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Synthesis of Some Novel Bis(Hetaryl)azo Disperse Dyes and Investigation of Their Absorption Spectra

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ABSTRACT: *3-Amino-2-cyano-4,6-disubstituted-thieno[2,3-b]pyridines and 3-aminopyridine were diazotized and coupled with 2-phenylindole, 2-methylindole, and 1-methyl-2-phenylindole, respectively. These dyes were characterized by UV-Visible, FT-IR, ^{1}H NMR, and mass spectroscopic techniques. Solvent effects on the visible absorption spectra of the dyes were evaluated. The color of the dyes is discussed with respect to the nature of the heterocyclic ring and substituent present therein. In addition, effects of temperature, concentration, as well as acid and base on the visible absorption maxima of the dyes are reported.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:622–630, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20361

INTRODUCTION

Azo compounds are very important in the fields of dyes, pigments, and advanced materials [1]. It has been known for many years that azo compounds are the most widely used class of dyes owing to their versatile application in various fields such as dyeing of textile fibers, coloring of different materials, colored plastics and polymers, biological-medical studies, and advanced applications in organic synthesis [2–7]. In addition, azo dye chromophores have excellent photoisomerization properties and sensitivity toward the polarized light. However, a number of studies have been conducted on all-optical poling in azo dye–doped polymers and glasses [8]. Azo dyes from synthesized heterocyclic coupling components have been investigated for the production of bright and strong color shades ranging from yellow to greenish blue on synthetic fabrics. These results have led commercial products to replace the conventional azobenzene disperse dyes [9]. There are some reports of azo dye derivatives of heterocycles such as pyridone, pyrazolone, and thiophene [10–24]. The visible absorption wavelength of these dyes are generally in the yellow to orange range due to poorly delocalized electrons in the heterocyclic ring; however, some of these dyes show more deeper color strength and shades such as red or violet [4,9,11,12]. On the other hand, the use of heteroaromatic amines as diazo components in the generation of disperse dyes having essentially color-deepening effect is well established [11,13,14].

Heterocyclic azo compounds tend to be more strongly affected by solvents than azobenzene-based dyes. This is a consequence of the increased polarity of the system, especially in the excited state. We have previously reported the synthesis of some novel heterocyclic systems such as hetarylazopyridones [22] and hetarylazopyrazolones [23], which exhibited the azo–hydrazone tautomerism and a strong solvent dependence in their absorption spectra. In continuation of our

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works, we herein investigate the solvatochromic behavior of bis(hetaryl)azo compounds, which do not exhibit the azo–hydrazone tautomerism, and an evaluation of their visible absorption spectra under the influence of solvents. Although many patents and papers describe the synthesis and properties of carbocyclic azoindole compounds [24–27], only few hetarylazoindole compounds have been synthesized [28–35]. However, the absorption spectroscopic properties of hetarylazoindole dyes were not investigated. In this study, 3-amino-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridines were synthesized according to literature method [36]. Diazotization of 3-amino-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridines and 3-aminopyridine and their subsequent coupling with 2-methylindole, 2-phenylindole, and 1-methyl-2-phenylindole gave a series of bis(hetaryl)monoazo disperse dyes. The effect of solvent, temperature, and concentration of the dyes on their visible absorption spectra was evaluated. In addition, spectroscopic properties of the azo compounds were examined with respect to 4,6-disubstituents present in the thieno[2,3-*b*]pyridine ring and 2-methyl and 2-phenyl substituents present in the indole nucleus.

EXPERIMENTAL

General

Chemicals used in the synthesis of these dyes were obtained from Aldrich Chemical Company and were used without further purification. Solvents used were of spectroscopic grade.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer using KBr. ^{1}H NMR spectra were recorded on a Bruker-Spectrospin Avance DTX 400 Ultra-Shield in DMSO-d_6 and $CDCl_3$. Chemical shifts are expressed in δ units (ppm). UV-Visible absorption spectra were recorded on Analytika-jena UV-200 spectrophotometer at the wavelength of maximum absorption (λ_{max}) of dyes in a range of solvents, that is, dimethylsulphoxide (DMSO), dimethylformamide (DMF), acetonitrile, methanol, acetic acid, and chloroform at various concentrations (approximately 1×10^{-6} to 1×10^{-8}). Change of λ_{max} was investigated when 0.1 ml piperidine was added to 1 ml dye solutions in DMSO, DMF, and chloroform, respectively, as well as when 0.1 ml base (potassium hydroxide, 0.1 M in methanol) or 0.1 ml hydrochloric acid (0.1 M in methanol) was added to 1 ml methanolic dye solutions. In addition, change of λ_{max} in DMSO and DMF was examined over the temperature range 25°C to 70°C. Mass spectra were recorded on Agilent 5973 Network Mass Selective Detector, SIS (Direct Insertion Probe, Germany), with an electron impact of 70 eV. All melting points were uncorrected and are reported in degree Celsius (°C).

