

# Synthesis and Spectral Properties of New Hetarylazo Indole Dyes\*

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**Abstract**—A series of new hetarylazo indole dyes were synthesized by azo coupling of 2-phenyl-, 2-methyl-, and 1-methyl-1-phenyl-1*H*-indole with diazonium salts derived from 5-methylsulfanyl-1*H*-1,2,4-triazol-3-amine, 1*H*-1,2,4-triazol-3-amine, 5-methylisoxazol-3-amine, and 5-amino-1,3,4-thiadiazole-2-thiol. The dyes were characterized by the IR spectra, electronic absorption spectra in the UV and visible regions, and <sup>1</sup>H NMR and mass spectra. The effects of solvent nature, acidity of the medium, temperature, and concentration on the electronic absorption spectra in the visible region and the dependence of the color of the dyes on the nature of heterocyclic fragment were examined.

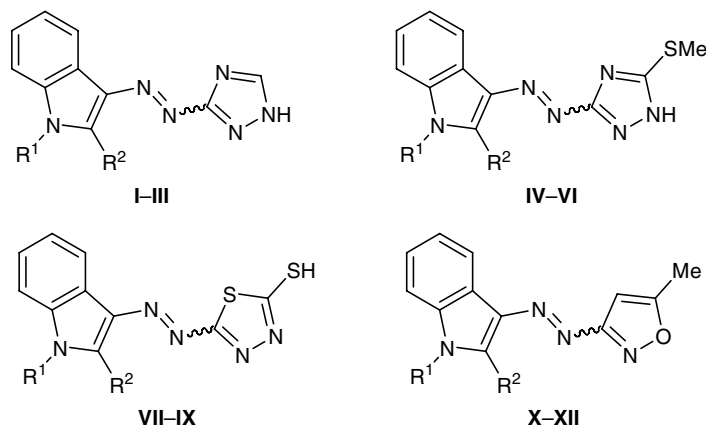
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Azo dyes are the largest group of organic dyes: they constitute more than 35% of the global production of all dyes and thus are used widely. Azo dyes based on heterocyclic amines have higher tinctorial strength and give brighter dyeing than those derived from aniline-based diazo components. For example, amino-substituted thiazoles, isothiazoles, and thiophenes afford very electronegative diazo components; therefore, dyes based thereon are characterized by a pronounced bathochromic effect as compared to the corresponding benzenoid derivatives [1–5].

Indole was discovered in 1866 by Baeyer and Knop as basic structure of the natural dye indigo from which it was obtained [6]. In the first published study on the coupling of diazonium salts with indoles Fischer ob-

served that 2-methylindole reacted rapidly to yield a crystalline azo compound [7]. Pauly and Gundermann [8] later confirmed that the azo coupling occurs preferentially at the 3-position of indole using reactions of diazotized sulfanilic acid with indole, tryptophan, and 2-methyl-, 3-methyl-, and 2,3-dimethylindoles as examples. Analogous conclusions followed from the results of reactions of indole, 2-methylindole, and 2-phenylindole with various diazonium salts [9–15]. The synthesis and spectral properties of disperse dyes on the basis of indole and carbocycles were described in numerous patents and papers [16–32].

We report here on the synthesis of hetarylazo dyes derived from 2-phenyl-, 2-methyl-, and 1-methyl-2-phenyl-1*H*-indole as azo components and four hetero-



I, IV, VII, X, R<sup>1</sup> = H, R<sup>2</sup> = Ph; II, V, VIII, XI, R<sup>1</sup> = H, R<sup>2</sup> = Me; III, VI, IX, XII, R<sup>1</sup> = Me, R<sup>2</sup> = Ph.

\* The text was submitted by the authors in English.

