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Synthesis of New Hetarylazoindole Dyes from Some 2-Aminothiazole Derivatives*

A. Saylam, Z. Seferoglu, and N. Ertan

Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölumü, 06500 Teknikokullar, Ankara, Turkiye
phone: +(90312)2323588; fax: +(90312)2323226; e-mail: znseferoglu@yahoo.com; znseferoglu@gazi.edu.tr

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Abstract—A new series of heterocyclic disperse dyes were prepared by diazotization of some 2-aminothiazole derivatives and subsequent coupling with indole compounds. The dyes were characterized by UV-Vis, FT-IR, ^{1}H NMR, and mass spectra (LC–MS). Solvent effects on their visible absorption spectra were estimated. The color of the dyes is discussed with respect to the substituent therein. The effects of acids and bases on the visible absorption maxima of the dyes are also reported. Replacement of methyl group in the 4-position of the thiazole ring by phenyl group leads to red shift of the absorption maximum due to π-electron-donating properties of the phenyl group, while weak electron-withdrawing chlorine or bromine atom in the *para*-position of the phenyl group in the 2-amino-4-phenylthiazole fragment induce a small blue shift relative to 2-amino-4-phenylthiazole derivatives. Introduction of an electron-withdrawing 4-nitrophenylsulfonyl group into the thiazole ring produces bathochromic shift of the absorption maximum in all solvents.

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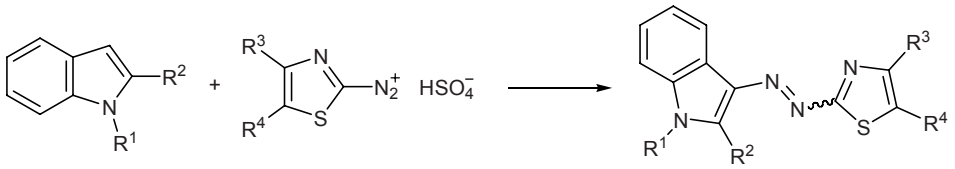
Disperse dyes are colorants that are poorly soluble in water and are suitable for dyeing and printing hydrophobic fibers and fabrics in the disperse colloidal form [1]. Azo dyes constitute the largest group of disperse dyes. The use of heterocyclic azo and diazo components in the synthesis of disperse azo dyes is well-established, and the resultant dyes exhibit good tinctorial strength and brighter dyeing than those derived from aniline-based components [2–4]. In the recent years many research teams reported on the synthesis of disperse azo dyes from heterocyclic amines and various heterocyclic coupling components and their applications for dyeing polyester fabrics [5, 6]. In addition, Wang and co-worker [7] described the synthesis of azo dyes from 2-amino-4-(*p*-substituted phenyl)thiazole derivatives and various heterocyclic coupling components and studied their spectroscopic properties with respect to substituent and solvent polarity. On the other hand, the use of amino-substituted thiazoles as very electronegative diazo component produces a pronounced bathochromic shift as compared to the corresponding benzoid compounds [8–12]. Moreover, some 2-aminothiazole derivatives have been used as a π-bridged chromophore for the prepara-

Scheme 1.

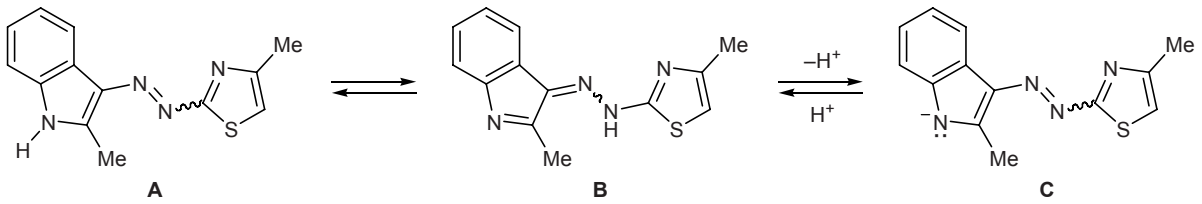


I–XVIII

I, $R^1 = R^4 = H$, $R^2 = R^3 = Me$; **II**, $R^1 = R^4 = H$, $R^2 = Ph$, $R^3 = Me$; **III**, $R^1 = R^3 = Me$, $R^2 = Ph$, $R^4 = H$; **IV**, $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = EtOCOCH_2$; **V**, $R^1 = R^4 = H$, $R^2 = Ph$, $R^3 = EtOCOCH_2$; **VI**, $R^1 = Me$, $R^2 = Ph$, $R^3 = EtOCOCH_2$, $R^4 = H$; **VII**, $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = Ph$; **VIII**, $R^1 = R^4 = H$, $R^2 = R^3 = Ph$; **IX**, $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = H$; **X**, $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = 4\text{-}ClC_6H_4$; **XI**, $R^1 = R^4 = H$, $R^2 = Ph$, $R^3 = 4\text{-}ClC_6H_4$; **XII**, $R^1 = Me$, $R^2 = Ph$, $R^3 = 4\text{-}ClC_6H_4$, $R^4 = H$; **XIII**, $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = 4\text{-}BrC_6H_4$; **XIV**, $R^1 = R^4 = H$, $R^2 = Ph$, $R^3 = 4\text{-}BrC_6H_4$; **XV**, $R^1 = Me$, $R^2 = Ph$, $R^3 = 4\text{-}BrC_6H_4$, $R^4 = H$; **XVI**, $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = 4\text{-}O_2NC_6H_4SO_2$; **XVII**, $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = 4\text{-}O_2NC_6H_4SO_2$; **XVIII**, $R^1 = Me$, $R^2 = Ph$, $R^3 = H$, $R^4 = 4\text{-}O_2NC_6H_4SO_2$.