Preparation of Hetarylazoindole Dyes **1–9**

Diazotization of various heterocyclic amines was achieved with nitrosyl sulphuric acid. The diazonium salts thus obtained were subsequently coupled with indole derivatives. A typical procedure starting from 3-aminopyridine is the one that is described below; all other dyes were prepared in a similar manner. Yields of the dyes are in the range of 55% to 80%. Characterization data are shown in Tables 1 to 2.

*Preparation of 2-phenyl-3-(3-pyridlylazo)-1*H*-indole* **7**. 3-Aminopyridine (2.0×10^{-3} mol, 0.18 g) was dissolved in a hot glacial acetic acid/propionic acid mixture (2:1, 6.0 ml) and was rapidly cooled in salt/ice bath to −5°C. The liquor was then added in portions in a 30 minute duration to a cold solution of nitrosyl sulphuric acid (prepared from sodium nitrite (0.15 g) and concentrated sulphuric acid (3 ml at 50°C)). The resulting mixture was stirred for an additional 2 h at 0°C. Excess nitrous acid was destroyed by the addition of urea. The resulting diazonium salt was cooled in salt/ice bath. After diazotization was complete, the diazo liquor was slowly added to vigorously stirred solution of 2-phenylindole (2.0×10^{-3} mol, 0.39 g) in acetic acid/propionic acid mixture (2:1, 8 ml). After 2 h, the reaction mixture was maintained at pH 4–6 by the simultaneous addition of saturated sodium carbonate solution. The mixture was then stirred for additional 1 h at 0°C to 5°C. The resulting product was filtered, washed with water, dried, and finally recrystallized from ethanol/H_2O mixture to give a yellow crystalline solid (yield: 65%; mp: 217°C–218°C).

RESULTS AND DISCUSSION

Characterization of the Novel Azocoupling Products (**1–9**) by Melting Point, FT-IR, ^{1}H NMR, and Mass Spectra

Hetarylazoindole dyes **1–9** were prepared by coupling 2-methylindole, 2-phenylindole, and 1-methyl-2-phenylindole with diazotized 3-amino-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridines and 3-aminopyridine in nitrosyl sulphuric acid (Scheme 1). These dyes were structurally characterized by FT-IR, ^{1}H NMR (Table 1), and mass spectral data (Table 2). The dyes prepared from

TABLE 1 IR and ^{1}H NMR Spectral Results of Dyes **1–9**

	FT-IR (cm^{-1}, in KBr)					*^{1}H NMR (δ, ppm)*			
Dye No.	ν_{N-H}	ν_{Aro-H}	ν_{Al-H}	$\nu_{C\equiv N}$	$\nu_{C=C}$	*Aro.-H*	*Alip.-H*	*X-H*	*Solvent*
1	3378	3044	2960–2921	2209	1580	8.28 (1H, d), 8.06 (2H, m), 7.73 (1H, s), 7.41–6.93 (6H, m)	2.72 (3H, s), 2.62 (3H, s)	12.01 (indole, b)	a,c
2	3435	3056	–	2203	1573	8.30 (1H, d), 8.18 (1H, d), 8.00 (1H, s), 7.81 (1H, d), 7.61–6.83 (16H, m)	–	11.93 (indole, b)	a,c
3	3358	3063	2973–2915	2198	1580	8.06 (1H, m), 7.21–7.08 (3H, m), 6.91 (1H, s)	2.73 (3H, s), 2.61 (3H, s), 2.44 (3H, s)	11.53 (indole, b)	a,c
4	3384	3056	2921	2215	1573	8.18 (1H, m), 7.82–7.24 (14H, m)	2.15 (3H, s)	9.11 (indole, b)	a,c
5	–	3050	2928	2209	1587	8.08 (1H, m),7.73 (2H, m), 7.84–7.08 (6H, m), 6.53 (1H, s)	3.88 (3H, s), 2.74 (3H, s), 2.62 (3H, s)	–	a,c
6	–	3056	2935	2210	1573	8.08 (1H, m), 7.83–7.16 (18H, m), 6.50 (1H, s)	3.75 (3H, s)	–	c
7	3371	3095	–	–	1541	9.09 (1H, d), 8.58 (2H, m), 8.13 (3H, m), 7.61–7.48 (5H, m), 7.29 (2H, m)	–	11.78 (indole, b)	a,c
8	3442	3048	2921	–	1548	9.06 (1H, d), 8.44 (1H, m), 8.38 (1H, m), 8.17 (1H, m), 7.38 (1H, m), 7.28 (1H, m), 7.16 (2H, m)	2.75 (3H, s)	11.16 (indole, b)	a,c
9	–	3070	2935	–	1478	9.02 (1H, d), 8.65 (1H, m), 8.57 (1H, m), 8.44 (1H, m), 7.81 (1H, m), 7.67–7.58 (4H, m), 7.53–7.43 (4H, m)	3.88 (3H, s)	–	a,c