**Table 1.** IR and  $^1\text{H}$  NMR spectra of dyes **I–XII**

Comp. no.	IR spectrum (KBr), $\nu$ , $\text{cm}^{-1}$				$^1\text{H}$ NMR spectrum, $\delta$ , ppm			
	N–H	C–H <sub>arom</sub>	C–H <sub>aliph</sub>	C=C	H <sub>arom</sub>	H <sub>aliph</sub>	NH (SH), br.s	solvent
<b>I</b>	3435	3050	–	1657	8.6–8.5 d (1H), 8.4–8.1 m (5H), 7.6–7.2 m (4H)	–	12.3 (indole), 14.0–13.0 (triazole)	$\text{CDCl}_3$ , $\text{DMSO-}d_6$
<b>II</b>	3403	3056	2928	1618	8.4–8.3 m (1H), 8.0–7.9 d (1H), 7.4–7.0 m (3H)	2.5 s (3H)	11.3 (indole), 14.2–13.1 (triazole)	$\text{CDCl}_3$ , $\text{DMSO-}d_6$
<b>III</b>	3167	3031	2870	1631	8.6–8.5 d (1H), 8.3 s (1H), 7.7–7.3 m (8H)	3.8 s (3H)	13.0–12.3 (triazole)	$\text{DMSO-}d_6$
<b>IV</b>	3397	3075	2928	1618	8.6–8.5 d (1H), 8.2–8.1 m (2H), 7.6–7.2 m (6H)	2.7 s (3H)	12.3 (indole), 14.0–13.4 (triazole)	$\text{DMSO-}d_6$
<b>V</b>	3416	3089	2935	1657	8.5–8.4 m (1H), 7.4–7.3 m (1H), 7.25–7.15 m (2H)	2.8 s (3H), 2.7 s (3H)	11.8 (indole), 14.0–13.0 (triazole)	$\text{DMSO-}d_6$
<b>VI</b>	3397	3056	2935	1585	8.6–8.5 m (1H), 7.6–7.3 m (8H)	3.8 s (3H), 2.7 s (3H)	14.0–13.5 (triazole)	$\text{CDCl}_3$ , $\text{DMSO-}d_6$
<b>VII</b>	3442	3056	–	1638	8.3 m (2H), 8.2 d (1H), 7.9–7.1 m (6H)	–	3.5–2.8 (SH), 11.4 (indole)	$\text{CDCl}_3$ , $\text{DMSO-}d_6$
<b>VIII</b>	3442	3063	2915	1657	8.4–8.3 m (1H), 7.4–7.0 m (3H)	2.7 s (3H)	3.6–3.2 (SH), 11.1 (indole)	$\text{CDCl}_3$
<b>IX</b>		3056	2938	1628	8.6–8.5 d (1H), 7.8–7.2 m (8H)	3.7 s (3H)	3.2–2.7 (SH)	$\text{CDCl}_3$ , $\text{DMSO-}d_6$
<b>X</b>	3391	3063	2921	1606	8.6–8.5 d (1H), 8.1–8.0 m (2H), 7.6–7.2 m (6H), 6.3 s (1H)	2.5 s (3H)	12.0 (indole)	$\text{CDCl}_3$ , $\text{DMSO-}d_6$
<b>XI</b>	3461	3075	2935	1618	8.5–8.4 m (1H), 7.4–7.2 m (3H), 6.4 s (1H)	2.8 s (3H), 2.5 s (3H)	11.7 (indole)	$\text{CDCl}_3$ , $\text{DMSO-}d_6$
<b>XII</b>		3050	2935	1645	8.7–8.6 m (1H), 7.6–7.3 m (8H), 6.1 s (1H)	3.8 s (3H), 2.4 s (3H)	–	$\text{CDCl}_3$

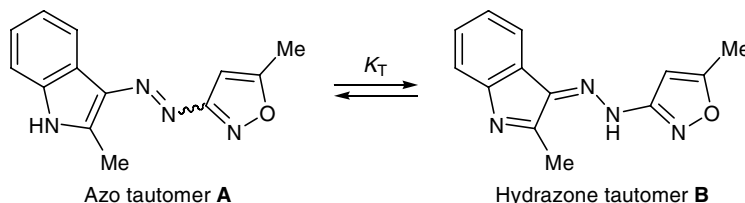
cyclic amines as diazo components. The electronic absorption spectra of the new dyes in the visible region were measured in various solvents.

