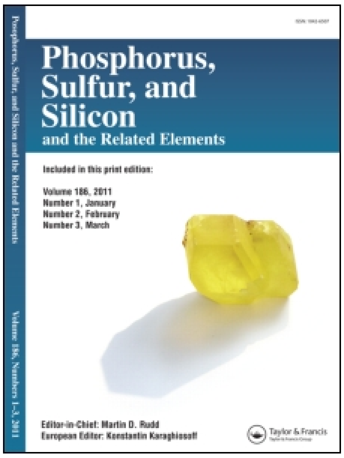

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Hetarylazoindoles 1. Synthesis, Characterization, and Spectroscopic Properties of New Hetarylazoindole Dyes

Zeynel Seferoĝlu[a]; Nermin Ertan[a]
[a] Faculty of Arts and Science, Department of Chemistry, Gazi University, Ankara, Turkey

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Hetarylazoindoles 1. Synthesis, Characterization, and Spectroscopic Properties of New Hetarylazoindole Dyes

Zeynel Seferoğlu and Nermin Ertan
Gazi University, Faculty of Arts and Science, Department of Chemistry,
Ankara, Turkey

Synthesis of some new hetarylazoindole dyes have been carried out by diazotization of 5-substituted 2-aminothiazoles in nitrosylsulphuric acid and coupling with various 2- and 1,2-disubstituted indole derivatives. The structures of the dyes were confirmed by UV-VIS, FT-IR, and ^1H NMR spectroscopy as well as by LC-MS or MS spectrometry and elemental analyses. The solvatochromism of the dyes was evaluated with respect to the absorption properties in various solvents. Absorption maxima of the dyes generally did not changed with the polarity of the solvent. The color of the dyes is discussed in relation to the substituents in the thiazole ring. The effects of an acid or a base on the visible absorption maxima of the dyes are also reported. In addition, the absorption spectra of the dyes were compared with those of corresponding model compounds, which do not exhibit azo-hydrazone tautomerism.

Keywords Hetarylazo indole dyes; heterocyclic disperse dyes; thiazolylazo dyes; solvent effect; substituent effect

INTRODUCTION

Azo dyes with heterocyclic coupling components have been investigated to produce bright and strong color shades ranging from yellow to greenish blue on synthetic fabrics. These results led to commercial products, which replaced the conventional azobenzene, disperse dyes.[1–3] There are reports of some azo dyes derived from heterocycles, such as pyridone, pyrazolone quinazoline-4-one, quinoxaline, and thiophene derivatives.[4–10] The visible absorption maxima of these dyes show wavelength mostly in the range of yellow to orange, due to poorly

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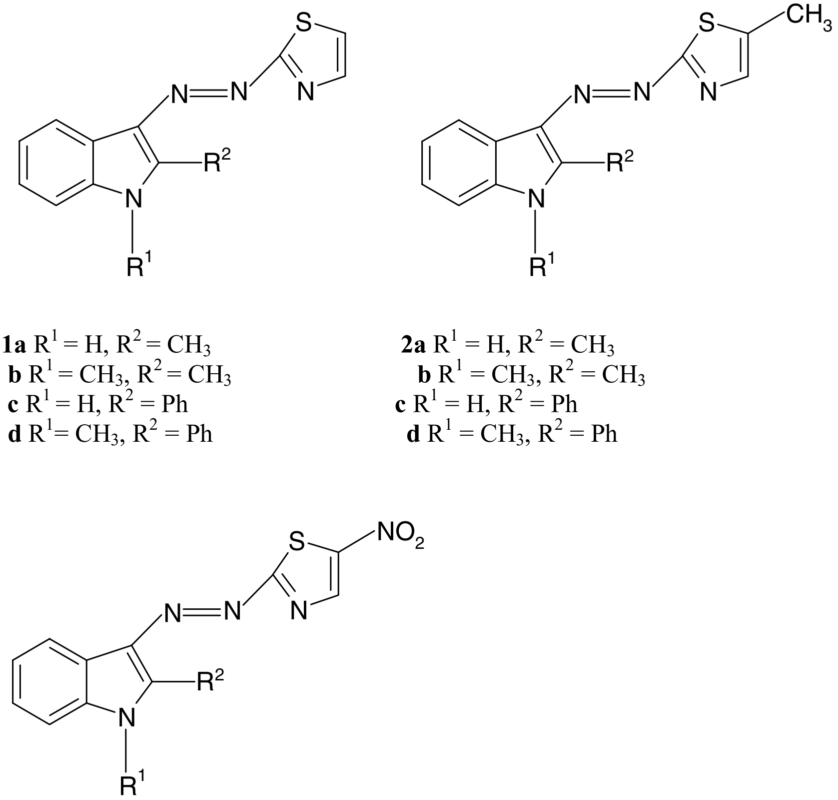
Address correspondence to Nermin Ertan, Gazi University, Faculty of Arts and Science, Department of Chemistry, 06500 Teknikokullar, Ankara, Turkey. E-mail: nertan@gazi.edu.tr

