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The synthesis, spectroscopic properties and crystal structure of novel, bis-hetarylazo disperse dyes

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Abstract

A series of hetarylazoindole dyes were obtained by coupling 2-methyl, 2-phenyl, 1,2-dimethyl and 1-methyl-2-phenylindoles with diazotized 2-amino-1,3,4-thiadiazoles and 3-amino-5-mercapto-1,2,4-triazole. The dyes were characterized by UV–vis, FT-IR, ^{1}H NMR, LC–MS or MS spectroscopic techniques and elemental analysis. The solvatochromism of the dyes was evaluated with respect to visible absorption properties in various solvents. The colours of the dyes were discussed with respect to the nature of heterocyclic rings and to the substituents therein; the effects of acid and alkali on the visible $\lambda_{\max}$ of the dyes are also reported. In addition, X-ray diffraction analysis of the crystal structure of 2-phenyl-3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole revealed that the dye was in the azo form and that intra- and intermolecular N–H···N hydrogen bonds link the molecules to form infinite chains in the [001] direction. The asymmetric unit of the dye contained two independent molecules.

Keywords: Hetarylazoindole dyes; Heterocyclic disperse dyes; Solvent effect; Azo–hydrazone tautomerism; Crystal structure

1. Introduction

It has been known for many years that the azo compounds are most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibres, the colouring of different materials, in biological-medical studies and advanced applications in organic synthesis [1–9]. They can also be used as materials for non-linear optics and for storage of optical information in laser disks [10–12]. Their optical properties depend not only on the spectroscopic properties of the molecules, but also on their crystallographic arrangements [13,14].

In recent years, many heteroaromatic systems have been used either as coupling components or diazo components in azo dyes to enhance colour strength and brilliant shades for synthetic fabrics. In this connection, both pyridones and pyrazolones have found wide utilization in textile industry as coupling components for the synthesis of azo and azamethine dyes [15–17]. It has also been reported that dyes made using heterocyclic amines, such as 2-aminothiazole and 2-aminothiophene derivatives as diazo components tend to show bathochromic shifts when compared to analogous dyes derived from benzenoid compounds [9,18–22]. On the other hand, it is well known that monoazo dyes prepared from enol-type coupling components exhibit azo–hydrazone tautomerism. Determination of azo–hydrazone tautomerism in solid state and in solution is quite interesting both from a theoretical viewpoint, and from practical standpoint since the tautomers have different technical properties and dyeing performance [23].

We have recently reported the synthesis of some new bis-hetarylazo dyes such as hetarylazopyridones [17], hetarylazopyrazolones [24], hetarylazoquinolines [25] and hetarylazoindoles

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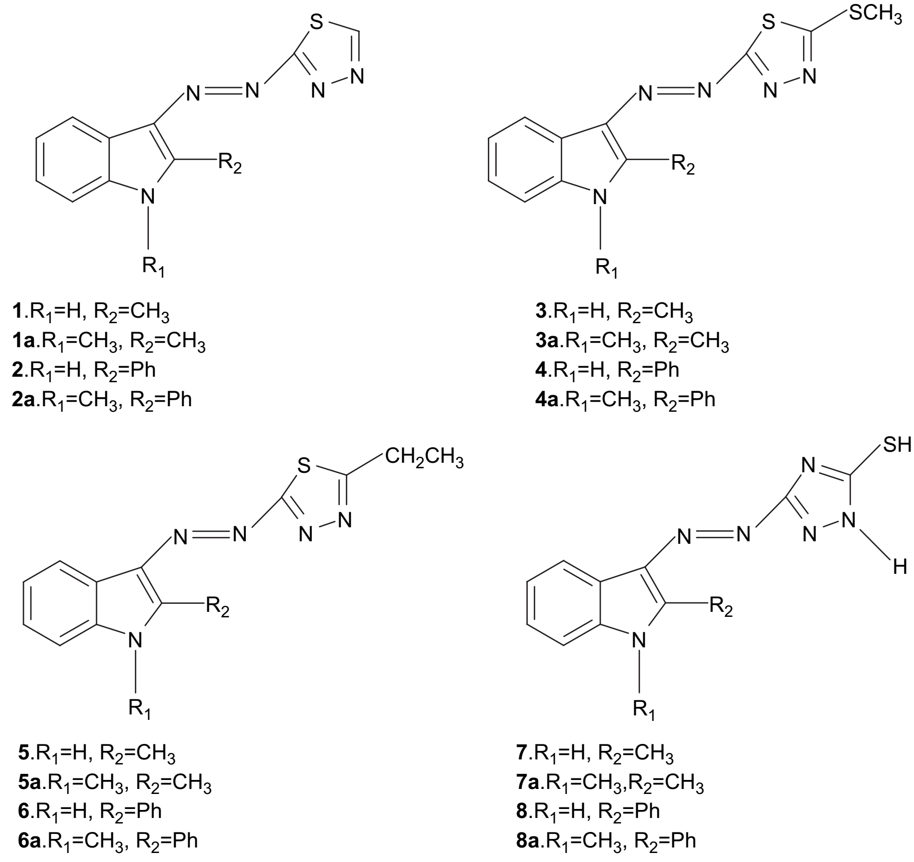
[26,27], which exhibit strong solvent dependence in their absorption spectra. In solution, these dyes theoretically may be involved in azo–hydrazone tautomerism. Furthermore, several data in our studies on visible absorption spectra of bis-hetarylazo dyes have suggested the manifestation of interconnected azo–hydrazone and acid–base equilibria. It has been reported that such interconnected equilibria was also observed in some hetarylazo compounds [2,24,28–35]. In this work, we aimed to find new data for supporting the structures of bis-hetarylazo dyes in solution and solid state. Although a few patents describe the application on textile materials of some cationic and neutral hetarylazoindole derivatives [36–43], synthesis of bis-hetarylazoindoles and solvatochromic behaviours were not investigated.