Dyes **I–XII** were synthesized by coupling of 2-phenyl-, 2-methyl-, and 1-methyl-2-phenyl-1*H*-indole with diazonium salts prepared from 5-methylsulfanyl-1*H*-1,2,4-triazol-3-amine, 1*H*-1,2,4-triazol-3-amine, 5-methylisoxazol-3-amine, and 5-amino-1,3,4-thiadiazole-2-thiol (the diazotization was carried out in nitrosylsulfuric acid). Dyes **I–XII** can exist as two tautomers: azo (**A**) and hydrazone (**B**) (Scheme 1).

Table 1 contains the IR and  $^1\text{H}$  NMR spectra of compounds **I–XII**; their yields, melting points, and

mass spectra are given in Table 2. The IR spectra (KBr) of all dyes, except for **III**, **VI**, **IX**, and **XII** displayed absorption bands at 3461–3391  $\text{cm}^{-1}$  due to NH group in the indole fragment. The corresponding proton gives a broadened singlet in the region  $\delta$  11.1–12.3 ppm of the  $^1\text{H}$  NMR spectra. The spectral data suggest that tautomeric equilibrium with 2-phenyl- and 2-methylindole derivatives is displaced toward the azo form (**A**) in the crystalline state and in solutions in  $\text{CHCl}_3$  and  $\text{DMSO}$ . Dyes **III**, **VI**, **IX**, and **XII** exist as a single tautomer (**A**).

The electronic absorption spectra of hetarylazo indole dyes **I–XII** were measured in various solvents

**Scheme 1.**

in the concentration range from  $10^{-6}$  to  $10^{-8}$  M (Table 3). In addition, pH of the medium was varied by adding piperidine or KOH as base or hydrochloric acid (Table 4). The choice of solvents was based on their polarity. We have revealed no regular relations between the solvent polarity and position of the visible absorption maxima for the examined dyes (Fig. 1). Bathochromic shift of the long-wave absorption maximum was observed in DMSO and DMF for all dyes except for **I** and **IV–VI** (**IX**:  $\lambda_{\max}$  481 nm in DMSO; 474 and 550 nm in DMF; 463 nm in  $\text{CHCl}_3$ ). In addition, red shift of the absorption maximum of compounds **III–VI** was observed in acetic acid (**VI**:  $\lambda_{\max}$  418 nm in acetic acid, 398 nm in DMSO, 400 nm in DMF, and 385 nm in  $\text{CHCl}_3$ ).

Disperse azo dyes containing heterocyclic fragments tend to show larger solvatochromic effect than azobenzene dyes due to stronger polarization of their electronic system, especially in the excited state. Similar effects were reported for dyes containing benzothiazole, thiazole, and thiophene fragments, as well as for some *N*-(2-cyanoethyl)-*N*-(2-hydroxyethyl)-aniline derivatives [33–37]. In the case of hetarylazo dyes of the indole series, possible tautomeric equilibria should be taken into account. These compounds can exist in two tautomeric forms. For example, dye **V** in DMF ( $\lambda_{\max}$  396 nm) and in a DMF–piperidine mixture ( $\lambda_{\max}$  437, 381 nm) may exist as the azo tautomer and anionic form. The spectrum of **VIII** in DMSO contains one absorption maximum, while in DMSO–piperidine two maxima appear. Presumably, compound **VIII** in DMSO–piperidine gives rise to equilibrium between one tautomer and anion ( $\lambda_{\max}$  466 nm in DMSO; 493 and 356 nm in DMSO–piperidine). The electronic absorption spectrum of dye **VIII** in DMF shows one maximum and two shoulders, while in DMF–piperidine one absorption maximum and one shoulder are present. These data suggest equilibrium between tautomeric and anionic forms of dye **VIII** in DMF and DMSO–piperidine (Fig. 2).