* The text was submitted by the authors in English.

Scheme 2.



tion of polymers with nonlinear optical properties [13]. Some thiazole derivatives are important from the pharmaceutical viewpoint. Heterocyclic systems containing a 1,3-thiazole ring exhibit a wide spectrum of biological activity, including antiviral and antifungal. 1,3-Thiazole ring was identified as a base structural unit of a number of biologically active natural products [14–16] and pharmacologically active compounds [17, 18]. Biological activity of thiazole derivatives originates mainly from their structural, electronic, and spectroscopic similarity to imidazole entities of proteins [19–21].

Many patents and papers described the synthesis and some properties of carbocyclic azo indole compounds [22–27], but only a few data are available on hetarylazo indole derivatives from patent literature [28–38]. We previously synthesized some hetarylazo indole dyes and evaluated their spectroscopic properties [39]. We now report on the synthesis of six series of 3-(1,3-thiazol-2-ylazo)indole derivatives **I**–**XVIII** using 2-methyl-1*H*-indole, 2-phenyl-1*H*-indole, and 1-methyl-2-phenyl-1*H*-indole as coupling components. The visible absorption spectra of these compounds in various solvents were discussed. In addition, spectroscopic properties of the azo dyes were examined with respect to the effects of substituents present in the thiazole and indole rings.

Hetarylazo indole dyes **I**–**XVIII** were prepared by diazo coupling of 2-methyl-, 2-phenyl-, and 1-methyl-2-phenyl-1*H*-indoles with diazotized 4-methyl-1,3-thiazol-2-amine, ethyl 2-amino-1,3-thiazol-4-ylacetate, 4-phenyl-1,3-thiazol-2-amine, 4-(4-chlorophenyl)-1,3-thiazol-2-amine, 4-(4-bromophenyl)-1,3-thiazol-2-amine, and 5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-amine in nitrosyl sulfuric acid (Scheme 1). The structure of the resulting dyes was confirmed by the FT-IR, ^{1}H NMR, and mass spectra. Dyes **I**, **IV**, **VII**, **X**, **XIII**, and **XVI** prepared from 2-methyl-1*H*-indole and compounds **II**, **V**, **VIII**, **XI**, **XIV**, and **XVII** obtained from 2-phenyl-1*H*-indole may exist as two tautomers, azo **A** and hydrazone **B**, as shown in Scheme 2. Deprotonation of both tautomers could lead to common anion **C**.

The IR spectra of **I**, **II**, **IV**, **V**, **VII**, **VIII**, **X**, **XI**, **XIII**, **XIV**, **XVI**, and **XVII** in KBr contained a broad absorption band in the region 3442–3210 cm^{-1} due to indole NH group. No such band was present in the IR spectra of *N*-methyl-2-phenylindole derivatives **III**, **VI**, **IX**, **XII**, **XV**, and **XVIII**. The spectra of all azo dyes **I**–**XVIII** displayed absorption bands in the regions 3082–3050 (C–H$_{arom}$) and 2973–2870 cm^{-1} (C–H$_{aliph}$). In the ^{1}H NMR spectra of **XVI** and **XVII** in DMSO-d_6–$CDCl_3$ we observed a signal at δ 12.54–12.51 ppm from the NH proton. The other dyes (except for those derived from 1-methyl-2-phenyl-1*H*-indole) showed the NH signal at δ 13.10–11.50 ppm. These results suggest that the azo tautomer of all dyes predominates in DMSO and DMSO–chloroform mixture.

The UV-Vis absorption spectra of hetarylazo indole dyes **I**–**XVIII** were measured in various solvents (Table 1) in the λ range from 300 to 800 nm at a concentration of 10^{-6} to 10^{-8} M. Almost all compounds displayed only one absorption band, indicating the presence of a single tautomer (azo). As follows from the data in Table 1, introduction of strongly electron-withdrawing 4-nitrophenylsulfonyl group into the thiazole ring (compounds **XVI** and **XVII**) leads to displacement of tautomeric equilibrium toward the hydrazone structure in DMSO and DMF. The same results were obtained for dyes **II**, **V**, **VIII**, **XI**, and **XIV** in DMSO and DMF. The absorption maximum of the hydrazone tautomer is located at longer wavelengths. These data are in good agreement with our previous results according to which hetarylazopyrazolone and hetarylazopyridone dyes in DMSO and DMF exist preferentially in the hydrazone form [11, 12].