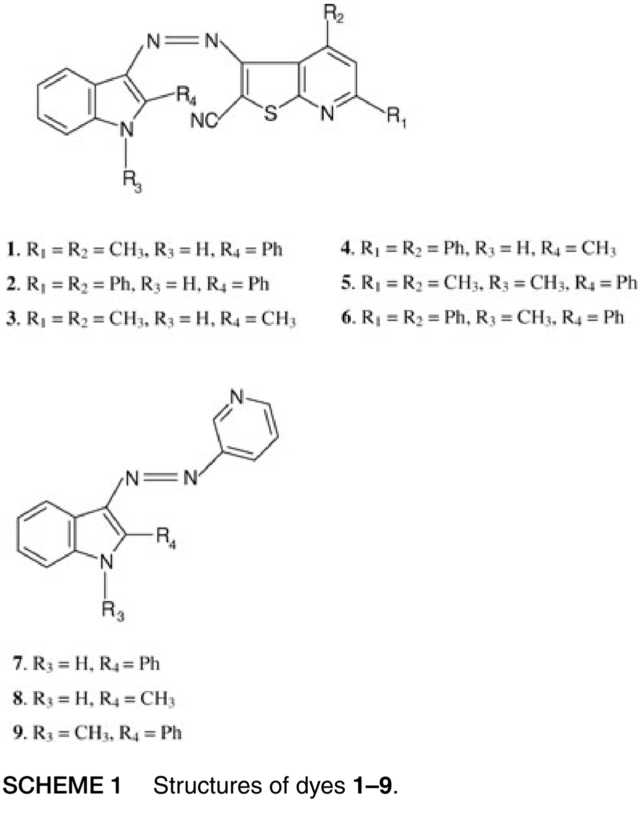
Abbreviations: X = –N; s, singlet; d, doublet; t, triplet; m, multiplet; b, broad; a, $CHCl_3$; and c, DMSO.

TABLE 2 Mass Spectra (MS), Isolated Yields, and Melting Points of Dyes **1–9**

Dye No.	*MS (m/z, M$^+$)*	*Isolated Yield^a (%)*	*Melting Point^b (°C)*
1	407	68	246–248
2	531	55	dec.> 300
3	345	78	dec.> 300
4	469	75	177–178
5	421	80	111–112
6	545	75	184–185
7	298	65	217–218
8	236	70	270–272
9	312	79	147–148

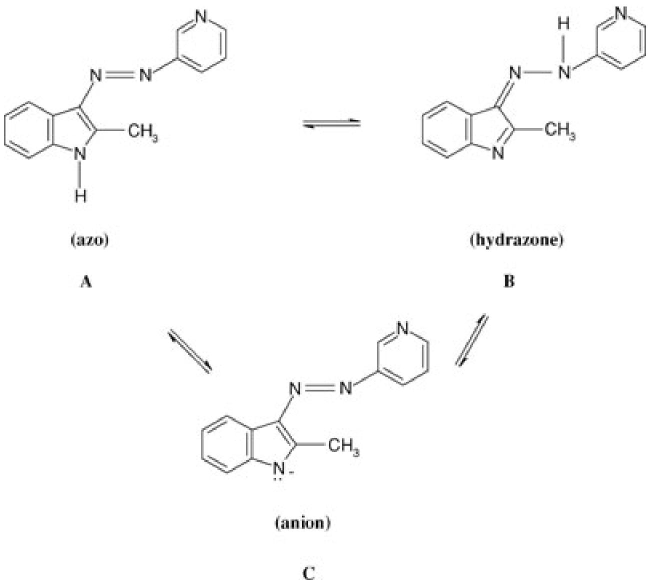
Abbreviation: dec., decomposition.
[a] Yield of pure product.
[b] Recrystallized from ethanol/H_2O.