Strong evidence for the existence of equilibrium between tautomeric forms of dyes **I–XII** and their anions in solution is provided by the presence of one or two isosbestic points in the visible region of the absorption spectrum of compound **VIII** in different solvents (Fig. 2). The state of the equilibrium is determined by acid–base properties of the medium, especially for dyes **I**, **VI**, and **IX** (Fig. 1). The absorption curves (except for dyes **VI** and **XII**) are very sensitive to the presence of bases. Addition of a small amount of piperidine to solutions of dyes in DMSO,

**Table 2.** Yields, melting points, and mass spectra of compounds **I–XII**

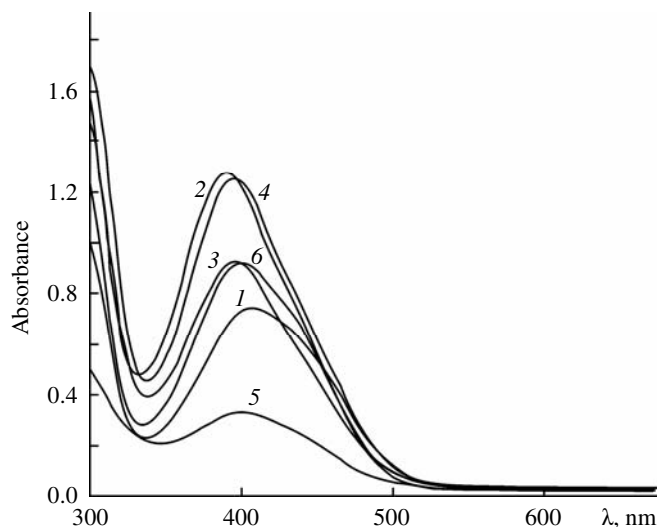
Compound no.	Yield, <sup>a</sup> %	mp, <sup>b</sup> °C	<i>m/z</i> ( <i>[M]</i> <sup>+</sup> )
<b>I</b>	75	268–270	288
<b>II</b>	81	>153 <sup>c</sup>	226
<b>III</b>	85	117–118	302
<b>IV</b>	79	184–185	334
<b>V</b>	76	98–99	272
<b>VI</b>	83	133–135	348
<b>VII</b>	80	240–241	337
<b>VIII</b>	82	>182 <sup>c</sup>	275
<b>IX</b>	75	115–116	351
<b>X</b>	85	210–211	302
<b>XI</b>	80	218–219	240
<b>XII</b>	79	>203 <sup>c</sup>	316

<sup>a</sup> Yield of isolated product.

<sup>b</sup> The products were recrystallized from aqueous ethanol.

<sup>c</sup> With decomposition.

DMF, or chloroform induces considerable long-wave shift of the absorption maxima (for dye **X**,  $\Delta\lambda_{\max}$  = 63 nm in going from DMF to DMF–piperidine). By contrast, the absorption maxima of dyes **I** and **III–V** in chloroform shift blue in the presence of a small amount of piperidine (for dye **I**,  $\Delta\lambda_{\max}$  = 50 nm). Red shifts of the absorption maxima of dyes **VII** and **VIII** ( $\Delta\lambda_{\max}$  = 25 nm for the latter) were observed upon addition of 0.1 M of KOH to their solutions in methanol (Fig. 3), whereas dyes **I–V** in methanol showed a blue



**Fig. 1.** Electronic absorption spectra of 5-(1-methyl-2-phenyl-1*H*-indol-3-yl-diazenyl)-1,3,4-thiadiazole-2-thiol (**IX**) in (1) acetic acid, (2) acetonitrile, (3) DMF, (4) DMSO, (5) chloroform, and (6) methanol.