The electronic absorption spectrum of dye **XVI** (Fig. 1) shows one or two isosbestic points at λ 497, 499, and 505 nm. The absorption maximum of **XVI** in acetic acid is located at the middle of these isosbestic points. This means that azo–hydrazone equilibrium exists in various solvents. On the other hand, tautomeric equilibria of dye **XVI** were observed in various solvent mixtures, and regular relations with dielectric constants of the solvents were revealed. Only the azo tautomer was identified in 100% chloroform, while

Table 1. Solvent effect on the absorption maxima (λ, nm) of dyes **I–XVIII**

Compound no.	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
I	469	469	417	442	476	419
II	515	513	469	466	476	464
III	461	456	450	454	469	450
IV	484	485	439	442	448	418
V	512	512	467	466	469	453
VI	461	455	451	453	461	454
VII	497	496	467	461	460	458
VIII	524	522	499	484	485	480
IX	482	478	472	473	476	473
X	486	487	451	452	453	447
XI	513	507	469	477	477	473
XII	473	469	464	467	469	467
XIII	480	491	452	452	454	448
XIV	521	519	484	476	475	469
XIV	474	469	464	406	467	466
XVI	531	523	478	480	494	479
XVII	550	551	503	504	521	504
XVIII	502	500	492	474	491	481

100% DMSO contained only the hydrazone tautomer. The absorption maximum shifts to the red region upon addition of a polar solvent (such as DMSO) to a solution of **XVI** in chloroform (Fig. 1). The dyes generally displayed a single main absorption peak without a shoulder in all solvents. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence; however, no regular variation with the solvent polarity was observed, except for compound **VII**. In going from DMSO (ε = 46.45) to less polar DMF (ε = 36.71), acetonitrile (ε = 35.94), methanol (ε = 32.66), acetic acid (ε = 6.17), and chloroform (ε = 4.81)), the absorption maximum shifts blue. Exceptions were dyes **XIII** ($\Delta\lambda_{max}$ = 32 nm for DMSO, 43 nm for DMF, 6 nm for acetic acid, and 4 nm for methanol relative to $CHCl_3$), **XVI** ($\Delta\lambda_{max}$ = 52 nm for DMSO, 44 nm for DMF, 15 nm for acetic acid, and 1 nm for methanol), and **XI** ($\Delta\lambda_{max}$ = 40 nm for DMSO, 34 nm for DMF, 4 nm for acetonitrile, 4 nm for acetic acid, and 4 nm for methanol) (Figs. 2, 3).

Substituent effect the on absorption maxima of hetarylazo indole dyes was also examined. Introduction of an electron-withdrawing $CH_2COOC_2H_5$ group instead of methyl into the 4-position of the thiazole ring (compounds **IV**–**VI**) induced a slight hypsochromic shift relative to dyes **I**–**III** in all solvents; an exception was compound **IV**. The $\Delta\lambda_{max}$ values for dye **V** relative to **II** were 3 nm in DMSO, 7 nm in acetic acid, and 1 nm in chloroform. The presence of an electron-donating phenyl group in the 4-position of the thiazole ring gives rise to a bathochromic shift relative to the corresponding 4-methylthiazole derivatives in all solvents, except for dye **VII** in acetic acid: **VII**,

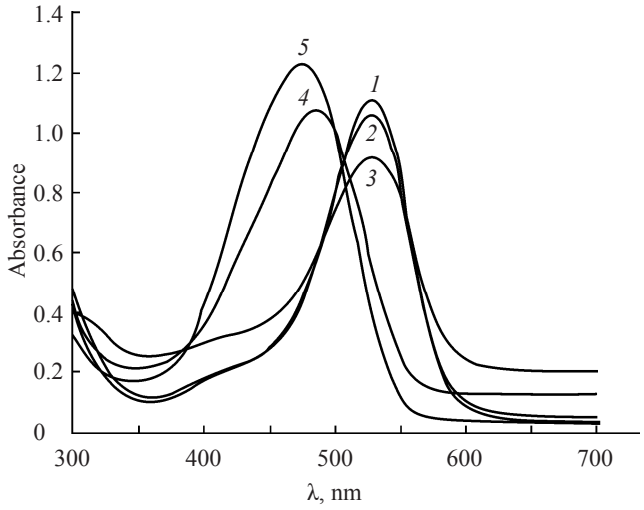


Fig. 1. Electronic absorption spectra of 2-methyl-3-[5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-yldiazenyl]-1*H*-indole (**XVI**) in (*1*) DMSO, (*2*) DMSO–$CHCl_3$ (80:20), (*3*) DMSO–$CHCl_3$ (50:50), (*4*) DMSO–$CHCl_3$ (20:80), and (*5*) $CHCl_3$.

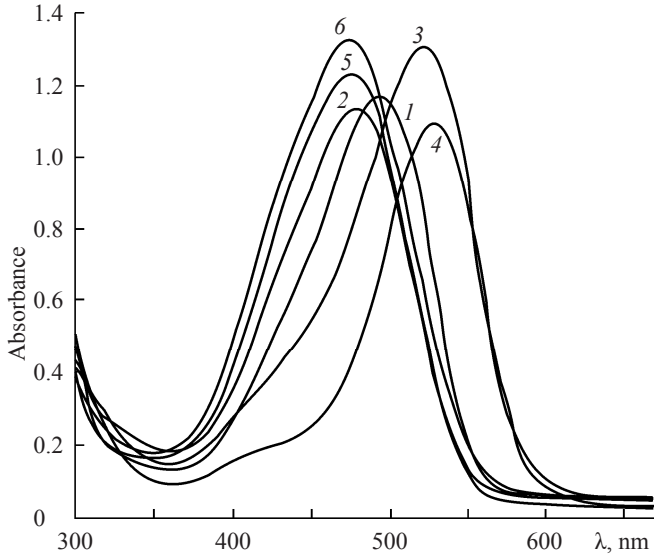


Fig. 2. Electronic absorption spectra of 2-methyl-3-[5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-yldiazenyl]-1*H*-indole (**XVI**) in (*1*) acetic acid, (*2*) acetonitrile, (*3*) dimethylformamide, (*4*) dimethyl sulfoxide, (*5*) chloroform, and (*6*) methanol.