delocalized electrons in the rings of the heterocycles. However, it has also been observed that some of these dyes show 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 those based on azobenzene; 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,[15] hetarylazonaphto-quinones,[16] hetarylazopyrazolones,[17] and hetarylazoquinolines,[18] which exhibited the azo-hydrazone tautomerism and a strong solvent dependency in their absorption spectra. Although many papers described the synthesis and some properties of phenylazo indolecompounds,[19–22] only a few hetarylazo indole compounds and their alkyl cations were synthesized and used in synthetic fibers in patent literature.[22–35] These dyes have not been characterized in these patents. In our previous papers on azo indoles, we have described the synthesis and the structural and spectroscopic properties of some hetarylazo and phenylazo indole dyes obtained by diazotization of some heterocyclic and carbocyclic amines using 2- and 1,2-disubstituted indoles as coupling components.[36–46] We observed a marked difference in the absorption maxima of the dyes when the polarity of the solvent was increased. In continuation of these investigations, we report here the solvatochromic behaviour of bis-hetarylazo compounds, which do not exhibit the azo-hydrazone tautomerism, and on the evaluation of their absorption spectra in the visible range with respect to the influence of the solvent. For this purpose we have prepared three series of 3-thiazolylazo indole derivatives (**1a–d**, **2a–d**, and **3a–d)** using 2-methylindole, 1,2-dimethylindole, 2-phenylindole and 1-methyl-2-phenylindole as coupling components. The dyes **1b**, 1d, **2b**, **2d**, **3b**, and **3d** were used as model compounds. In this study, some of the dyes prepared (**1a**, **1c**, **1d**, and **3a**, Scheme 1) have been mentioned in the patent literature, but have not been characterized. The visible absorption spectra of these compounds in various solvents are discussed. The influences of the substituents at the 5-position of thiazole ring and at the 2-position of the indole nucleus on the visible absorption maxima of the dyes have been evaluated.

RESULTS AND DISCUSSION

The hetarylazoindole dyes (**1a–d**, 2a-**d**, and **3a–d)** were prepared by coupling of 2-methyl, 1,2-dimethyl, 2-phenyl and



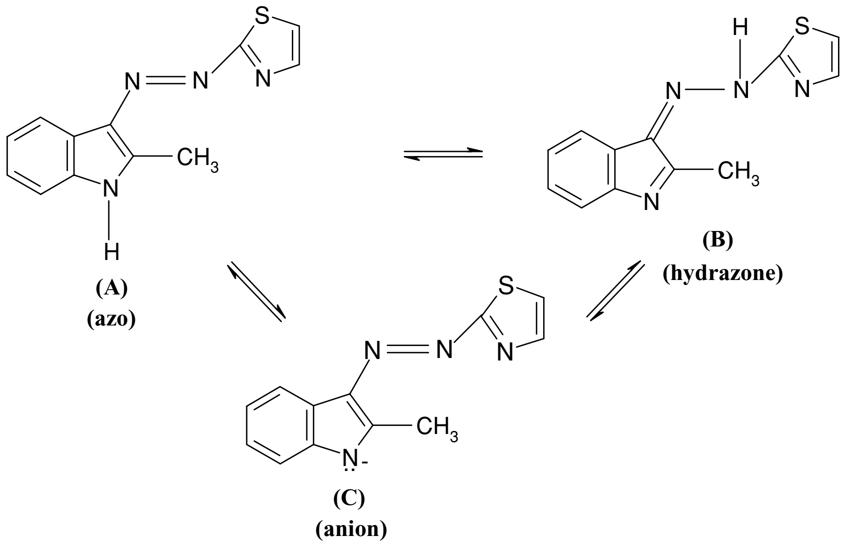
1a R^1 = H, R^2 = CH_3
b R^1 = CH_3, R^2 = CH_3
c R^1 = H, R^2 = Ph
d R^1= CH_3, R^2 = Ph

2a R^1 = H, R^2 = CH_3
b R^1 = CH_3, R^2 = CH_3
c R^1 = H, R^2 = Ph
d R^1 = CH_3, R^2 = Ph

3a R^1 = H, R^2 = CH_3
b R^1 = CH_3, R^2 = CH_3
c R^1 = H, R^2 = Ph
d R^1 = CH_3, R^2 = Ph

SCHEME 1 Structures of dyes **1–12.**

1-methyl-2-phenylindole with diazotized 2-aminothiazole, 2-amino-5-methylthiazole and 2-amino-5-nitrothiazole in nitrosyl sulphuric acid (Scheme 1). The structures of the dyes were confirmed by UV-VIS, FT-IR, and ^{1}H NMR spectroscopy as well as by LC-MS or MS spectrometry and elemental analyses. The dyes prepared from 2-methylindole (**1a**, **2a**, and **3a**) and 2-phenylindole (**1c**, **2c**, and **3c**) may exist in two possible tautomeric forms, namely the azo form **A**, and the hydrazone form **B** (Scheme 2). The deprotonation of the two tautomers leads to the common anion **C**.



SCHEME 2 Azo-hydrazone tautomeric forms and anionic form of hetarylazo indole dyes (**1a** and **c**, **2a** and **c**, **3a** and **c**).