With this object in view, we now report here the synthesis of a new series of hetarylazoindole dyes using 2-methyl and 2-phenylindoles as coupling components which may be involved in azo–hydrazone tautomerism. For comparison, we prepared 1,2-disubstituted derivatives of these dyes as model compounds from 1,2-disubstituted indoles as coupling components which exist solely in azo form. Then, we studied the effect of the solvents, acid and base on the visible absorption spectra of the dyes. The crystalline and molecular structures of dye **6** obtained by X-ray diffraction analysis were also discussed.

2. Results and discussion

The hetarylazoindole dyes (**1–8** and **1a–8a**) were prepared by coupling 2-methylindole, 1,2-dimethylindole, 2-phenylindole and 1-methyl-2-phenylindole with diazotized 2-amino-1,3,4-thiadiazole, 2-amino-5-methylthio-1,3,4-thiadiazole, and 2-amino-5-ethyl-1,3,4-thiadiazole, 3-amino-5-mercapto-1,2,4-triazole in nitrosylsulphuric acid (Scheme 1). The dyes (**1–8** and **1a–8a**) were obtained generally in excellent yields (91–77%); the structure of these dyes was verified by elemental analysis and by spectroscopic methods (FT-IR, Mass and ^{1}H NMR). Physical and spectral data of dyes prepared are given in Section 3. The dyes prepared from 2-methylindole (**1**, **3**, **5** and **7**) and 2-phenylindole (**2**, **4**, **6** and **8**) may exist in two possible tautomeric forms, namely azo form **A** and hydrazone form **B**, as depicted in Scheme 2. The deprotonation of two tautomers leads to the common anion **C**.

The infrared spectra of the dyes **1–8** (in KBr) showed weak and broad bands within the range 3462–3180 cm^{-1}, due to –NH band of the indole rings. These bands were not observed in the infrared spectra of the dyes prepared from 1,2-dimethylindole and 1-methyl-2-phenylindole (**1a–6a**). In addition, the infrared spectra of the dyes **7a** and **8a** (in KBr) showed broad bands within the range 3418–3264 cm^{-1}, due to –SH and –NH bands of the triazole ring. The other ν_{max}



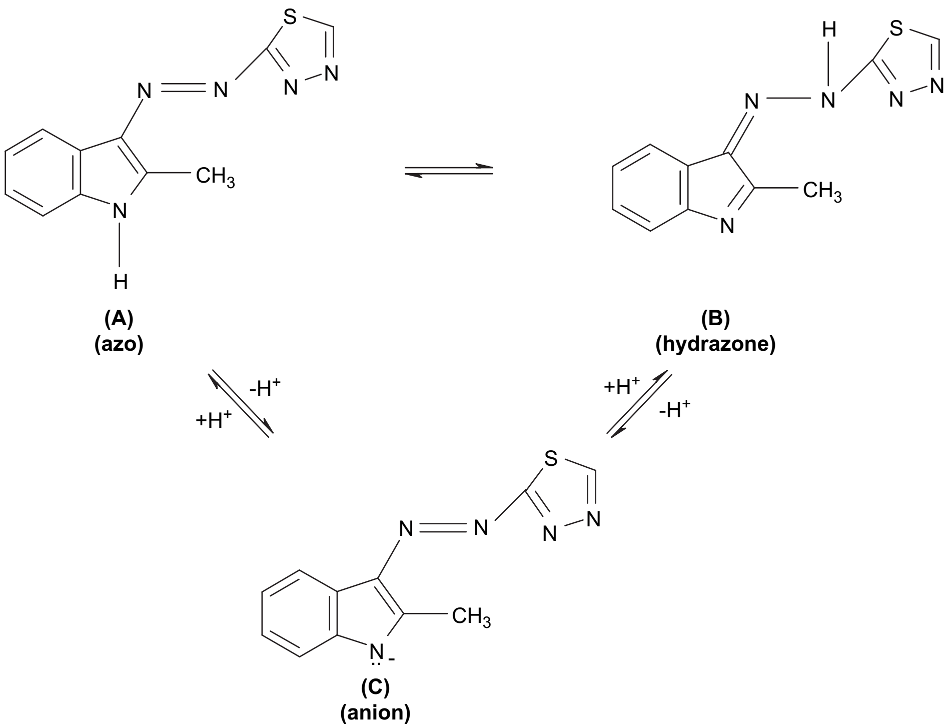
1.R_1=H, R_2=CH_3
1a.R_1=CH_3, R_2=CH_3
2.R_1=H, R_2=Ph
2a.R_1=CH_3, R_2=Ph