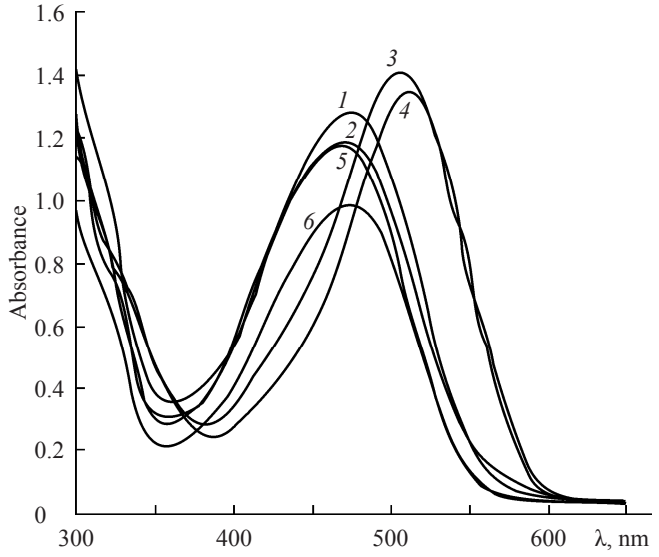


Fig. 3. Electronic absorption spectra of 3-[4-(4-chlorophenyl)-1,3-thiazol-2-yldiazenyl]-2-phenyl-1*H*-indole (**XI**) in (*1*) acetic acid, (*2*) acetonitrile, (*3*) dimethylformamide, (*4*) dimethyl sulfoxide, (*5*) chloroform, and (*6*) methanol.

$\Delta\lambda_{max}$(**VII**/**I**) = 28 nm in DMSO; **VIII**, $\Delta\lambda_{max}$(**VIII**/**II**) = 30 nm in acetonitrile; **IX**, $\Delta\lambda_{max}$(**IX**/**III**) = 23 nm in methanol). Weak electron-withdrawing chloro and bromo substituents in the *para* position of the phenyl group on the thiazole ring produced hypsochromic shift in all solvents: $\Delta\lambda_{max}$(**X**/**VII**) = 11 nm in DMSO; $\Delta\lambda_{max}$(**XI**/**VIII**) = 30 nm in acetonitrile; $\Delta\lambda_{max}$(**XII**/**IX**) = 6 nm in chloroform; $\Delta\lambda_{max}$(**XIII**/**VII**) = 17 nm in DMSO; $\Delta\lambda_{max}$(**XIV**/**VIII**) = 8 nm in methanol; $\Delta\lambda_{max}$(**XV**/**IX**) = 7 nm in chloroform). These results are in agreement with the data reported for 4-substituted thiazolylazopyrazolone and thiazolylazopyridone derivatives [7]. On the other hand, introduction of an electron-withdrawing 4-nitrophenylsulfonyl group into the 5-position of the thiazole ring resulted in a bathochromic shift of the absorption maximum in all solvents: $\Delta\lambda_{max}$(**XVI**/**I**) = 62 nm in DMSO; $\Delta\lambda_{max}$(**XVII**/**XI**) = 34 nm in acetonitrile and 60 nm in chloroform; $\Delta\lambda_{max}$(**XVIII**/**IX**) = 22 nm in DMF. Analogous patterns were observed previously for substituted thiazolylazo dyes [4]. The presence of a phenyl group in the 2-positon of the indole ring induces a bathochromic shift relative to 2-methylindole derivatives: $\Delta\lambda_{max}$(**II**/**I**) = 46 nm in DMSO, 52 nm in acetonitrile, and 45 nm in chloroform; $\Delta\lambda_{max}$(**XI**/**X**) = 20 nm in DMF, 25 nm in methanol, 24 nm in acetic acid.

The effect of the acidity of the medium on the electronic absorption spectra of helarylazo indole dyes is illustrated by the data in Table 2 and Fig. 4. Addition of 0.1 M hydrochloric acid to solutions of compounds **I**–**XVIII** (except for dye **XVII**) in methanol induces a bathochromic shift of the absorption maximum relative to its position in pure methanol: **III**, $\Delta\lambda_{max}$ = 1 nm; **V**, $\Delta\lambda_{max}$ = 55 nm; **XIII**, $\Delta\lambda_{max}$ = 49 nm). These data indicate that dyes **I**–**XVI** and **XVIII** undergo protonation. However, analogous effect (red shift) was observed upon addition of 0.1 M KOH to solutions of the dyes in methanol: **V**, $\Delta\lambda_{max}$ = 16 nm; **XI**, $\Delta\lambda_{max}$ = 22 nm; **XVI**, $\Delta\lambda_{max}$ = 33 nm. Presumably, dyes **I**–**XVIII** exist in the anionic form (Scheme 2) in 0.1 M methanolic alkali. In contrast, addition of a small amount of piperidine to solutions of the dyes in DMSO, DMF, and $CHCl_3$ did not produce any significant variation of the λ_{max} values.