The infrared spectra of the dyes prepared from 2-methylindole (**1a**, **2a**, and **3a**) and 2-phenylindole (**1c**, 2c, and **3c**) showed a weak and broad band within the range 3454-3278 cm^{-1} due to the -NH moiety of the indole ring. The broadening of this band suggests that this group is strongly involved in intermolecular hydrogen bonding in the solid state.[47] This band was not observed in the infrared spectra (in KBr) of the dyes prepared from 1,2-dimethylindole and 1-methyl-2-phenylindole. Characteristic bands at 3114–3031 cm^{-1} for aromatic –CH and at 2972–2903 cm^{-1} for aliphatic —CH were observed. The ^1H NMR spectra of the dyes prepared from 2-methylindole (**1a**, **2a**, and **3a**) and from 2-phenylindole (**1c**, **2c**, and **3c**) showed for the -NH group a broad signal in the range 8.95–13.82 ppm, depending on the solvent used. In the ^1H NMR spectrum of **1c** in $CDCl_3$ the signal at 8.95 ppm can be attributed to the -NH proton at 1-position of the indole ring. When the ^1H NMR spectrum of **1c** was measured in DMSO-d_6, the —NH signal shifted to lower field by 3.88 ppm and appeared at 12.83 ppm.[47] On the other hand, the ^1H NMR chemical shift of the -NH proton in **1a**, **1c**, **2a**, **2c**, **3a** and **3c** in DMSO-d_6 and $CDCl_3$/DMSO-d_6 mixtures was within the range of 11.64–13.82 ppm. This downfield shift in DMSO-d_6 is probably due to intermolecular hydrogen bonding between the indole —NH and DMSO. Assignments for the signal of the —NH proton of the indole ring are in accord with data for analogous indole derivatives.[48]

It was reported that the resonance of the hydrazone —NH proton in o- and p-hydroxyazo compounds appears at approximately 13.0–16.0 ppm.[49—50] These results suggest that the dyes **1a**, **1c**, **2a**, **2c**, **3a**, and **3c** are predominantly in the azo form in the solid state and in solution (Scheme 2).

Solvent Effect on the Absorption Spectra

The absorption spectra of the new dyes (**1a–d**, **2a–d**, and **3a–d)** were recorded in various solvents at a concentration range of approximately 10^{-6}–10^{-8} M and at different concentrations because of solubility problems. The results are given in Table I. Although many papers on azo-hydrazone tautomerism of hydroxyazo dyes have been published, the assignment of the tautomeric structure is difficult because the tautomeric equilibrium strongly depends on the nature of the corresponding medium. On the other hand, it was observed that the absorption spectra of hetarylazo dyes exhibited a strong dependency on the solvent. In order to settle this assignment problem, we prepared 1,2-disubstituted indole derivatives of the dyes as model compounds and compared their absorption spectra in various solvents with those of the other dyes. The model compounds exist in the azo form and their absorption maxima in different solvents were found to show little dependency on the solvent except in the case of acetic acid (Table I). For example, λ_{max} for **1b** are 438 nm in chloroform, 455 nm in acetic acid, 444 nm in methanol, 438 nm in acetonitrile, 443 nm in DMF, and 449 nm in DMSO. Similar results were observed for λ_{max} of the other model compounds. The small shifts in λ_{smax} of the model compounds in different solvents

TABLE I Influence of the Solvent on λ_{max} (nm) of Dyes 1–12

Dye no	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
1a	441,421s	438,418s	411,435s	419,439s	477	415,437s
1b	449,418s	443,418s	438,419s	444,419s	455,421s	438,419s
1c	465,432s	467,432s	442	459	488	437,465s
1d	452,429s	449,428s	431,449s	444	487	431,454s
2a	448,417s	443,416s	414,438s	444,418s	491	416,437s
2b	448,417s	444,417s	438,420s	443,417s	456,420s	442,420s
2c	469	471	453	464	483	452
2d	460	456	450	453	501	451
3a	525,399	586,393	504,425	509,429	502	504,424s
”3b	531	527	517	522	515	514
3c	605	603	593	539	527	526
3d	538	532	525	522	514	524

S: shoulder

are due to solute-solvent interactions.[51] The absorption maxima of the model compounds in acetic acid were observed in the range of 455–515 nm. The observed large bathochromic shifts are considered to be the consequence of protonation of the nitrogen atom in the thiazole ring. It has been reported that the protonation of the nitrogen atom of heteroaromatic rings in acidic media sometimes leads to a bathochromic shift of the absorption bands.[52]

The absorption band of dye **1a** and **1b** shows a small bathochromic shift, $\Delta\lambda_{max} = 1\text{-}8$ nm, with the change of solvent except in the case of acetic acid. This is attributed to substituent effect. The same shift was observed for the other dyes except the nitro substituted compounds. It was found, that the absorption maxima of the nitro substituted compounds showed larger bathochromic shifts in DMSO and DMF as compared to the shifts in other solvents (for **3a**, λ_{max} values are 525, 399 nm in DMSO, 586, 393 nm in DMF, 502 nm in acetic acid; for **3b**, λ_{max} values are 531 in DMSO, 527 nm in DMF, 515 nm in acetic acid; for **3c**, λ_{max} values are 605 in DMSO, 603 nm in DMF, 527 nm in acetic acid; for **3d** λ_{max} values are 538 nm in DMSO, 532 nm in DMF, 514 nm in acetic acid).