3.R_1=H, R_2=CH_3
3a.R_1=CH_3, R_2=CH_3
4.R_1=H, R_2=Ph
4a.R_1=CH_3, R_2=Ph

5.R_1=H, R_2=CH_3
5a.R_1=CH_3, R_2=CH_3
6.R_1=H, R_2=Ph
6a.R_1=CH_3, R_2=Ph

7.R_1=H, R_2=CH_3
7a.R_1=CH_3,R_2=CH_3
8.R_1=H, R_2=Ph
8a.R_1=CH_3, R_2=Ph

Scheme 1. Structures of dyes.



Scheme 2. Azo–hydrazone tautomeric forms and anionic form of hetarylazoindole dyes (**1**–**8**).

values at 3085–3005 cm^{-1} (aromatic CH) and at 2986–2851 cm^{-1} (aliphatic CH) were recorded. ^1H NMR spectra of the dyes showed –NH peaks in the range 13.21–12.49 ppm in DMSO-d_6 except for the 1,2-dimethylindole and 1-methyl-2-phenylindole derivatives. In our previous study, in the ^1H NMR spectrum of 2-phenyl-3-(2-thiazol-2-yl-diazenyl)-1*H*-indole in $CDCl_3$, –NH proton signal was located at 8.95 ppm which could be attributed to –NH proton of indole ring at 1-position, and when the ^1H NMR spectrum of 2-phenyl-3-(2-thiazol-2-yldiazenyl)-1*H*-indole was measured in DMSO-d_6, the –NH peak shifted to downfield by 3.88 ppm and appeared at 12.83 ppm [44]. The downfield chemical shift of the –NH proton signal in DMSO-d_6 is probably attributed due to intermolecular hydrogen bonding between indole ring –NH and DMSO. Assignments for the indole –NH proton signal of coupler moiety supported the ^1H NMR data for 2-methyl and 2-phenylindole derivatives in DMSO-d_6 and $CDCl_3$ [45].

To determine the tautomeric forms of the dyes in solid state, X-ray data for dye **6** were recorded (Table 1). Suitable single crystals were obtained by slow evaporation from ethanol in one week. The asymmetric unit of the dye **6**, containing two crystallographically independent molecules, was denoted by primed and unprimed labels (Fig. 1). The atomic coordinates are given in Table 2. The bond lengths and angles (Table 3) were in normal ranges [46].

An examination of the deviations from the least-squares planes through the individual rings showed that all of the rings are planar. The indole ring systems were planar, with dihedral angles of 2.28(9)° and 1.32(11)° between rings A(N1/C3–C5/C10) and B(C5–C10) and between rings A′(N1′/C3′–C5′/C10′) and B′(C5′–C10′). In the closely related compounds, 3-(4-chlorophenyldiazenyl)-1-methyl-2-phenyl-1*H*-indole **17** [47], *N*-{4-[(2-phenyl-1*H*-indol-3-yl)diazenyl]phenyl}acetamide **18** [48], ethyl[2-(2-phenyl-1*H*-indol-3-yldiazenyl)-1,3-thiazol-4-yl]acetate **19** [49], ethyl-2-{2-[(1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl]thiazol-4-yl}acetate

Table 1
Crystallographic data

Empirical formula	$C_{18}H_{15}N_5S$
Formula weight	333.41
Color/shape	Red/block
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	15.1778(5)
b (Å)	14.4514(2)
c (Å)	15.4628(4)
β (°)	94.687(2)
Volume (Å^3)	3380.28(15)
Z	8
D_{calc} (g cm^{-3})	1.310
μ (mm^{-1})	0.200
Crystal dimensions (mm)	0.35 × 0.25 × 0.20
$2\theta_{max}$ (°)	61.14
No. of reflections measured	10334
No. of reflections observed [$I > 2\sigma(I)$]	6932
No. of variables	515
R	0.0769
R_w	0.1891
Largest diffraction peak and hole (e Å^{-3})	0.594 and −0.340
Maximum shift in final cycles	0.000

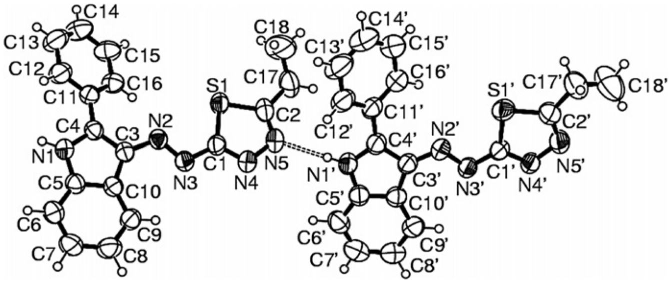


Fig. 1. An ORTEP-3 [58] drawing with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

