterocyclic Ring on the Absorption Maximum

As shown in Fig. 1, comparison of the absorption maximum for disazo dyes **4**, **5** and **7**, these contain *N*,*N*-diethylaniline group in the coupling moiety, revealed more bathochromic

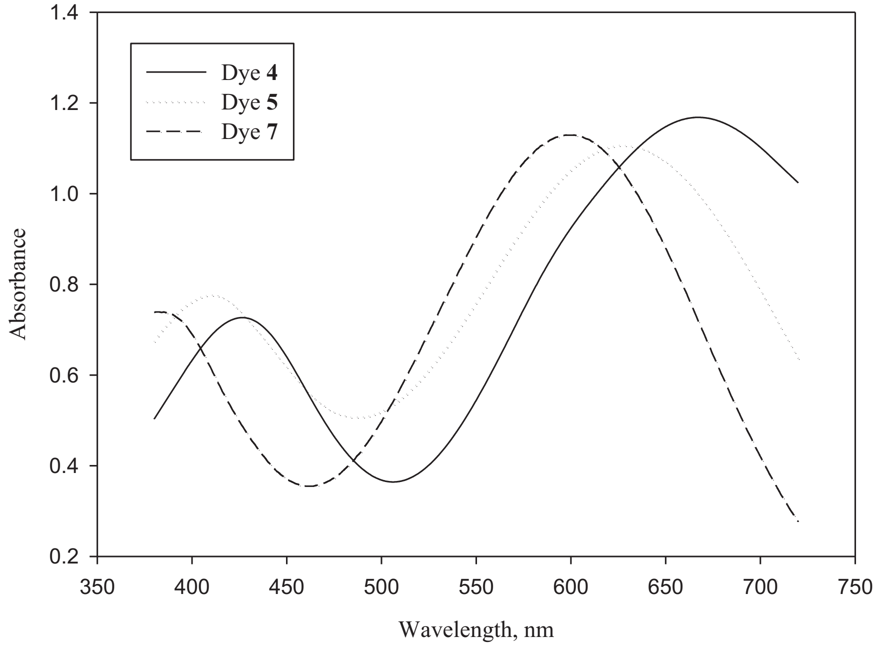


Figure 1. Absorption spectra of dyes **4**, **5** and **7** derived from three types of heterocyclic rings.

shift by the heterocyclic ring in the diazo moiety ordered from benzothiazole, thiazole to thiophene. Therefore the most bathochromic disazo dye, in this series, was found with dye **4** that derived from 2-amino-3,5-dinitrothiophene which absorbs maximally at 668 nm. By comparing with that of corresponding disazo dye **5** contains 2-amino-5-nitrothiazole, a large bathochromic shift of 40 nm was observed which is mostly attributable to the strong withdrawing effect exerted by two nitro groups of the thiophene ring. In contrast, dye **7** derived from 2-amino-6-nitrobenzothiazole diazo moiety showed a hypsochromic shift compared to that of corresponding dye **5** which was 28 nm. In this case, the diene effect arisen by a 5-membered heterocyclic ring, such as thiophenes and thiazoles, could be mainly contributed to the red shift observed [14–18]. Therefore, all disazo dyes prepared could afford blue to greenish-blue shades, irrespective of heterocyclic diazo component. It can be concluded that the bathochromic effect depending on heterocyclic rings as a diazo component increases in the following order: 2-amino-3,5-dinitrothiophene > 2-amino-5-nitrothiazole > 2-amino-6-nitrobenzothiazole.

Effects of Coupler Ring (Donor) on the Absorption Maximum

In Table 1, the absorption maxima of disazo dyes **6–10** derived from 2-amino-6-nitrobenzothiazole, as a diazo moiety, coupled with five different electron donors were summarized. The most bathochromic dye was dye **10** which contains a *N*,*N*-dimethylnaphthalene ring absorbing maximally at 615nm, whereas the dye **9** containing *N*,*N*-unsubstituted naphthalene analogue exhibited absorption maximum of 597 nm that to be hypsochromically shifted by 18 nm. This result can be explained by the presence of stronger electron donating substituents, *N*,*N*-dimethyl group, in the coupling moiety of dye **10** leading to lower energy level in the excited state. In similar, dye **7** containing an *N*,*N*-diethylaniline group exhibited a bathochromic shift of 8nm in comparison with corresponding dye **6** substituted by aniline ring.