The absorption spectra of the dyes **2c**, **2d**, and **3c–d** showed only one absorption maximum in all of the solvents used, whereas the other dyes prepared showed two absorption maxima or one absorption maximum with a shoulder in all of the solvents used. The shifts of **2c** in various solvents are shown in Figure 1. It was observed that the λ_{max} values

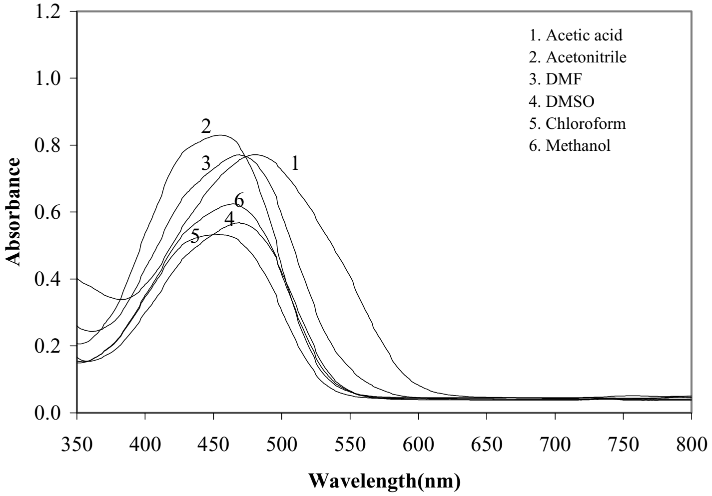


FIGURE 1 Absorption spectra of dye **7** in various solvents.

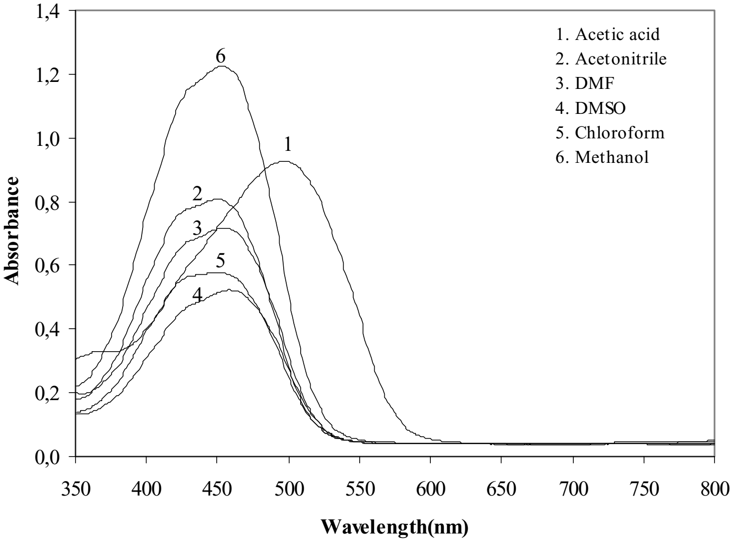


FIGURE 2 Absorption spectra of dye **8** in various solvents.

of **2c** and its model compound **2d** have similar absorption maxima in all of the solvents investigated (Figure 2). Therefore, dye **2c** is present in the azo form in all of the solvents used. In addition, compound **3a** showed two absorption maxima or shoulder in DMSO, DMF, acetonitrile, methanol and chloroform while dye **3b** showed one absorption maximum in all of the solvents used. Two absorption maxima may indicate the presence of an azo-hydrazone tautomeric equilibrium or of equilibrium between one of the tautomeric forms and an anionic form. However, **3c** showed one maximum in all of the solvents used, which indicates that the compound is present in only one tautomeric form (azo form) in these solvents. It was observed that λ_{max} values of **3c** and its model compound **3d** have similar absorption maxima in these solvents.

The effect of an acid or a base on the absorption maxima of the dyes in solution was also investigated and the results are shown in Table II. The absorption maxima of the dyes in DMSO and DMF were quite sensitive to the addition of piperidine, with exception of the model compounds (**1b**, **1d**, **2b**, **2d**, **3b**, and **3d**). λ_{max} of the dyes (except the model compounds) showed large bathochromic shifts when a small amount of piperidine was added to each of the solutions in DMSO and DMF. A typical example is shown in Figure 3. For **2c**, $\Delta\lambda_{max}$ is 44 nm in DMSO + piperidine relative to DMSO and 42 nm in DMF + piperidine relative to DMF. There was no significant change in the spectra of the compound **3c** when a small amount of piperidine was added to its solutions

TABLE II Absorption Maxima of Dyes 1–12 in Acidic and Basic Solution

	λ_{max}(nm)								
Dye	DMSO	DMSO+ piperidine	DMF	DMF+ piperidine	Methanol	Methanol+ KOH	Methanol + HCl	Chloroform	Chloroform + piperidine
1a	441,421s	486	438,418s	481	419,439s	467	492	415,437s	418,440s
1b	449,418s	449,418s	443,418s	442,418s	444,419s	436,420s	487	438,419s	436,418s
1c	465,432s	513	467,432s	509	459	496	517	437,465s	449
1d	452,429s	450,429s	449,428s	443,428s	444	444	506	431,454s	433,456s
2a	448,417s	486	443,416s	470,417s	444,418s	459,417s	496	416,437s	418,441
2b	448,417s	448,417s	444,417s	442,417s	443,417s	441,417s	495	442,420s	441,420s
2c	469	513	471	513	464	477	521	452	461
2d	460	459	456	455	453	454	512	451	449
3a	525,399	587,442	586,393	586, 442	509,429	565,438	510	504,424s	538
3b	531	531	527	526	522	521	523	514	514
3c	605	604	603	602	539	583	535	526	537
3d	538	540	532	536	522	527	530	524	524