EXPERIMENTAL

All initial compounds used in the synthesis of dyes **I**–**XVIII** were purchased from Aldrich Chemical Company and were used without additional purification. The solvent used were of spectroscopic grade. The IR spectra were recorded in KBr on a Mattson 1000 FT-IR spectrophotometer. The ^{1}H NMR spectra were obtained on a Bruker Spectrospin Avance DTX 400 Ultra-Shield instrument from solutions in DMSO-d_6 and $CDCl_3$ using tetramethylsilane as internal reference. The electronic absorption spectra were measured on an Analytika Jena UV-200 spectrophotometer. Analysis by liquid chromatography–mass spectrometry (LC–MS) was performed on an Agilent 1100 MSD

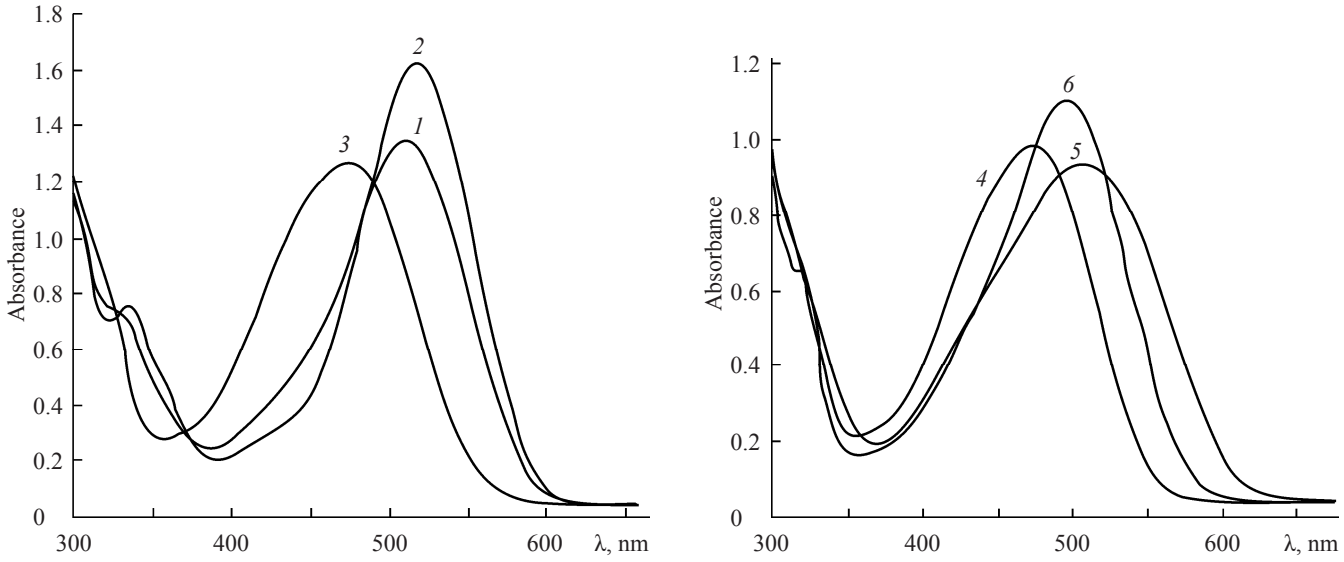


Fig. 4. Electronic absorption spectra of 3-[4-(4-chlorophenyl)-1,3-thiazol-2-yldiazenyl]-2-phenyl-1*H*-indole (**XI**) in acidic and basic solutions: (*1*) DMSO, (*2*) DMSO + piperidine, (*3*) acetic acid, (*4*) methanol, (*5*) methanol + 0.1 M HCl, and (*6*) methanol + 0.1 M KOH.

instrument at the TUBITAK ATAL Laboratories (Center of Science and Technology Research of Turkey). All melting points were uncorrected.

General procedure for the synthesis of thiazolylazo indole dyes I–XVIII. The corresponding substituted 2-amino-1,3-thiazole, 2 mmol, was dissolved in 6.0 ml of a hot 2:1 glacial acetic acid–propionic acid mixture, and the solution was quickly cooled to –5°C using an ice–salt bath. The solution was then added in portions over a period of 30 min under stirring to a cold solution of nitrosyl sulfuric acid (prepared from 0.15 g of sodium nitrite and 3 ml of concentrated sulfuric acid at 70°C). The mixture was stirred for 2 h at 0°C, excess nitrous acid was decomposed by adding urea, and the resulting diazonium salt solution was cooled in an ice–salt bath and added dropwise under stirring to a solution of 2 mmol of the corresponding substituted indole in 8 ml of a 3:1 acetic acid–propionic acid mixture, preliminarily cooled in an ice–salt bath. The mixture was stirred for 2 h at 0–5°C, maintaining the pH value at 4 to 6 by simultaneous addition of a saturated sodium carbonate solution. The mixture was then stirred for 24 h at room temperature, and the precipitate was filtered off, washed with cold water, dried, and recrystallized from ethanol.