2-methylindole (dyes **3, 4**, and **8**) and 2-phenylindole (dyes **1, 2**, and **7**) may exist in two possible tautomeric forms, namely, azo form A and hydrazone B, as depicted in Scheme 2. The deprotonation reaction of two tautomers leads to a common anion C.



1. $R_1 = R_2 = CH_3$, $R_3 = H$, $R_4 = Ph$
2. $R_1 = R_2 = Ph$, $R_3 = H$, $R_4 = Ph$
3. $R_1 = R_2 = CH_3$, $R_3 = H$, $R_4 = CH_3$
4. $R_1 = R_2 = Ph$, $R_3 = H$, $R_4 = CH_3$
5. $R_1 = R_2 = CH_3$, $R_3 = CH_3$, $R_4 = Ph$
6. $R_1 = R_2 = Ph$, $R_3 = CH_3$, $R_4 = Ph$
7. $R_3 = H$, $R_4 = Ph$
8. $R_3 = H$, $R_4 = CH_3$
9. $R_3 = CH_3$, $R_4 = Ph$

SCHEME 1 Structures of dyes **1–9**.



SCHEME 2 Azo–hydrazone tautomerization of hetarylazoindole dyes **1–4, 7**, and **8**.

IR spectra of the dyes prepared from 2-methylindole (dyes **3, 4**, and **8**) and 2-phenylindole (dyes **1, 2**, and **7**) showed a weak and a broad band within the range 3442 to 3358 cm^{-1} due to indole ν_{NH} (Table 1). These bands were not observed in the IR spectra (in KBr) of the dyes prepared from 1-methyl-2-phenylindole (dyes **5, 6**, and **9**). The other ν_{max} values at 3095–3044 cm^{-1} (aromatic CH) and 2973–2915 cm^{-1} (aliphatic CH) were also recorded. ^{1}H NMR spectra except for dyes **5, 6**, and **9** exhibit one broad peak at 12.01 to 9.11 ppm, which were due to —NH indole protons. These spectral data generally conclude that the tautomeric equilibrium of the dyes derived from 2-methylindole and 2-phenylindole is in favor of the azo form in the solid state as well as in DMSO or DMSO/chloroform mixtures. Dyes **5, 6**, and **9** exhibit one tautomeric form (azo) and are used as model compounds. Mass spectra show the molecular ion peaks of the dyes and are given in Table 2.

UV-Visible Spectroscopic Study

Since the tautomeric equilibrium strongly depends on the nature of media, the behavior of hetarylazoindole dyes in various solvents was studied. For this purpose, absorption spectra of hetarylazoindole dyes **1–9** were recorded in various solvents at a concentration range of approximately 10^{-6} to 10^{-8} M and were run at different concentrations because of solubility problem. The results are given Table 3. It was found that the absorption maxima of these dyes are strongly dependent on solvents and vary with solvent polarity. The dyes generally show bathochromic shifts with the increasing polarity of the solvents, but do not show a regular variation. The influence of

TABLE 3 Influence of Solvent, Temperature, and Sample Concentration on Absorption Maxima (in nm) of Dyes **1–9**

Dye No.	DMSO conc. (25°C)	DMSO dil. (25°C)	DMSO (70°C)	DMF conc. (25°C)	DMF dil. (25°C)	DMF (70°C)	A.nitrile conc. (25°C)	A.nitrile dil. (25°C)	Meth. conc. (25°C)	Meth. dil. (25°C)	A. Acid. conc. (25°C)	A. Acid. dil. (25°C)	Chl. conc. (25°C)	Chl. dil. (25°C)
1	450	458	455	450	450	451	428	426	438	435	441	439	423	423
2	462	466	462	457	457	459	447	447	452	452	448	446	441	443
3	461	461	455	453	452	449	438	440	444	446	448	448	436	438
4	449	450	447	442	443	441	435	438	431	433	470	472	429	429
5	446	443	440	440	440	442	416	418	434	431	487	489	411	411
6	442	442	443	438	438	436	420	421	432	434	480	477	408	408
7	410	409	412	406	407	411	404	402	405	404	424	426	398	398
8	390	390	392	388	387	388	379	381	387	385	409	410	377	379
9	400	401	403	398	398	399	399	397	396	395	426	426	394	394

Abbreviations: s, shoulder; A. acid, acetic acid; Chl., chloroform; Meth., methanol; A. nitrile, acetonitrile; conc., concentrated; and dil., diluted.

solvents for the dyes increase in the order DMSO > DMF > acetonitrile ~ methanol > acetic acid > chloroform. The spectral shifts of dyes **9** and **3** in various solvents are shown in Figs. 1 and 2, respectively.