**Table 3.** Positions of absorption maxima ( $\lambda_{\max}$ , nm) in the electronic spectra of dyes **I–XII** in different solvents

Compound no.	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
<b>I</b>	398	396	391	400	409	401
<b>II</b>	382	382	379	384	388	386
<b>III</b>	399	388	390	393	401	403
<b>IV</b>	417, 447 sh	417, 468 sh	411	413	426	419
<b>V</b>	398	396	395	394	401	396
<b>VI</b>	398	400	400	394	418	385
<b>VII</b>	515, 388	506, 386 sh	382, 476 sh	393, 469 sh	399, 467 sh	393, 469 sh
<b>VIII</b>	466	461, 372 sh, 522 sh	447	455	456	450
<b>IX</b>	481, 547 sh	474, 550 sh	463	468	471	463
<b>X</b>	398	394	386	390	391	386
<b>XI</b>	375, 432 sh	373	367	371	373	368
<b>XII</b>	388	385	382	384	386	384

**Table 4.** Positions of absorption maxima ( $\lambda_{\max}$ , nm) in the electronic spectra of dyes **I–XII** in acidic and basic media

Comp. no.	DMSO	DMSO–piperidine	DMF	DMF–piperidine	MeOH	MeOH–KOH	MeOH–HCl	CHCl <sub>3</sub>	CHCl <sub>3</sub> –piperidine
<b>I</b>	398	476, 401	396	473, 397, 348 sh	400	384	459	401	351
<b>II</b>	382	448, 367	382	373, 435 sh	384	369	439	386	384
<b>III</b>	399	382	388	384	393	379	451	403	391
<b>IV</b>	417, 447 sh	474	417, 468 sh	478	413	399	473	419	410
<b>V</b>	398	383, 431	396	437, 381	394	379	449	396	390
<b>VI</b>	398	395	400	397	394	391	467	385	385
<b>VII</b>	515, 388	521, 389	506, 386	522, 388	393, 469 sh	505, 365	380, 435 sh	393, 469 sh	440
<b>VIII</b>	466	493, 356 sh	461, 372 sh, 522 sh	491, 359 sh	455	480	474	450	461, 348 sh
<b>IX</b>	481, 547 sh	481, 551 sh	474, 550 sh	478, 548 sh	468	469	485	463	469
<b>X</b>	398	459	394	457	390	397	395	386	389
<b>XI</b>	375, 432 sh	374, 433	373	367, 435 sh	371	374	376	368	369
<b>XII</b>	388	386	385	385	384	384	385	384	386

shift of the absorption maximum on addition of a small amount of 0.1 M KOH ( $\Delta\lambda_{\max} = 14$  nm for **IV**). The spectra of **VI** and **IX–XII** in methanol change insignificantly in the presence of 0.1 M KOH. These findings indicate that some hetarylazo indole dyes undergo dissociation when a base is added to their solutions in DMSO, DMF, chloroform, and methanol.

Acid medium induces bathochromic shifts of the absorption maxima of all the examined dyes, except for **VII** and **X–XII**. The  $\Delta\lambda_{\max}$  values for dyes **I**, **IV**, **VI**, and **VIII** in methanol in the presence of 0.1 M HCl are 59, 60, 73, and 19 nm, respectively, relative to pure

methanol (Fig. 3). Compound **VII** displayed a blue shift of the absorption maximum in going from methanol to MeOH–0.1 M HCl ( $\Delta\lambda_{\max} = 13$  nm). The spectra of **X–XII** almost do not change upon addition of 0.1 M HCl to their solutions in methanol. These data suggest that dyes **I–IX** in acidic proton-donor solvents (such as acetic acid or a solution of hydrochloric acid in methanol) are converted into the corresponding cations.

Table 5 contains the data on the effects of dye concentration and temperature on the electronic absorption spectra. It is seen that the position of the long-wave absorption maximum of compounds **I–XII** almost does

**Table 5.** Effects of temperature and concentration on the position of absorption maxima ( $\lambda_{\max}$ , nm) in the electronic spectra of dyes **I–XII**