20 [50], 1-methyl-2-phenyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole **2a** [51] 1,2-dimethyl-3-(thiazol-2-yldiazenyl)-1*H*-indole **21** [52], 3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1-methyl-2-phenyl-1*H*-indole **6a** [53] and 3-(6-methoxybenzothiazol-2-yldiazenyl)-1-methyl-2-phenyl-1*H*-indole **22** [54], the observed A/B and/or A′/B′ dihedral angles were 1.56(11) and 0.77(12)° in (**17**), 1.63(14)° in (**18**), 0.99(10)° in (**19**), 0.59(7)° in (**20**), 4.26(7)° in (**2a**), 2.07(9) and 2.04(9)° in (**21**), 0.59(12)° in (**6a**) and 1.16(7)° in (**22**). The orientations of rings C(S1/C1/N4/N5/C2), D(C11–C16) and C′(S1′/C1′/N4′/N5′/C2′), D′(C11′–C16′) with respect to the indole ring systems might be described by the dihedral angles of 5.83(6)°, 27.98(8)° (for the unprimed molecule) and 8.87(6)°, 36.78(9)° (for the primed molecule), respectively.

As can be seen from the packing diagram (Fig. 2), intra- and intermolecular N–H···N hydrogen bonds (Table 4) linked the molecules to form infinite chains along the [001] direction. Dipole–dipole and van der Waals interactions were effective in the molecular packing. These results suggested that the dyes prepared exist in azo form in solid state.

Table 2
Selected bond lengths (Å) and angles (°)

S1–C1	1.729(3)	S1′–C1′	1.726(2)
S1–C2	1.724(3)	S1′–C2′	1.717(3)
N1–C4	1.357(3)	N1′–C4′	1.351(3)
N1–C5	1.390(3)	N1′–C5′	1.384(4)
N2–N3	1.289(3)	N3′–N2′	1.292(3)
N2–C3	1.363(3)	N2′–C3′	1.359(3)
N3–C1	1.396(3)	N3′–C1′	1.382(3)
N4–N5	1.380(3)	N4′–N5′	1.383(3)
N5–C2	1.296(4)	N5′–C2′	1.300(3)
C1–N4	1.299(3)	N4′–C1′	1.308(3)
C2–S1–C1	86.54(12)	C2′–S1′–C1′	86.68(12)
C4–N1–C5	110.20(19)	C4′–N1′–C5′	110.3(2)
N3–N2–C3	115.11(19)	N3′–N2′–C3′	116.3(2)
N2–N3–C1	109.92(19)	N2′–N3′–C1′	110.07(19)
C1–N4–N5	111.1(2)	C1′–N4′–N5′	112.2(2)
C2–N5–N4	113.6(2)	C2′–N5′–N4′	111.9(2)
N4–C1–N3	121.2(2)	N4′–C1′–N3′	120.9(2)
N4–C1–S1	114.94(18)	N4′–C1′–S1′	114.19(18)
N3–C1–S1	123.84(17)	N3′–C1′–S1′	124.89(17)
N5–C2–S1	113.8(2)	N5′–C2′–S1′	115.0(2)
N2–C3–C4	121.2(2)	N2′–C3′–C4′	120.1(2)
N2–C3–C10	131.2(2)	N2′–C3′–C10′	132.6(2)