2-Methyl-3-(4-methyl-1,3-thiazol-2-yldiazenyl)-1*H*-indole (I) was synthesized from 4-methyl-1,3-thiazol-2-amine and 2-methyl-1*H*-indole. Yield 0.45 g (87%), brown crystals, mp 238°C. IR spectrum, ν, cm^{-1}: 3397 (NH); 3056 (C–H_{arom}); 2960, 2870 (C–H_{aliph}); 1548 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.50 br.s (NH), 8.92 s (1H), 8.53 m (1H), 7.20–7.30 m (2H), 6.80 s (1H), 2.98 s (3H), 2.65 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 257 (100) $[M + 1]^+$, 158 (33.0), 130 (13.3).

3-(4-Methyl-1,3-thiazol-2-yldiazenyl)-2-phenyl-1*H*-indole (II) was synthesized from 4-methyl-1,3-thiazol-2-amine and 2-phenyl-1*H*-indole. Yield 0.51 g (80%), red–brown crystals, mp 158 °C. IR spectrum, ν, cm^{-1}: 3442 (NH); 3050 (C–H_{arom}); 2960, 2877 (C–H_{aliph}); 1490 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.50 br.s (NH), 8.40 d (1H), 8.10 d (1H), 7.90 d (2H), 7.65–7.30 m (3H), 7.10 m (1H), 7.00 m (1H), 6.90 s (1H), 2.50 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 319 (100) $[M + 1]^+$, 220 (91.4), 192 (47.8).

1-Methyl-3-(4-Methyl-1,3-thiazol-2-yldiazenyl)-2-phenyl-1*H*-indole (III) was synthesized from 4-methyl-1,3-thiazol-2-amine and 1-methyl-2-phenyl-1*H*-indole. Yield 0.56 g (85%), red crystals, mp 116°C. IR spectrum, ν, cm^{-1}: 3050 (C–H_{arom}), 2947 (C–H_{aliph}), 1471 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.40 d (1H), 7.73 m (2H), 7.45–7.61 m (4H), 7.20 m (1H), 7.10 m (1H), 6.60 s (1H), 3.88 s (3H), 2.40 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 333 (100) $[M + 1]^+$, 234 (65.9), 206 (29.0).

Ethyl [2-(2-methyl-1*H*-indol-3-yldiazenyl)-1,3-thiazol-4-yl]acetate (IV) was synthesized from ethyl 2-amino-1,3-thiazol-4-ylacetate and 2-methyl-1*H*-indole. Yield 0.57 g (87%), orange crystals, mp 183°C. IR spectrum, ν, cm^{-1}: 3275 (NH), 3082 (C–H_{arom}),

Table 2. Absorption maxima of dyes **I–XVIII** in acidic and basic solutions

Compound no.	λ_{max}, nm								
	DMSO	DMSO + piperidine	DMF	DMF + piperidine	MeOH	MeOH + KOH	MeOH + HCl	$CHCl_3$	$CHCl_3$ + piperidine
I	469	469	469	483	442	451	496	419	422
II	515	516	513	514	466	485	522	464	461
III	461	461	456	456	454	453	512	450	448
IV	484	490	485	487	442	453	493	418	423
V	512	515	512	513	466	482	521	453	462
VI	461	460	455	455	453	453	510	454	448
VII	497	499	496	497	461	484	479	458	460
VIII	524	524	522	523	484	510	495	480	482
IX	482	482	478	477	473	473	492	473	473
X	486	495	487	492	452	468	498	447	452
XI	513	520	507	520	477	499	511	473	474
XII	473	473	469	469	467	467	509	467	466
XIII	480	498	491	493	452	467	501	448	453
XIV	521	521	519	519	476	498	520	469	473
XIV	474	473	469	469	466	467	499	466	466
XVI	531	532	523	531	480	513	489	479	490
XVII	550	550	551	551	504	533	505	504	516
XVIII	502	504	500	502	474	475	500	481	484

2979 (C–H_{aliph}), 1708 (C=O), 1472 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.50 br.s (NH), 8.20 d (1H), 7.40 d (1H), 7.30 s (1H), 7.20–7.10 m (2H), 4.05 q (2H), 3.75 s (2H), 2.65 s (3H), 1.15 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 329 (62.2) $[M + 1]^+$, 172 (31.2), 158 (100).

Ethyl [2-(2-phenyl-1*H*-indol-3-yldiazenyl)-1,3-thiazol-4-yl]acetate (V) was synthesized from ethyl 2-amino-1,3-thiazol-4-ylacetate and 2-phenyl-1*H*-indole. Yield 0.68 g (87%), red crystals, mp 188°C. IR spectrum, ν, cm^{-1}: 3288 (NH); 3056 (C–H_{arom}); 2979, 2870 (C–H_{aliph}); 1715 (C=O); 1522 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.80 br.s (NH), 8.30 d (1H), 8.00 d (2H), 7.40–7.60 m (4H), 7.30 s (1H), 7.20 m (2H), 4.10 q (2H), 1.20 t (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 391 (100) $[M + 1]^+$, 220 (28.8), 192 (6.8).