Heterocyclic-based azo disperse dyes tend to show larger solvatochromic effects than azobenzene-based dyes because of increased polarity of the dye system, especially in the excited state. Similar effects for some derivatives of these dyes containing benzothiazolyl, thiazolyl, thiadiazolyl, and thienyl moieties have been reported [37–42]. On the other hand, the tautomeric equilibrium in hetarylazo dyes prepared from indole-type coupling components needs further consideration.

Absorption spectra of these dyes showed only one absorption maxima without shoulder in the solvents used. The results show that only one tautomeric form is present in the solvents used. In proton-donating solvents such as acetic acid, dyes **4–9** give a bathochromic shift relative to other solvents (Fig. 1) (for dye **5**, $\lambda_{max} = 443$ nm in DMSO, 440 nm in DMF, 418 nm in acetonitrile, 431 nm in methanol, 411 nm in chloroform, and 489 nm in acetic acid; for dye **9**, $\lambda_{max} = 401$ nm in DMSO, 398 nm in DMF, 397 nm in acetonitrile, 395 nm in methanol, 394 nm in chloroform, and 426 nm in acetic acid). In addition, in proton-accepting solvents, such as DMSO and DMF, dyes **1–3** give a bathochromic shift of λ_{max} relative to other solvents (for dye **1**, $\Delta\lambda_{max} = 35$ nm in DMSO and 27 nm in DMF relative to chloroform; for dye **3**, $\Delta\lambda_{max} = 23$ nm in DMSO and 14 nm in DMF relative to chloroform) (Fig. 1).

In addition, it was observed that the absorption curves of dyes **1–9** were very sensitive to acid and bases. For dyes **1–4, 7**, and **8**, λ_{max} showed a large bathochromic shift when 0.1 ml piperidine was added to each of the dye solutions in DMSO and DMF (Table 4). For dyes **1–4, 7**, and **8**, both a shoulder (dyes **7** and **8**) at the long wavelength region and a maxima at the short wavelength region were observed as a result of the addition of 0.1 ml piperidine to their DMSO and DMF solutions. In contrast, dye **2** has two absorption maxima in basic DMSO and DMF solutions. This equilibrium may exist between the tautomeric and anionic forms. The other dyes (**1, 3**, and **4**) exhibit only one absorption maxima at long wavelength. This suggests that the dyes exist mainly in the common anionic form (Figs. 3a and 3b) (for dye **1**, $\Delta\lambda_{max} = 97$ nm in DMSO and 104 nm in DMF relative to DMF + piperidine; for dye **3**, $\Delta\lambda_{max}$ is 83 nm and 89 nm in DMF relative to DMF + piperidine).

However, similar results were not observed when 0.1 ml piperidine was added to each of the dye solutions in chloroform. For dyes **1–4, 7**, and **8**,

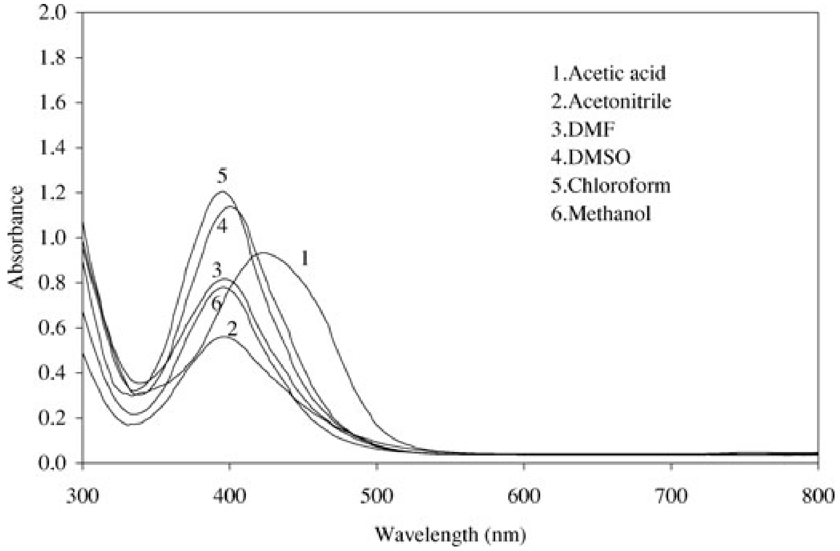


FIGURE 1 Absorption spectra of dye **9** in various solvents.