Table 3
Atomic coordinates and equivalent isotopic displacement parameters

	x	y	z	U_{eq}
S1	0.03055(4)	0.77382(5)	0.03164(4)	0.06188(18)
N1	−0.14850(14)	1.07410(14)	−0.20833(13)	0.0575(5)
N2	−0.00904(12)	0.92125(12)	−0.08321(12)	0.0513(4)
N3	0.07578(13)	0.91300(13)	−0.07881(13)	0.0572(5)
N4	0.18509(14)	0.81649(15)	−0.01101(16)	0.0706(6)
N5	0.19576(15)	0.74220(16)	0.04496(17)	0.0741(6)
C1	0.10245(15)	0.83992(15)	−0.02375(15)	0.0545(5)
C2	0.12234(19)	0.71289(18)	0.07246(17)	0.0662(6)
C3	−0.04277(15)	0.99062(15)	−0.13565(14)	0.0501(5)
C4	−0.13446(15)	1.00503(15)	−0.14939(14)	0.0518(5)
C5	−0.06831(16)	1.10790(16)	−0.23238(15)	0.0556(5)
C6	−0.0527(2)	1.1800(2)	−0.28819(18)	0.0723(7)
C7	0.0340(2)	1.2023(2)	−0.2978(2)	0.0823(9)
C8	0.1031(2)	1.1535(2)	−0.2540(2)	0.0786(8)
C9	0.08793(17)	1.08115(19)	−0.19946(17)	0.0622(6)
C10	0.00017(15)	1.05761(15)	−0.18754(14)	0.0523(5)
C11	−0.20881(15)	0.96071(16)	−0.11092(15)	0.0551(5)
C12	−0.29173(19)	0.9587(2)	−0.1560(2)	0.0763(8)
C13	−0.3627(2)	0.9195(3)	−0.1181(2)	0.0922(10)
C14	−0.3525(2)	0.8838(3)	−0.0366(2)	0.0887(10)
C15	−0.2706(2)	0.8849(2)	0.0087(2)	0.0775(8)
C16	−0.19858(19)	0.92276(19)	−0.02786(16)	0.0634(6)
C17	0.1170(2)	0.6332(2)	0.1332(2)	0.0890(9)
C18	0.0404(3)	0.5739(4)	0.1138(4)	0.198(3)
S1′	0.55406(5)	0.27847(5)	0.12019(5)	0.0720(2)
N1′	0.36606(16)	0.65693(17)	0.08041(15)	0.0669(6)
N2′	0.50810(12)	0.46750(14)	0.12258(13)	0.0589(5)
N3′	0.58588(12)	0.46154(14)	0.16293(13)	0.0586(5)
N4′	0.68957(13)	0.34726(14)	0.20612(14)	0.0632(5)
N5′	0.70529(15)	0.25313(16)	0.20186(16)	0.0729(6)
C1′	0.61343(15)	0.37035(17)	0.16626(16)	0.0559(5)
C2′	0.6407(2)	0.20969(19)	0.1590(2)	0.0765(8)
C3′	0.47280(16)	0.55376(18)	0.11447(16)	0.0590(6)
C4′	0.38498(16)	0.56559(18)	0.07983(17)	0.0622(6)
C5′	0.43874(17)	0.70674(19)	0.11438(17)	0.0628(6)
C6′	0.4467(2)	0.8014(2)	0.1269(2)	0.0744(8)
C7′	0.5272(2)	0.8337(2)	0.1616(2)	0.0832(9)
C8′	0.5977(2)	0.7738(2)	0.1821(2)	0.0793(8)
C9′	0.58979(19)	0.6797(2)	0.16921(19)	0.0703(7)
C10′	0.50782(16)	0.64455(18)	0.13636(16)	0.0604(6)
C11′	0.31991(16)	0.4972(2)	0.04691(18)	0.0660(6)
C12′	0.26057(19)	0.5180(3)	−0.0238(2)	0.0826(9)
C13′	0.2005(2)	0.4533(3)	−0.0571(3)	0.1067(12)
C14′	0.1976(3)	0.3677(4)	−0.0194(3)	0.1150(14)
C15′	0.2543(2)	0.3459(3)	0.0524(3)	0.1002(11)
C16′	0.3161(2)	0.4101(2)	0.0850(2)	0.0794(8)
C17′	0.6395(3)	0.1068(2)	0.1405(4)	0.1248(16)
C18′	0.6947(4)	0.0545(3)	0.1953(3)	0.1451(19)

$U\text{eq} = (1/3)\ \sum_i \sum_j U_{ij} a_i a_j$.

2.1. Solvent effects on absorption spectra of the dyes

Since the tautomeric equlibria strongly depend on the nature of media, the behaviour of hetarylazoindole dyes in various solvents was studied and also effect of acid and base on the absorption spectra of the dyes prepared was investigated. For this purpose, the absorption spectra of hetarylazoindole dyes (**1–8**) were measured in various solvents at a concentration of approximately 10^{-6}–10^{-8} M and were compared with those of corresponding model compounds (**1a–8a**) which contain 1,2-disubstituted indole ring. The results are given in

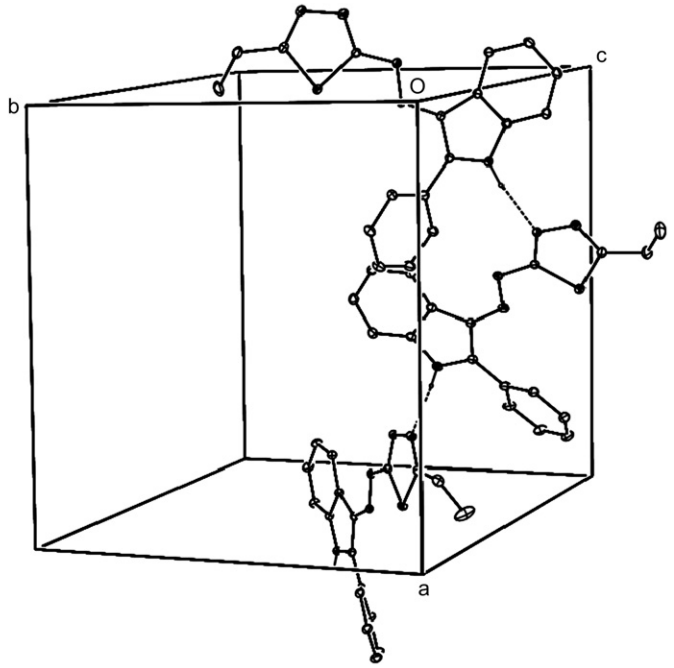


Fig. 2. A partial packing diagram of dye **6** showing hydrogen bonds as dashed lines. H atoms not involved in hydrogen bonds have been omitted.