S: shoulder

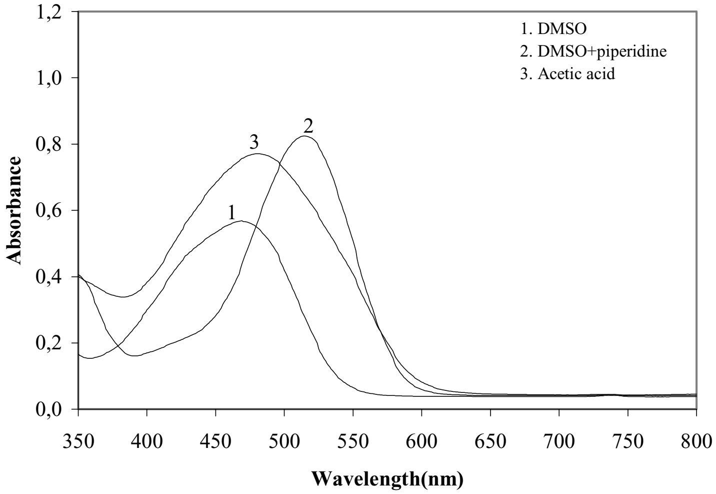


FIGURE 3 Absorption spectra of dye **7** in acidic and basic solution.

in DMSO. Similar effects were observed when a small amount of the piperidine was added to the solution of **3c** in DMF. This indicates that compound **3c** exist in its anionic form in DMSO and DMF. Same results were observed for **3a** in DMF. On the other hand, λ_{max} of the dyes (except the model compounds) showed small bathochromic shifts when a small amount of piperidine was added to each of the dye solutions in chloroform. For compound **2c** $\Delta\lambda_{max}$ is 9 nm in chloroform + piperidine relative to chloroform; similarly for **3c** $\Delta\lambda_{max}$ is 11 nm in chloroform + piperidine relative to chloroform.

When a small amount of 0.1 M KOH was added to the methanolic solutions of the dyes (except the model compounds), $\Delta\lambda_{max}$ values showed bathochromic shifts and only one absorption maximum was observed except for **2a** and **3a**. These dyes (**2a** and **3a**) showed two absorption maxima or one absorption maximum with a shoulder in basic methanolic solution. The dyes **1a–d** and **2a–d** may exist in the anionic form in basic methanolic solution. For compound **1c** $\Delta\lambda_{max}$ is 37 nm in methanol + KOH relative to methanol; similarly for **3c** $\Delta\lambda_{max}$ is 44 nm in methanol + KOH relative to methanol. When a small amount of 0.1 M HCl was added to the methanolic solutions of dyes (except for compounds **3a-d**), the λ_{max} values showed large bathochromic shifts and also only one absorption maximum was observed. This indicates that the dyes **1a–d** and **2a–d** exist in the cationic form in acidic methanolic solution. For compound **2c** $\Delta\lambda_{max}$ is 57 nm in methanol + HCl relative to methanol; similarly for **2d** $\Delta\lambda_{max}$ is 59 nm in methanol + HCl relative to methanol (Figure 4).

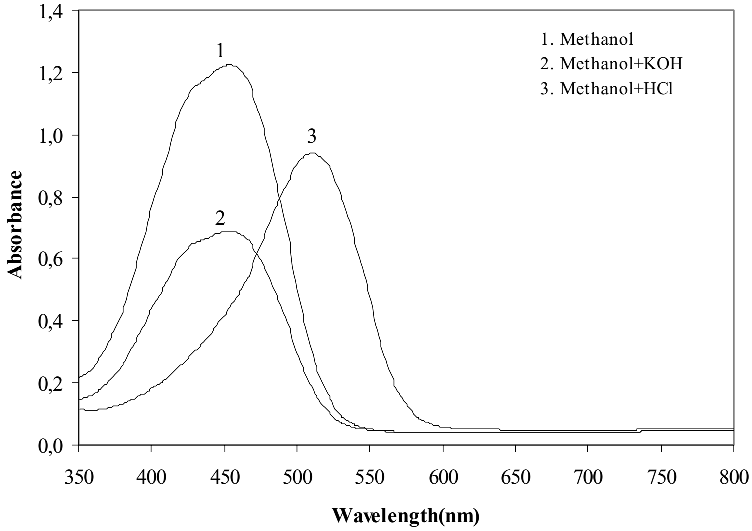


FIGURE 4 Absorption spectra of dye **8** in acidic and basic solution.

The effects of dye concentration and temperature on the positions of the absorption maxima were examined. The λ_{max} values of the dyes did not change with concentration in all solutions investigated. Since in these experiments the dyes were not fully dissolved in acetonitrile, methanol, acetic acid or chloroform (undissolved material was filtered off), the actual concentration of dye in the solution was not precisely known. More dilute solutions were therefore prepared, and it was found in all cases, that λ_{max} was unaffected by the dye concentration. When solutions of the dyes **1a–d**, **2a–d**, and **3a–d** in DMSO and DMF were examined over the temperature range 25–70°C , the λ_{max} values did not change significantly. These findings support the dissociation equilibrium of hetarylazoindoles in proton-accepting solvents, which does not involve a change in energy.