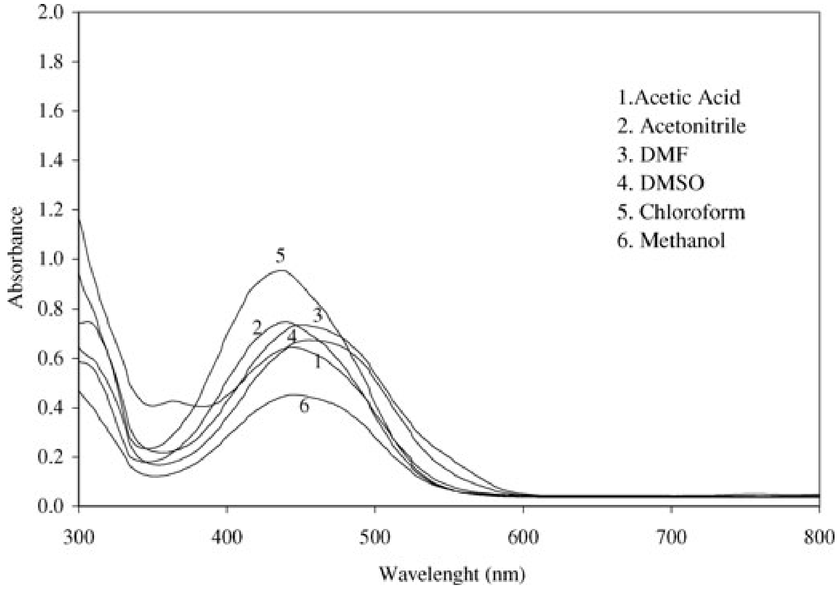


FIGURE 2 Absorption spectra of dye **3** in various solvents.

TABLE 4 Absorption Maxima (in nm) of Dyes **1–9** in Acidic and Basic Solutions

Dye No	*DMSO*	*DMSO + Piperidine*	*DMF*	*DMF + Piperidine*	*Methanol*	*Methanol + KOH*	*Methanol + HCl*	*Chloroform*	*Chloroform + Piperidine*
1	458	555	450	554	435	522, 439 s	483	423	428, 478 s
2	466	439, 583	457	580, 441	452	533, 442 s	488	443	451
3	461	544	452	541	446	520, 447 s	481	438	444
4	450	555	443	560	433	511	464	429	438
5	443	442	440	438	431	429	458	411	413
6	442	444	438	439	434	430	448	408	409
7	409	492	407	408, 491 s	404	433	442	398	402
8	390	389, 472 s	387	386, 481 s	385	428	421	379	388
9	401	400	398	398	395	396	428	394	394

Abbreviation: s, shoulder.