Ethyl [2-(1-methyl-2-phenyl-1*H*-indol-3-yldiazenyl)-1,3-thiazol-4-yl]acetate (VI) was synthesized from ethyl 2-amino-1,3-thiazol-4-ylacetate and 1-methyl-2-phenyl-1*H*-indole. Yield 0.69 g (86%), red crystals, mp 178°C. IR spectrum, ν, cm^{-1}: 3063 (C–H_{arom}); 2940, 2896 (C–H_{aliph}); 1727 (C=O); 1529 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.40 d (1H), 7.75 d (3H), 7.63 d (3H), 7.40–7.50 m (2H), 7.30 s (1H), 4.10 q (2H), 3.90 s (3H), 3.80 s (2H), 1.20 t (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 405 (100) $[M + 1]^+$, 234 (30.3), 206 (7.7).

2-Methyl-3-(4-phenyl-1,3-thiazol-2-yldiazenyl)-1*H*-indole (VII) was synthesized from 4-phenyl-1,3-thiazol-2-amine and 2-methyl-1*H*-indole. Yield 0.50 g (79%), red crystals, mp 185°C. IR spectrum, ν, cm^{-1}: 3275 (NH); 3056 (C–H_{arom}); 2921, 2870 (C–H_{aliph}); 1464 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 12.80 br.s (NH), 8.25 m (1H), 8.00 m (2H), 7.55 m (2H), 7.45 m (3H), 7.30 m (2H), 2.80 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 319 (100) $[M + 1]^+$, 158 (21.7), 130(6.0).

2-Phenyl-3-(4-phenyl-1,3-thiazol-2-yldiazenyl)-1*H*-indole (VIII) was synthesized from 4-phenyl-1,3-thiazol-2-amine and 2-phenyl-1*H*-indole. Yield 0.62 g (81%), claret red crystals, mp 127°C. IR spectrum, ν, cm^{-1}: 3416 (NH), 3063 (C–H_{arom}), 1458 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 13.10 br.s (NH), 8.40 d (1H), 8.12 d (1H), 7.98 d (1H), 7.50–7.40 m (12H). Mass spectrum, *m*/*z* (I_{rel}, %): 381 (100) $[M + 1]^+$, 220 (14.7), 192 (5.9).

1-Methyl-2-phenyl-3-(4-phenyl-1,3-thiazol-2-yldiazenyl)-1*H*-indole (IX) was synthesized from

4-phenyl-1,3-thiazol-2-amine and 1-methyl-2-phenyl-1*H*-indole. Yield 0.67 g (85%), red crystals, mp 230°C. IR spectrum, ν, cm^{-1}: 3056 (C–H_{arom}), 2935 (C–H_{aliph}), 1471 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.40 d (1H), 8.00 d (1H), 7.42–7.81 m (10H), 7.20 s (1H), 7.10 s (1H), 6.60 s (1H), 3.90 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 395 (100) $[M + 1]^+$, 234 (55.5), 220 (3.5), 206 (17.0).

3-[4-(4-Chlorophenyl)-1,3-thiazol-2-yldiazenyl]-2-methyl-1*H*-indole (X) was synthesized from 4-(4-chlorophenyl)-1,3-thiazol-2-amine and 2-methyl-1*H*-indole. Yield 0.56 g (79%), orange crystals, mp 220°C. IR spectrum, ν, cm^{-1}: 3281 (NH), 3070 (C–H_{arom}), 2921 (C–H_{aliph}), 1458 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.30 m (1H), 8.05 d (2H), 8.00 s (1H), 7.53 d (2H), 7.45 m (1H), 7.30 m (2H), 2.75 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 353 (100) $[M + 1]^+$, 196 (11.8), 158 (40.8).

3-[4-(4-Chlorophenyl)-1,3-thiazol-2-yldiazenyl]-2-phenyl-1*H*-indole (XI) was synthesized from 4-(4-chlorophenyl)-1,3-thiazol-2-amine and 2-phenyl-1*H*-indole. Yield 0.65 g (78%), claret red crystals, mp 147°C. IR spectrum, ν, cm^{-1}: 3218 (NH), 3070 (C–H_{arom}), 1458 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.45 d (1H), 8.15 d (1H), 8.10 m (2H), 7.50–7.60 m (8H), 7.40 m (2H). Mass spectrum, *m*/*z* (I_{rel}, %): 415 (100) $[M + 1]^+$, 220 (34.3), 192 (12.4).

3-[4-(4-Chlorophenyl)-1,3-thiazol-2-yldiazenyl]-1-methyl-2-phenyl-1*H*-indole (XII) was synthesized from 4-(4-chlorophenyl)-1,3-thiazol-2-amine and 1-methyl-2-phenyl-1*H*-indole. Yield 0.69 g (81%), orange crystals, mp 200°C. IR spectrum, ν, cm^{-1}: 3050 (C–H_{arom}); 2940, 2877 (C–H_{aliph}); 1471 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.50 d (1H), 8.00–8.10 m (3H), 7.80 d (3H), 7.65 d (3H), 7.40–7.60 m (4H), 3.90 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 429 (100) $[M + 1]^+$, 234 (68.7), 206 (43.3).