Substituent Effect on the Absorption Spectra in Various Solvents

The effect of the substituents in the hetarylazoindole dyes was also studied. As becomes apparent from Table II, introduction of an electron donating -CH_3 group at 5-position of the thiazole ring results in small bathochromic shifts in DMSO, DMF, acetonitrile and methanol. For compound **2c** $\Delta\lambda_{max}$ values are 4 nm in DMSO, 4 nm in DMF, 11 nm in acetonitrile, and 5 nm in methanol relative to λ_{max} of **1c** in the same solvents. The introduction of the strong electron-withdrawing nitro group at the 5-position of the thiazole ring results in large bathochromic shifts in all of the solvents investigated. For compound **3c** $\Delta\lambda_{max}$ values are 140 nm in DMSO, 136 nm in DMF, 151 nm in acetonitrile, 80 nm in methanol, 39 nm in acetic acid, and 89 nm in chloroform relative to λ_{max} of **1c** in the same solvents. Similar shifts were observed for **3a** and **3b** in DMF ($\Delta\lambda_{max} = 59$ nm) and for **3c** and **3d** in DMSO ($\Delta\lambda_{max} = 67$ nm) and in DMF ($\Delta\lambda_{max} = 71$ nm). These large bathochromic shifts suggest that for the nitro substituted compounds **3a** – **3d** azo-hydrazone or anionic equilibria are present in DMSO and DMF. The introduction of an electron accepting nitro group in the 5-position of the thiazole ring causes large bathochromic shifts of the absorption bands of the dyes. This could be attributed to a more extensive π-conjugation in these compounds. The absorption spectra of the dyes showed bathochromic shifts in all solvents used when the phenyl group at the 2-position of indole rings is replaced with the methyl group. For compound **1a** $\Delta\lambda_{max}$ values are 24 nm in DMSO, 29 nm in DMF, 31 nm in acetonitrile, 10 nm in methanol, 11 nm in acetic acid and 22 nm in chloroform relative to $\lambda_{max}$of **1c** in the same solvents. In general the same results are observed also for the model compounds. For compound **2b** $\Delta\lambda_{max}$ values are 12 nm in DMSO, 12 nm in DMF, 12 nm in acetonitrile, 10 nm in methanol, 45 nm in acetic acid and 9 nm in chloroform relative to λ_{max} of **2d** in the same solvents. These behaviors may be attributed to the π-donor properties of the phenyl rings.

As a result, the dyes prepared (**1a-d**, **2a-d**, and **3a-d)** might be used for polyester materials as disperse dyes. In addition, the dyes derived from the model compounds could be used as cationic dyes.

EXPERIMENTAL

The chemicals used for the syntheses of all dyes were obtained from Aldrich and were used without further purification. Solvents of spectroscopic grade purity were used. IR spectra were recorded with a Mattson 1000 FT-IR spectrophotometer in KBr. ^{1}H NMR spectra were recorded with a Bruker-Spectrospin Avance DPX 400 in DMSO-d_6 and $CDCl_3$ with TMS as internal reference. Chemical shifts are expressed in δ units (ppm). Ultraviolet-visible (UV-VIS) absorption spectra were recorded with a Analytik-Jena Specord 200 spectrophotometer at the wavelength of maximum absorption (λ_{max}) in dimethylsulphoxide (DMSO), dimethylformamide (DMF), acetonitrile, methanol, acetic acid and chloroform. Changes of λ_{max} were investigated by adding of 0.1 mL of piperidine to 1 mL of the dye solutions in chloroform, DMSO and DMF. Similarly 0.1 mL of potassium hydroxide (0.1 M aqueous soln) or 0.1 mL of hydrochloric acid (0.1 M aqueous soln) was added to 1 mL of the dye solutions in methanol. Mass spectra were recorded with a Agilent 5973 Network Mass Selective Detector instrument equipped with SIS (Direct Insertion Probe) in electron impact mode at 70 and 100 eV and with an AGILENT 1100 MSD instrument. Elemental analyses were obtained with a LECO CHNS 932 instrument by the Turkish Research Council Laboratories (Center of Science and Technology Research of Turkey). All melting points are uncorrected and given in °C.

Preparation of the Hetarylazoindole Dyes

Diazotization of various heterocyclic amines was performed with nitrosylsulphuric acid. A typical procedure is described below for 2-aminothiazole; all other dyes were prepared in a similar manner. The yields of the dyes are in range of 65–90%.

2-Methyl-3-(thiazol-2-yldiazenyl)-1H-indole (1a)

2-Aminothiazole (0.2 g, 2 mmol) was dissolved in hot glacial acetic acid—propionic acid mixture (2:1, 6.0 mL) and was rapidly cooled in an salt/ice bath to $-5°$C. The mixture was stirred for 1 h at 0–5°C. Then the resulting liquor was added in portions during 30 min to a cold solution of nitrosylsulphuric acid, prepared from sodium nitrite (0.15 g) and concentrated sulphuric acid (3 mL) at 50°C . The mixture was stirred for additional 2 h at 0°C . The excess of nitrous acid was destroyed by addition of urea. The resulting diazonium salt was cooled in an salt/ice bath. 2-methylindole (0.26 g, 2 mmol) was dissolved in a mixture of acetic acid and propionic acid (3:1, 8.0 mL) and cooled in a salt/ice bath. To this cooled solution the cold diazonium solution was added dropwise with stirring. The solution was stirred at 0–5°C for 2 h and while the pH of the reaction mixture was maintained at 4–6 by simultaneous addition of saturated aqueous sodium carbonate solution. The mixture was stirred for further 1 h at 5°C . The resulting product was filtered, washed with water, dried and crystallized from ethanol to give orange crystals. Yield: 0.39 g, 81%; m.p: 212–213°C), FT–R (KBr) $\nu_{\max}$: 3391 (indole —NH), 3050, 3031 (aromatic C—H), 2921, 2851 (aliphatic C—H), 1503 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d$_6$/CDCl$_3$): $\delta = 12.78$ (br, 1H, indole -NH), 8.39 (m, 1H), 7.81 (d, 1H), 7.37 (d, 1H), 7.27 (d, 1H), 7.23-7.19 (m, 2H). Anal. Calcd. for $C_{12}H_{10}N_4S$: C, 54.48; H, 4.16; N, 23.12; S, 13.23%. Found: C, 54.59; H, 4.19; N, 22.96; S, 13.22%. MS (m/z, 70 eV): 242 (M$^+$).