In comparison of aniline ring and aminonaphthalene analogue, $\lambda_{\max}$ of dye **9** was measured to be 597 mn which is 45 mn longer than corresponding dye **6** due to the longer conjugation of π–electrons arisen by naphthalene ring.

Furthermore, *N*,*N*-Dibutyl group in the coupling moiety of the dye **8** contributed to the red shift by 7nm compared with diethyl analogue (dye **7**) that could suggest the longer carbon chain of *N*,*N*-dialkyl group results in a bathochromic shift.

Comparison of the Absorption Maximum Between Disazo Dyes and Monoazo Precursors

As shown in Table 2, all disazo dyes prepared absorbed maximally at much longer wavelength compared with that of corresponding monoazo dyes. The most difference in $\lambda_{\max}$ was observed with disazo dye **7** which exhibited 600nm of $\lambda_{\max,}$ whereas the monoazo analogue (dye **3**) absorbed maximally at 531 nm, leading to a bathochromic shift of 69 nm. The other disazo dyes **4–6** also showed longer $\lambda_{\max}$ values in the range of 21∼51 nm. Thus, it is clearly explained that the extension of azo linkage from monoazo to disazo leads to the longer conjugation of π-systems of the dye molecules affording smaller energy gab between the ground state and excited state.

Solvatochromism

Solvatochromism can be best described as the effect of a solvent on the color of a dye. Solvent-solute interactions have various influences on the absorption spectrum, such as

Table 2. Comparison of absorption maxima of disazo dyes and their corresponding precursors

Disazo dye		Monoazo dye		
No.	λ_{max}(nm)	No.	λ_{max}(nm)	$\Delta\ \lambda_{max}$* (nm)
4	668	**1**	638	30
5	628	**2**	577	51
6	552	**3**	531	21
7	600	**3**	531	69

*Determined in DMSO.

the λ_{max} value and the intensity of a band. Generally in many neutral dye molecules, the ground state is less polar than the excited state so that a polar solvent will tend to stabilize the excited state more than the ground state, leading to a bathochromic shift in the absorption maximum. This effect is termed positive solvatochromism. In contrast with positive solvatochromism, negative solvatochromism is relatively rare and is most often observed with colorants which contain a delocalized charge.

The dielectric constant of the solvent reflects its polarity, as shown in Table 3. For example, water (very polar) has a dielectric constant of 80.1 at 20°C while n-hexane (very non-polar) has a dielectric constant of 1.89 at 20°C [19]. The dielectric constant of DMSO is 46.7 which is highest polar among three solvents used, and ethyl acetate has the lowest dielectric constant.

As summarized in Table 3, a positive solvatochromism was observed for all disazo dyes when these dyes were dissolved in four different solvents, where significant changes in absorption maxima toward longer wavelengths were consistently observed. The most change was found in dye **5** which shifted its absorption maximum bathochromically by 64 nm in DMSO compared with in ethyl acetate. In contrast, the smallest value was observed with dye **9**.

Table 3. Dielectric constants of solvents used and absorption maxima of disazo dyes **4–10** in various solvents

	Dielectric constant		
	46.7 DMSO	21 Acetone	6.02 Ethyl acetate
Dye no.	λ_{max}(nm)		
4	668	631	624
5	628	586	564
6	552	522	517
7	600	574	567
8	607	578	569
9	597	576	568
10	615	589	566

Conclusions

A series of seven disazo dyes based on heterocyclic rings, as a diazo moiety, has been prepared by the diazotization of monoazo precursor with a subsequent coupling reaction. The absorption maxima of the disazo dyes prepared varied from 552 nm to 668 nm depending on the heterocyclic rings and *N*,*N*-disubstituents in the coupler moiety. The most bathochromic shift was observed with dye containing a thiophene ring as a diazotizer, whereas benzothiazole analogues were comparatively blue-shifted. However, the presence of naphthalene ring affords a bathochromic shift compared to corresponding phenyl group.

A significant positive solvatochromism was found when dissolved disazo dyes in three different solvents responding to the conventional neutral dye molecules.

Therefore, these disazo dyes can be used for blue dichroic dyes where suitable affinity is confirmed with substrates.

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