3-[4-(4-Bromophenyl)-1,3-thiazol-2-yldiazenyl]-2-methyl-1*H*-indole (XIII) was synthesized from 4-(4-bromophenyl)-1,3-thiazol-2-amine and 2-methyl-1*H*-indole. Yield 0.62 g (78%), orange crystals, mp 254°C. IR spectrum, ν, cm^{-1}: 3288 (NH); 3070 (C–H_{arom}); 2935, 2870 (C–H_{aliph}); 1458 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 12.60 br.s (NH), 8.30 m (1H), 8.10 s (1H), 8.00 d (2H), 7.60 d (2H), 7.40 m (1H), 7.30 m (2H), 2.80 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 397 (100) $[M]^+$, 240 (6.7), 158 (45.1).

3-[4-(4-Bromophenyl)-1,3-thiazol-2-yldiazenyl]-2-phenyl-1*H*-indole (XIV) was synthesized from 4-(4-bromophenyl)-1,3-thiazol-2-amine and 2-phenyl-1*H*-indole. Yield 0.77 g (84%), light claret red crystals, mp 166°C. IR spectrum, ν, cm^{-1}: 3210 (NH), 3050 (C–H_{arom}), 1458 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.50 d (1H), 8.20 d (1H), 8.10 s (1H), 8.00 d (1H), 7.50–7.70 m (3H), 7.40 m (2H). Mass spectrum, *m*/*z* (I_{rel}, %): 459 (100) $[M]^+$, 220 (37.4), 192 (16.0).

3-[4-(4-Bromophenyl)-1,3-thiazol-2-yldiazenyl]-1-methyl-2-phenyl-1*H*-indole (XV) was synthesized from 4-(4-bromophenyl)-1,3-thiazol-2-amine and 1-methyl-2-phenyl-1*H*-indole. Yield 0.79 g (83%), light orange crystals, mp 240°C. IR spectrum, ν, cm^{-1}: 3056 (C–H_{arom}), 2935 (C–H_{aliph}), 1471 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.50 d (1H), 8.05 s (1H), 8.00 d (2H), 7.80 d (2H), 7.60–7.70 m (5H), 7.50 m (2H), 3.90 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 475 (100) $[M + 2]^+$, 473 (96.0). 234 (91.6), 206 (49.2), 158 (21.3).

2-Methyl-3-[5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-yldiazenyl]-1*H*-indole (XVI) was synthesized from 5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-amine and 2-methyl-1*H*-indole. Yield 0.70 g (82%), red crystals, mp 236°C. IR spectrum, ν, cm^{-1}: 3416 (NH); 3070 (C–H_{arom}); 2973, 2870 (C–H_{aliph}); 1535 (C=C); 1310, 1157 (SO_2), 1093 (S=O). ^1H NMR spectrum (DMSO-d_6–$CDCl_3$), δ, ppm: 12.51 br.s (NH), 8.36 d (2H), 8.28 m (1H), 8.23 s (1H), 8.17 d (2H), 7.31 m (1H), 7.21 m (2H), 2.71 s (3H). Mass spectrum, *m*/*z* (I_{rel}, %): 428 (100) $[M + 1]^+$, 306 (5.5), 220 (13.5), 192 (5.6), 158 (30.7).

3-[5-(4-Nitrophenylsulfonyl)-1,3-thiazol-2-yldiazenyl]-2-phenyl-1*H*-indole (XVII) was synthesized from 5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-amine and 2-phenyl-1*H*-indole. Yield 0.76 g (78%), red crystals, mp 290°C. IR spectrum, ν, cm^{-1}: 3326 (NH); 3070 (C–H_{arom}); 1541 (C=C); 1329, 1143 (SO_2); 1047 (S=O). ^1H NMR spectrum (DMSO-d_6–$CDCl_3$), δ, ppm: 12.54 br.s (NH), 8.47 m (1H), 8.31 m (3H), 8.16 d (2H), 8.01 m (2H), 7.52–7.42 m (4H), 7.28 m (2H). Mass spectrum, *m*/*z* (I_{rel}, %): 490 (100) $[M + 1]^+$, 220 (19.2), 192 (6.8), 158 (2.8).

1-Methyl-3-[5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-yldiazenyl]-2-phenyl-1*H*-indole (XVIII) was synthesized from 5-(4-nitrophenylsulfonyl)-1,3-thiazol-2-amine and 1-methyl-2-phenyl-1*H*-indole. Yield 0.79 g (79%), orange crystals, mp 184°C. IR spectrum, ν, cm^{-1}: 3063 (C–H_{arom}); 2940, 2870 (C–H_{aliph}); 1535 (C=C); 1317, 1157 (SO_2); 1092 (S=O). ^1H NMR spectrum (DMSO-d_6–$CDCl_3$), δ, ppm: 8.58 m (1H), 8.29 d

(2H), 8.09 d (2H), 7.61–7.51 m (5H), 7.38–7,31 m (2H), 3.79 s (3H). Mass spectrum, m/z (I_{rel}, %): 504 (10.8) $[M + 1]^+$, 234 (2.3), 208 (100), 193 (4.6).

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