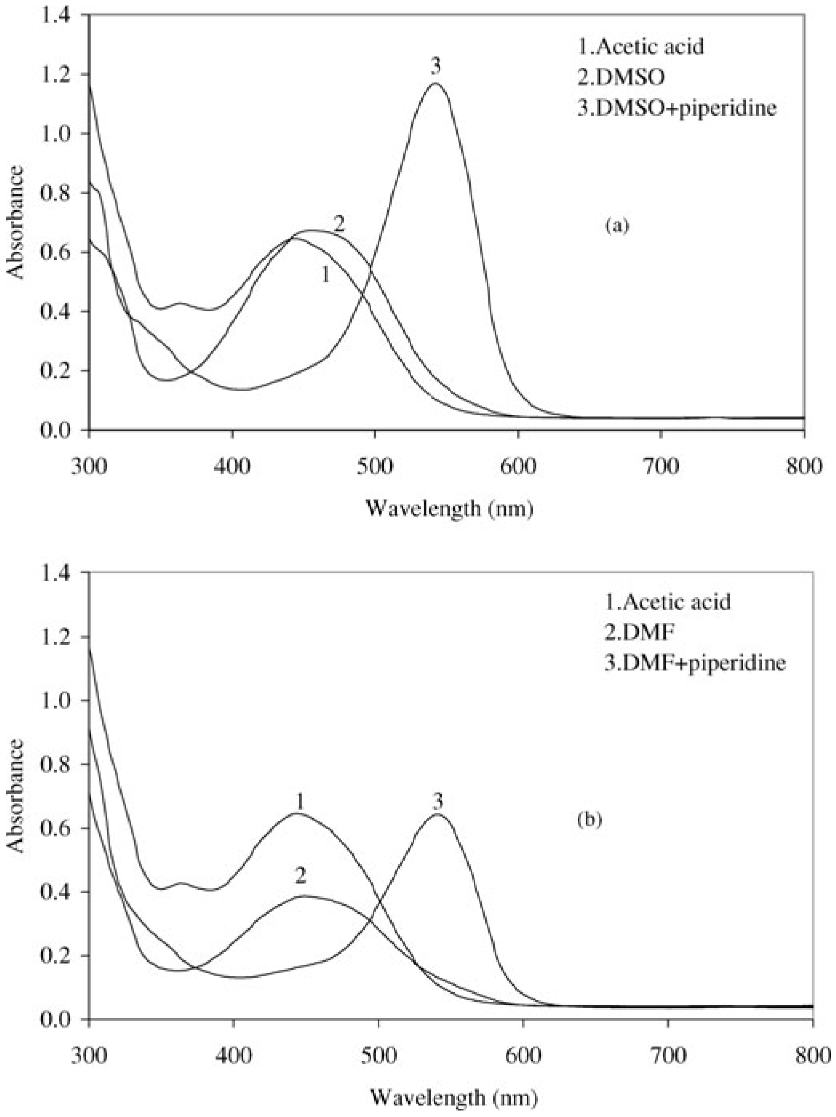


FIGURE 3 Absorption spectra of dye **3** in acidic and basic solution: (a) acetic acid, DMSO, and DMSO + piperidine; (b) acetic acid, DMF, and DMF + piperidine.

λ_{max} showed a slight bathochromic shift when 0.1 ml piperidine was added to each of the dye solutions in chloroform, whereas dyes **1–4, 7**, and **8** exhibit one absorption maxima with the exception of dye **1** (for dye **3**, $\Delta\lambda_{max} = 8$ nm in chloroform relative to chloroform + piperidine; for dye **4**, $\Delta\lambda_{max} = 9$ nm in chloroform relative to chloroform + piperidine) (Fig. 4a).

Similarly, when 0.1 mL KOH was added to a methanolic solution of dyes **1–4, 7**, and **8**, both a shoulder (dyes **1–3**) at the short wavelength region and a maxima at the long wavelength region was observed (Fig. 4b). This equilibrium may exist between the tautomeric and anionic forms. The other dyes (**4, 7**, and **8**) exhibit only one absorption maxima at long wavelength. This findings show that dyes **4, 7**, and **8** may exist mainly in the common anion form (for dye **4**, $\Delta\lambda_{max} = 78$ nm in methanol relative to methanol + KOH; for dye **7**, $\Delta\lambda_{max} = 29$ nm in methanol relative to methanol + KOH). This indicates that hetarylazoindole dyes **1–4, 7**, and **8** exist in a dissociated state when a small amount of base was added to each of the dye solutions in DMSO, DMF, chloroform, and methanol (Table 4).

On the other hand, λ_{max} values of the dyes in methanol showed bathochromic shifts when 0.1 ml HCl was added, being nearly the same as those observed in acetic acid. This suggests that these dyes exist in the cationic form in the acidic medium (for dye **5**, $\Delta\lambda_{max} = 27$ nm in methanol relative to methanol + HCl; for dye **1**, $\Delta\lambda_{max} = 48$ nm in methanol relative to methanol + HCl).