Table 5. We found that the absorption maxima of thiadiazolylazoindole dyes (**1**–**6**) and their 1,2-disubstituted derivatives (**1a**–**6a**) generally indicated bathochromic shifts as the polarity of solvent was increased except in acetic acid. Apparently, these dyes exhibit a strong solvent dependence. The influence of solvents for dyes increases in the order acetic acid > DMSO > DMF > acetonitrile ~ methanol > chloroform.

The absorption curves of dyes **6** and **6a** in various solvents are shown in Figs. 3 and 4, respectively. Dye **6** showed absorption maxima at 509 nm in acetic acid, 499 nm in DMSO, 469 nm in DMF, 458 nm in methanol, 440 nm in acetonitrile, and 437 nm in chloroform. The same trend was observed for dye **6a** [e.g. 499 nm in acetic acid, 450 nm in DMSO, 443 nm in DMF, 445 nm in methanol, 438 nm in acetonitrile, and 430 nm in chloroform].

In addition, dye **6** exhibited significantly larger bathochromic shifts compared to dye **6a** in all solvents used. For instance, $\Delta\lambda_{max}$ values are 62 nm for dye **6** and 20 nm for **6a** in DMSO relative to chloroform. As can be seen in Table 5, the similar results were observed in $\Delta\lambda_{max}$ values of the other thiadiazolylazoindole dyes (**1**–**5**) when compared with their model compounds (**1a**–**5a**). On the other hand, dyes **7** and **7a**, and **8** and **8a**, in which diazonium salts of substituted 3-amino-5-mercapto-1,2,4-triazole was used as diazo components, showed properties somewhat different to those of **1**–**6** and **1a**–**6a** in which substituted diazotized 2-aminothiadiazoles were used as diazo components. Absorption maxima for dyes **7** and **7a**, and **8** and **8a** did not significantly change with the polarity of solvents except for acetic acid (e.g. for dye **7** $\Delta\lambda_{max}$ is 7 nm, for dye **7a** $\Delta\lambda_{max}$ is 4 nm in DMSO relative to those in chloroform; for dye **7** $\Delta\lambda_{max}$ is 50 nm, for dye **7a** $\Delta\lambda_{max}$ is 21 nm in acetic acid relative to those in chloroform).

Table 4
Hydrogen bond geometry (Å, °)

D−H⋯A	D−H	H⋯A	D⋯A	DH⋯A
N1−H1⋯$N4'^{i}$	0.87(3)	2.07(3)	2.924(3)	169(3)
N1′−H1′⋯N5	0.80(3)	2.08(3)	2.875(3)	174(3)

Symmetry codes: (i) $x - 1$, $3/2 - y$, $z - 1/2$.

Table 5
Influence of solvents on λ_{max} (nm) values of dyes **1**–**8** and **1a**–**8a**

Dye	λ_{max}					
	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
1	394s, 469	397s, 467	428	434	477	419
1a	441	437	434	439	443	429
2	496	465	437	454	503	438
2a	452	452	431	444	493	434
3	462	454	445	450	491	442
3a	460	455	451	454	468	451
4	509	484	467	472	521	465
4a	466	465	459	464	510	459
5	469	436	420	434	483	428
5a	442	438	432	440	453	431
6	499	469	440	458	509	437
6a	450	443	438	445	499	430
7	388	388	392	395	431	381
7a	402	397	401	399	419	398
8	411	408	411	410	470	410
8a	394	394	408	405	465	409

s, shoulder.

It was also observed that the λ_{max} values of all dyes prepared showed larger bathochromic shifts in acetic acid than in high polar solvents, e.g. DMSO and DMF, as shown in Table 5. These large bathochromic shifts in proton-donating acetic acid were considered due to intermolecular hydrogen bonding between dye molecules and acetic acid which is capable of stabilizing the ground state of the dyes leading to a resultant bathochromic shift.