1,2-Dimethyl-3-(thiazol-2-yldiazenyl)-1H-indole (1b)

This compound was obtained from 2-aminothiazole and 1,2-dimethylindole as orange crystals. Yield: 0.44 g, 86%%; m.p.:

168–170°C; FT–IR (KBr) ν_{max}: 3051 (aromatic C—H), 2941 (aliphatic C—H), 1527 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ = 8.31 (m, 1H), 7.87 (d, 1H), 7.63 (m, 1H), 7.56 (d, 1H), 7.39-7.31 (m, 2H), 3.83 (s, 3H, —NCH$_3$), 2.79 (s, 3H). Anal. Calcd. for $C_{13}H_{12}N_4S$: C, 60.92; H, 4.72; N, 21.86; S, 12.51%. Found: C, 60.90; H, 4.66; N, 21.90; S, 12.48%. LC-MS (m/z, 100 eV): 257.1 (48.7%) (M+1)$^+$, 172.1 (100%), 144.1 (58.0%).

2-Phenyl-3-(thiazol-2-yldiazenyl)-1H-indole (1c)

This compound was obtained from 2-aminothiazole and 2-phenylindole as red crystals. Yield: 0.42 g, 69%; m.p.: 280°C (dec.); FT–IR (KBr) ν_{max}: 3454 (indole —NH), 3114, 3056 (aromatic C—H), 1464 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 8.95 (br, 1H, indole —NH), 8.69 (m, 1H), 8.07 (m, 1H), 7.93 (d, 1H), 7.62–7.52 (m, 4H), 7.48–7.33 (m, 4H). Anal. Calcd. for $C_{17}H_{12}N_4S$: C, 67.08; H, 3.97; N, 18.41; S, 10.53%. Found: C, 67.19; H, 4.06; N, 18.59; S, 10.49%. MS (m/z, 70 eV): 304 (M$^+$).

1-Methyl-2-phenyl-3-(thiazol-2-yldiazenyl)-1H-indole (1d)

This compound was obtained from 2-aminothiazole and 1-methyl-2-phenylindole as orange crystals. Yield: 0.49 g, 77%; m.p.: 196–199°C; FT–IR (KBr) ν_{max}: 3070 (aromatic C—H), 2935 (aliphatic C—H), 1464 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d$_6$/CDCl$_3$): δ = 8.34 (m, 1H), 7.58 (d, 1H), 7.50-7.10 (m, 8H), 6.92 (d, 1H), 3.68 (s, 3H, —NCH$_3$). Anal. Calcd. for $C_{18}H_{14}N_4S$: C, 67.90; H, 4.43; N, 17.60; S, 10.07%. Found: C, 67.98; H, 4.46; N, 17.59; S, 10.09%. MS (m/z, 70 eV): 318 (M$^+$).

2-Methyl-3-(5-methylthiazol-2-yldiazenyl)-1H-indole (2a)

This compound was obtained from 2-amino-5-methylthiazole and 2-methylindole as orange crystals. Yield: 0.41 g, 80%; m.p.: 243°C (dec.); FT-IR (KBr) ν_{max}: 3442 (indole —NH), 3050, 3034 (aromatic C—H), 2954, 2928 (aliphatic C—H), 1541 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d$_6$/CDCl$_3$): δ = 11.64 (br, 1H, indole —NH), 7.93 (m, 1H), 7.16 (s, 1H), 6.91 (m, 1H), 6.77 (m, 2H), 2.44 (s, 3H), 2.04 (s, 3H). Anal. Calcd. for $C_{13}H_{12}N_4S$: C, 60.92; H, 4.72; N, 21.86; S, 12.51%. Found: C, 61.09; H, 4.80; N, 22.01; S, 12.44%. MS (m/z, 70 eV): 256 (M$^+$).

1,2-Dimethyl -3-(5-methylthiazol-2-yldiazenyl)-1H-indole (2b)

This compound was obtained from 2-amino-5-methylthiazole and 1,2-dimethylindole as orange crystals. Yield: 0.49 g, 90%; m.p.: 200–202°C ; FT–IR (KBr) ν_{max}: 3067 (aromatic C—H), 2910 (aliphatic C—H), 1519 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ = 8.28 (m, 1H), 7.62 (m, 1H), 7.57 (s, 1H), 7.38–7.27 (m, 2H), 3.81 (s, 3H, -NCH$_3$), 2.79 (s, 3H), 2.42 (s, 3H). Anal. Calcd. for $C_{14}H_{14}N_4S$: C, 62.20; H, 5.22; N, 20.72; S, 11.86%.

Found: C, 62.39; H, 5.10; N, 20.61; S, 11.84%. LC-MS (m/z, 100 eV): 271.1 (100%) $(M+1)^+$, 172.1 (83.7%), 144.1 (13.0%).