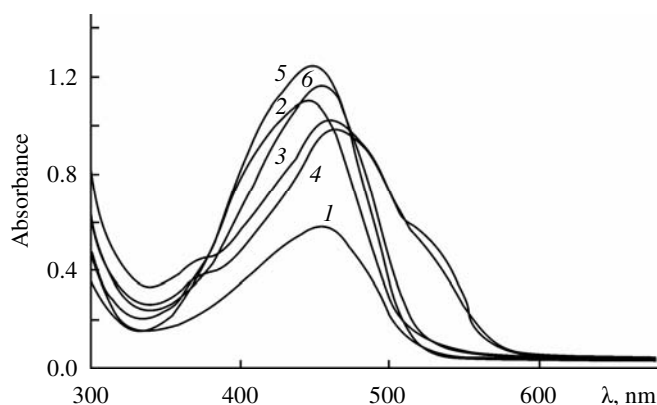
Comp. no.	DMSO			DMF			Acetonitrile		Methanol		Acetic acid		Chloroform	
	25°C		70°C	25°C		70°C	25°C		25°C		25°C		25°C	
	concd.	dilute		concd.	dilute		concd.	dilute	concd.	dilute	concd.	dilute	concd.	dilute
<b>I</b>	395	398	396	396	396	396	391	391	401	400	408	409	400	401
<b>II</b>	382	382	382	382	382	380	379	379	385	384	388	388	386	386
<b>III</b>	385	399	401	387	388	386	388	390	392	393	400	401	402	403
<b>IV</b>	418, 449 sh	417, 447 sh	417, 445	416, 459 sh	417, 468 sh	415, 466 sh	411	411	413	413	393	426	421	419
<b>V</b>	399	398	399	399	396	399	395	395	395	394	401	401	397	396
<b>VI</b>	400	398	399	401	400	400	399	400	394	394	415	418	385	385
<b>VII</b>	516, 387	515, 388	517, 388	506, 385 sh	506, 386 sh	505, 388 sh	380	382, 476 sh	391	393, 469 sh	398	399, 467 sh	395, 467 sh	393, 469 sh
<b>VIII</b>	465	466	465	464, 373 sh, 522 sh	461, 372 sh, 522 sh	466, 372 sh, 522 sh	448	447	458	455	456	456	450	450
<b>IX</b>	482, 547 sh	481, 547 sh	482, 544 sh	469, 551 sh	474, 550 sh	471, 551 sh	463	463	467	468	470	471	463	463
<b>X</b>	397	398	396	395	394	396	388	386	393	390	390	391	388	386
<b>XI</b>	376, 431 sh	375, 432 sh	375, 432 sh	372	373	371	367	367	369	371	372	373	368	368
<b>XII</b>	387	388	387	385	385	385	381	382	383	384	386	386	383	384

not depend on the dye concentration. Likewise, no appreciable change in the absorption patterns of dyes **I–XII** in DMSO and DMF was observed upon raising the temperature from 25 to 70°C. Presumably, acid–base and tautomeric equilibria of compounds **I–XII** in proton-acceptor solvents do not involve considerable variations in energy.

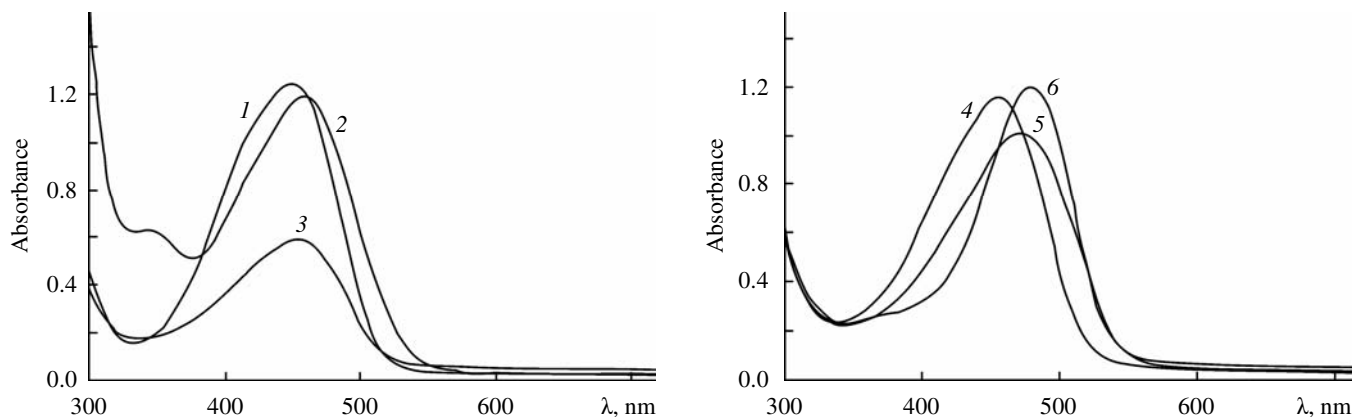
Thus we have synthesized new azo dyes on the basis of 2-phenyl-, 2-methyl-, and 1-methyl-2-phenyl-1*H*-indole and heterocyclic amines (5-methylsulfanyl-1*H*-1,2,4-triazol-3-amine, 1*H*-1,2,4-triazol-3-amine, 5-methylisoxazol-3-amine, and 5-amino-1,3,4-thiadiazole-2-thiol) as diazo components. The electronic absorption spectra of the obtained dyes in the visible region revealed some dependence of the position of the absorption maxima on the solvent nature; however, no regular relation with the solvent polarity was found. Acid–base properties of the medium also affect the spectral patterns. Our results showed that compound **VIII** is quite promising for use in both acidic and basic media (Fig. 3).