Heterocyclic based azo disperse dyes tend to show larger solvatochromic effects than azo-benzene based dyes because of increased polarity of the dye system, especially in the excited

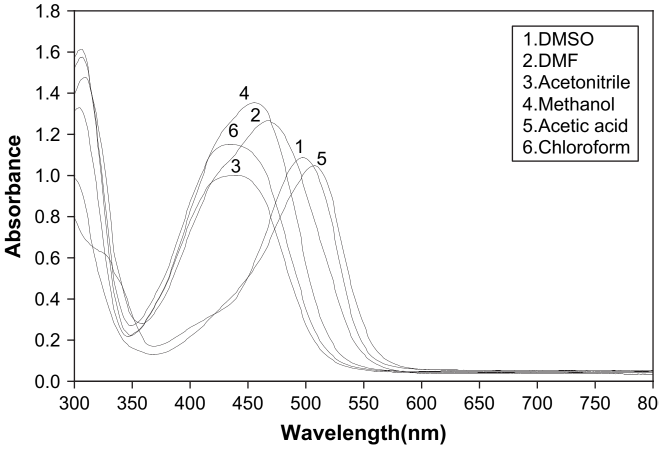


Fig. 3. Absorption spectra of dye **6** in various solvents.

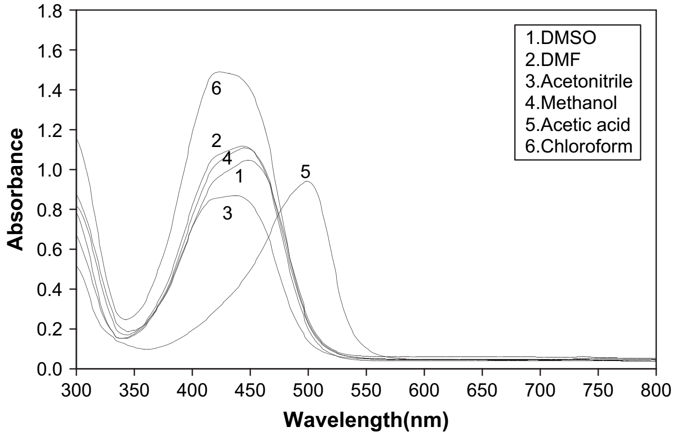


Fig. 4. Absorption spectra of dye **6a** in various solvents.

state. On the other hand, in hetarylazo dyes prepared from enamine-type coupling components, their tautomeric equilibria need to be considered. Hetarylazoindole dyes (**1**–**8**) theoretically may be involved in azo–hydrazone tautomerism (Scheme 2). Thus, the role of the azo–hydrazone tautomerism in relation to the visible absorption spectra and solvatochromic behaviour of the dyes have also been investigated. The visible absorption spectra of the dyes **1**–**8** showed one absorption maximum in all the solvents used, with the exception of the dye **1** in DMSO and DMF. It is known that two maxima are observed for compounds exhibiting azo–hydrazone tautomerism [26,27]. These results showed that the dyes **1**–**8** are in favour of the predominantly single tautomeric form in the solvents used. In addition, a comparison between λ_{max} values of the dyes (**1**–**8**) and their corresponding model compounds (**1a**–**8a**), which are in the azo form, in chloroform, methanol and acetonitrile reveals that the additional substitution of methyl group in the 1-position of indole ring brings about small hypsochromic shifts of λ_{max} values than 2-methyl and 2-phenyl substituted dyes, such as in dyes **3** and **3a** ($\Delta\lambda_{max}$ values are 9 nm in chloroform, 4 nm in methanol and 6 nm in acetonitrile) due to substituent effect (Table 5). Therefore, we assigned the structures of the dyes **1**–**8** to azo form in chloroform, methanol and acetonitrile. The small shifts in λ_{max} of the dyes in these solvents are due to solute–solvent interactions.

It was also observed that the differences in the λ_{max} values between the thiadiazolylazoindole dyes (except dye **3** in DMSO and dyes **3** and **5** in DMF) and their corresponding model compounds (in DMSO and DMF) were larger than those in the other mentioned solvents (e.g. $\Delta\lambda_{max}$ values are 44 nm for dye **2**, 49 nm for dye **6** in DMSO with the respect to the dyes **2a** and **6a**). The similar results were observed for dyes **1**, **3** and **5** in acetic acid (i.e. $\Delta\lambda_{max}$ values are 34 nm for dye **1**, 23 nm for dye **3** and 30 nm for dye **5** with the respect to the dyes **1a**, **3a** and **5a**). In addition, the λ_{max} values of thiadiazolylazoindole dyes in DMSO (except dye **3**) and in DMF (except dyes **3** and **5**) are strongly shifted bathochromically relative to the other solvents whilst the λ_{max} of their corresponding model compounds are slightly shifted bathochromically in DMSO and DMF. This result suggests that these dyes may present the different tautomeric form in DMSO and DMF. However, the chemical shifts of –NH peaks for dyes **1**–**6** in DMSO-d_6 were nearly the same for dyes **3** and **5** in DMSO-d_6. Moreover, comparison with the λ_{max} values of dyes **3** and **3a** in DMSO and dyes **5** and **5a** in DMF suggests that these dyes are in azo form in these solvents. Because the λ_{max} values of these dyes in above mentioned solvents are slightly greater than that for their model compounds to the exten of 1–2 nm as illustrated in Table 5. And, we assigned the structures of the dyes **3** and **5** as the azo form in DMSO and DMF, respectively. Therefore, it is reasonable to assume that the azo form is predominant in these solvents used.