2-Phenyl-3-(5-methylthiazol-2-yldiazenyl)-1H-indole (2c)

This compound was obtained from 2-amino-5-methylthiazole and 2-phenylindole as orange crystals. Yield: 0.41 g, 65%; m.p.: 285°C (dec.); FT–IR (KBr) ν_{max}: 3448 (indole —NH), 3070, 3052 (aromatic C—H), 2954, 2903 (aliphatic C—H), 1464 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): $\delta = 12.31$ (br, 1H, indole -NH), 8.42 (m, 1H), 8.08 (m, 2H), 7.53-7.42 (m, 5H), 7.28–7.17 (m, 2H), 2.48 (s, 3H). Anal. Calcd. for $C_{18}H_{14}N_4S$: C, 67.90; H, 4.43; N, 17.60; S, 10.07%. Found: C, 68.04; H, 4.44; N, 17.59; S, 10.11%. MS (m/z, 70 eV): 318 (M^+).

1-Methyl-2-phenyl-3-(5-methylthiazol-2-yldiazenyl)-1H-indole (2d)

This compound was obtained from 2-amino-5-methylthiazole and 1-methyl-2-phenylindole as orange crystals. Yield: 0.56 g, 84%; m.p.: 222–224°C), FT–IR (KBr) ν_{max}: 3044 (aromatic C—H), 2940, 2920 (aliphatic C—H), 1464 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): $\delta = 8.72$ (m, 1H), 7.70–7.40 (m, 9H), 3.88 (s, 3H, $-NCH_3$), 2.44 (s, 3H). Anal. Calcd. for $C_{19}H_{16}N_4S$: C, 68.65; H, 4.85; N, 16.86; S, 9.65%. Found: C, 68.58; H, 4.88; N, 16.79; S, 9.66%. MS (m/z, 70 eV): 332 (M^+).

2-Methyl-3-(5-nitrothiazol-2-yldiazenyl)-1H-indole (3a)

This compound was obtained from 2-amino-5-nitrothiazole and 2-methylindole as violet purple powder. Yield: 0.45 g, 79%; m.p.: 194°C (dec.); FT–IR (KBr) ν_{max}: 3409–3278 (indole —NH), 3072, 3056 (aromatic C—H), 2972, 2921 (aliphatic C—H), 1562 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): $\delta = 12.67$ (br, 1H, indole —NH), 8.48 (s, 1H), 8.31 (m, 1H), 7.32 (m, 1H), 7.25 (m, 2H), 2.71 (s, 3H). Anal. Calcd. for $C_{12}H_9N_5O_2S$: C, 50.17; H, 3.16; N, 24.38; S, 11.16%. Found: C, 50.39; H, 3.29; N, 24.46; S, 11.25%. MS (m/z, 70 eV): 287 (M^+).

1,2-Dimethyl-3-(5-nitrothiazol-2-yldiazenyl)-1H-indole (3b)

This compound was obtained from 2-amino-5-nitrothiazole and 1,2-dimethylindole as dark red powder. Yield: 0.45 g, 77%; m.p.: 234°C (dec.); FT–IR (KBr) ν_{max}: 3093 (aromatic C—H), 2940, 2920 (aliphatic C—H), 1490 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): $\delta = 8.78$ (s, 1H), 8.27 (m, 1H), 7.50 (m, 1H), 7.44 (m, 2H), 3.88 (s, 3H, $-NCH_3$), 2.79 (s, 3H). Anal. Calcd. for $C_{13}H_{11}N_5O_2S$: C, 51.82; H, 3.68; N, 23.24; S, 10.64%. Found: C, 51.59; H, 3.62; N, 23.11; S, 10.44%. LC-MS (m/z, 100 eV): 302.1 (100%) $(M+1)^+$, 172.1 (76.7%), 144.2 (42.3%).

2-Phenyl-3-(5-nitrothiazol-2-yldiazenyl)-1H-indole (3c)

This compound was obtained from 2-amino-5-nitrothiazole and 2-phenylindole as violet purple powder. Yield: 0.46 g, 66%; m.p.: 234°C (dec.), FT–IR (KBr) ν_{max}: 3442 (indole –NH), 3056 (aromatic C–H), 1529 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): $\delta = 13.82$ (br, 1H, indole –NH), 8.31 (m, 2H), 8.12 (m, 1H), 7.66–7.33 (m, 7H). Anal. Calcd. for $C_{17}H_{11}N_5O_2S$: C, 58.44; H, 3.17; N, 20.05; S, 9.18%. Found: C, 58.59; H, 3.26; N, 20.19; S, 9.25%. MS (m/z, 70 eV): 349 (M^+).

1-Methyl-2-phenyl-3-(5-nitrothiazol-2-yldiazenyl)-1H-indole (3d)

This compound was obtained from 2-amino-5-nitrothiazole and 1-methyl-2-phenyl-indole as violet purple powder. Yield: 0.54 g, 75%; m.p.: 236°C (dec.); FT–IR (KBr) ν_{max}: 3056, 3031 (aromatic C–H), 2935 (aliphatic C–H), 1496 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): $\delta =$ 8.53 (s, 1H), 7.62–7.41 (m, 7H), 7.28 (m, 1H), 7.08 (m, 1H), 3.78 (s, 3H, –NCH_3). Anal. Calcd. for $C_{18}H_{13}N_5O_2S$: C, 59.49; H, 3.61; N, 19.27; S, 8.82%. Found: C, 59.77; H, 3.66; N, 19.36; S, 8.85%. MS (m/z, 70 eV): 363 (M^+).

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