## EXPERIMENTAL

All chemicals used in this work were commercial products (Aldrich) which were not subjected to additional purification. Spectroscopic-grade solvents were



**Fig. 2.** Electronic absorption spectra of 5-(2-methyl-1*H*-indol-3-yl-diazenyl)-1,3,4-thiadiazole-2-thiol (**VIII**) in (1) acetic acid, (2) acetonitrile, (3) DMF, (4) DMSO, (5) chloroform, and (6) methanol.



**Fig. 3.** Electronic absorption spectra of 5-(2-methyl-1*H*-indol-3-yl)diazenyl)-1,3,4-thiadiazole-2-thiol (**VIII**) in (1) chloroform, (2) chloroform with addition of piperidine, (3) acetic acid, (4) methanol, (5) methanol with addition of 0.1 M hydrochloric acid, and (6) methanol with addition of 0.1 M KOH.

used. The IR spectra were recorded in KBr on a Mattson 1000 FT-IR spectrometer. The  $^1\text{H}$  NMR spectra of solutions in  $\text{DMSO}-d_6$  and  $\text{CDCl}_3$  were obtained on a Bruker Spectrospin Avance DTX 400 Ultra-Shield instrument using tetramethylsilane as internal reference. The electronic absorption spectra were measured on an Analytika-Jena UV-200 spectrophotometer. The electron-impact mass spectra (70 eV) were run on an Agilent HP 5973 mass-selective detector equipped with a direct inlet probe. The melting points were not corrected.

**3-(5-Methyl-1,2-oxazol-3-yl)diazenyl)-2-phenyl-1*H*-indole (X).** 5-Methylisoxazol-3-amine, 2 mmol, was dissolved in 6.0 ml of a hot mixture of glacial acetic acid and propionic acid at a ratio of 2:1. The solution was quickly cooled to  $-5^\circ\text{C}$  in an ice-salt bath and was added in portions over a period of 30 min under stirring to a cold solution of nitrosylsulfuric acid prepared from 1 g of sodium nitrite and 7 ml of concentrated sulfuric acid at  $70^\circ\text{C}$ . The mixture was stirred for 2 h at  $0^\circ\text{C}$ , excess nitrous acid was quenched by addition of urea and the resulting diazo solution was slowly added under vigorous stirring to a solution of 2 mmol of 2-phenyl-1*H*-indole in 6 ml of a 2:1 mixture of acetic and propionic acids. The mixture was stirred for 2 h, maintaining its pH value at 4 to 6 by adding a saturated solution of sodium carbonate, and was then stirred for 1 h at  $0-5^\circ\text{C}$ . The precipitate was filtered off, washed with water, dried, and recrystallized from aqueous ethanol. Yield 85%, mp  $210-211^\circ\text{C}$ .

Dyes **I-IX**, **XI**, and **XII** were synthesized in a similar way; the yields were 75–85% (Tables 1, 2).

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