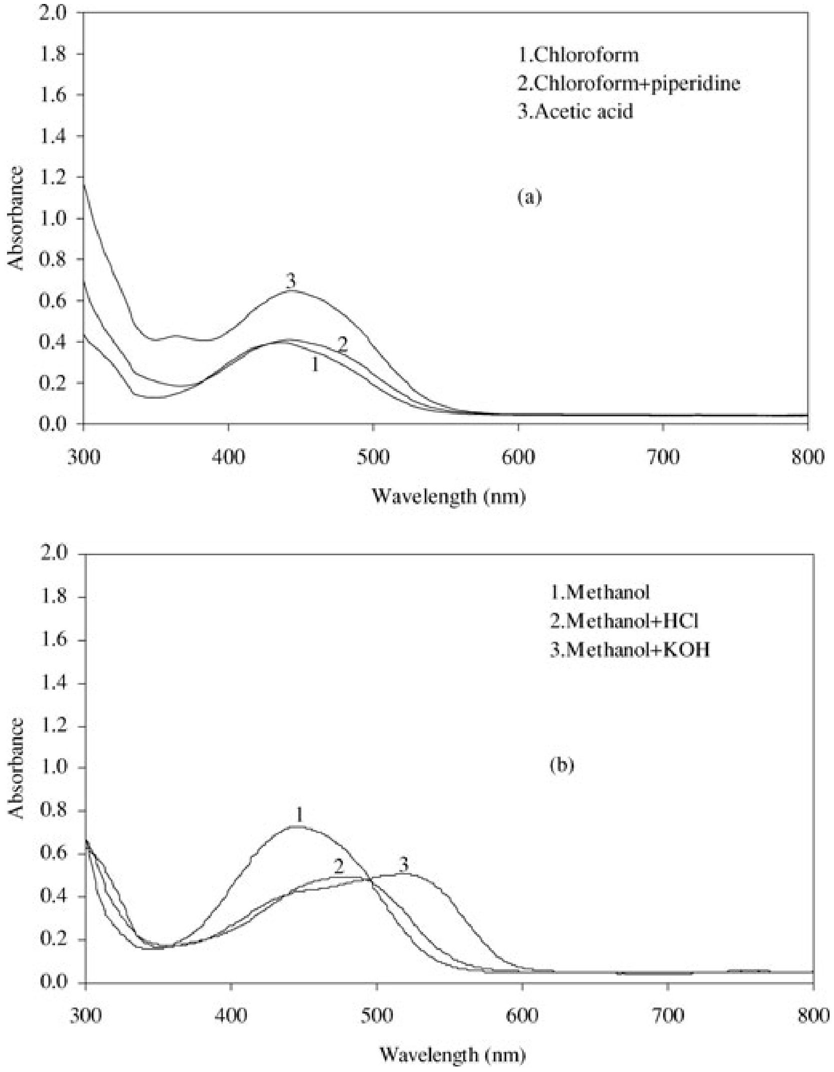


FIGURE 4 Absorption spectra of dye **3** in acidic and basic solution: (a) chloroform, chloroform + piperidine, and acetic acid; (b) methanol, methanol + HCl, and methanol + KOH.

The effect of dye concentration and temperature on absorption maxima was also examined. For dyes **1–9**, $\lambda_{\max}$ values did not change significantly with dye concentration in all solutions and in the temperature range 25°C to 70°C for dye solutions in DMSO and DMF (Table 3). These findings support the dissociation equilibrium of hetarylazoindoles in proton-accepting solvents, which do not involve a change in energy.

A thiophene ring is fused to the pyridine ring and substituted cyano group in dyes **1–6**. For dyes **1–6**, $\lambda_{\max}$ showed a bathochromic shift relative to dyes **7–9** in solvents used (for dye **3**, $\Delta\lambda_{\max} = 71$ nm relative to dye **8** in DMSO; for dye **5** $\Delta\lambda_{\max} = 42$ nm relative to dye **9** in DMSO). In addition, absorption spectra of dyes **7** and **8** change significantly in solvents used when a phenyl group was replaced with a methyl group in the indole ring (for dye **7**, $\Delta\lambda_{\max} = 19$ nm relative to dye **8** in DMSO). In contrast, absorption spectra of dyes **1–4** did not show regular variation when a phenyl group was replaced with a methyl group in the indole ring. The bathochromic and hypsochromic shifts were observed for dyes **1, 3** and dyes **2, 4**, respectively, in solvents used, when a methyl group was introduced in position 2 of the indole ring instead of a phenyl group (for dye **1**, $\Delta\lambda_{\max} = 3$ nm relative to dye **3** in DMSO; for dye **2**, $\Delta\lambda_{\max} = 16$ nm relative to dye **4** in DMSO). On the other hand, the hypsochromic and bathochromic shifts were observed for dyes **1, 2** and dyes **3, 4**, respectively, in solvents used, when a methyl group was introduced in both positions 4 and 6 of the thieno[2,3-*b*]pyridine ring instead of a phenyl group (for dye **1**, $\Delta\lambda_{max} = 8$ nm relative to dye **2** in DMSO; for dye **3**, $\Delta\lambda_{max} = 11$ nm relative to dye **4** in DMSO). In contrast, absorption spectra of dyes **5** and **6** did not change significantly in solvents used when a phenyl group was replaced with a methyl group in both positions 4 and 6 of the thieno[2,3-*b*]pyridine ring.

CONCLUSIONS

In this study, a series of novel heterocyclic disperse azo dyes were prepared by coupling 2-methylindole, 2-phenylindole, and 1-methyl-2-phenylindole with 3-amino-2-cyano-4,6-disubstituted-thieno[2,3-*b*]pyridine and 3-aminopyridine in nitrosyl sulphuric acid. These dyes were characterized by UV-Visible, FT-IR, ^{1}H NMR, and mass spectroscopic techniques. In addition, the solvent effect on the visible absorption spectra of the dyes was evaluated. It was found that the absorption maxima of these dyes strongly depend on the solvent used and vary with solvent polarity. On the other hand, the color of the dyes was discussed with respect to the nature of the heterocyclic ring and the substituents present therein. The effect of temperature, concentration, as well as acid and base on the visible absorption maxima of the dyes was also reported. Finally, it was observed that the absorption curves of the synthesized dyes were very sensitive to acid and bases.

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