On the other hand, the electronic absorption spectra of the dye **1** in DMSO and DMF solutions differ significantly from those in the other dyes (Fig. 5). Thus, the spectra of the dye **1** in DMSO and DMF showed one absorption maximum with a shoulder at shorter wavelengths (λ_{max} value is 469 nm with a shoulder at 394 nm in DMSO and λ_{max} value is 467 nm with a shoulder at 397 nm in DMF) whereas it showed one absorption maximum in the other solvents used (Table 5). The position of both shoulders is practically closer to their absorption maxima in chloroform which may be indicated in the azo tautomer. So, the absorption at longer wavelengths may be assigned to the hydrazone form. Furthermore, λ_{max} values of dye **1** showed large bathochromic shifts in DMSO, DMF and acetic acid with respect to the λ_{max} values in chloroform, methanol and acetonitrile. In addition, dramatic increases in λ_{max} values are observed in these solvents in contrast to the behaviour of its model compound **1a** (e.g. $\Delta\lambda_{max}$ values are 50 and 12 nm in DMSO with respect to chloroform for dyes **1** and **1a**, respectively). These results suggest that dye **1** was present in more than one tautomeric form in DMSO and DMF.

The effects of the acid and base on the absorption maxima of the dye solutions were investigated and the results are shown in Table 6. The absorption maxima of the thiadiazolylazoindole dyes (**1**–**6**) in DMF and methanol were quite sensitive to the addition of base (piperidine and KOH, respectively) with λ_{max} values of the dyes **1**–**6** showing large bathochromic shifts (Table 6) with the exception of dye **1** in DMF (Fig. 6). When piperidine was added to chloroform

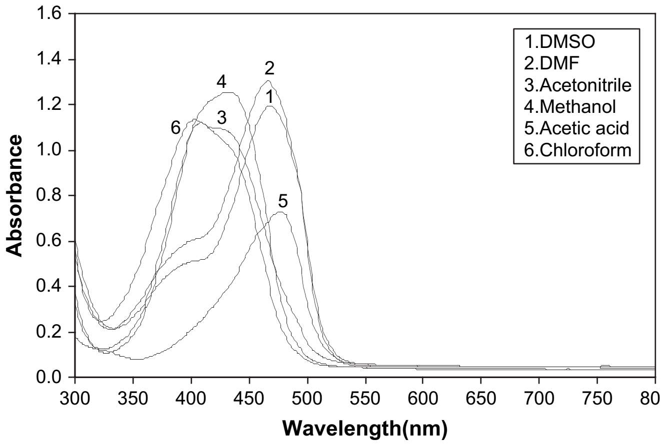


Fig. 5. Absorption spectra of dye **1** in various solvents.

Table 6
Absorption maxima of dyes **1**–**8** and **1a**–**8a** in acidic and basic solution

Dye	λ_{max}								
	DMSO	DMSO + piperidine	DMF	DMF + piperidine	Methanol	Methanol + HCl	Methanol + KOH	Chloroform	Chloroform + piperidine
1	394s, 469	386, 473	397s, 467	394, 472	434	466	465	419	424
1a	441	442	437	437	439	474	439	429	428
2	496	497	465	495	454	477	485	438	451
2a	452	448	452	441	444	469	443	434	433
3	462	487	454	486	450	460	475	442	450
3a	460	459	455	456	454	471	456	451	450
4	509	508	484	508	472	488	500	465	471
4a	466	466	465	466	464	478	463	459	458
5	469	474	436	474	434	480	465	428	437
5a	442	441	438	438	440	480	440	431	429
6	499	500	469	500	458	499	489	437	451
6a	450	449	443	444	445	491	444	430	429
7	388	364, 420s	388	362, 431	395	432	383, 420s	381	381
7a	402	382, 425s	397	382, 419s	399	440	384, 422s	398	397, 427s
8	411	410, 469	408	412s, 476	410	466	402, 458s	410	408
8a	394	391, 437s	394	390, 431s	405	456	391, 426s	409	404, 438s

s, shoulder.

solutions, λ_{max} values of the dyes showed a small bathochromic shifts. There was no significant change when piperidine was added to solutions of the dyes in DMSO with exception of dyes **1** and **3** which showed a large bathochromic shift. In the case of dye **1**, with the addition of piperidine to their DMSO and DMF solutions, shoulders were converted to maximum and λ_{max} at longest wavelength did not significantly change (Table 6). A typical example is shown in Fig. 7. It is interesting that the absorption spectra obtained in basic solutions of DMSO, DMF and methanol for dyes **1**–**6** are very similar to the corresponding spectra registered in acetic acid. Therefore, absorption maxima in these basic solutions are assigned to azo tautomer. On the other hand, λ_{max} values of the dyes in chloroform showed small bathochromic shifts when piperidine was added, being nearly the same as those observed in chloroform. This indicates that dyes **1**–**6** exist in azo form in chloroform and they are very stable even in basic solutions. These results are in agreement with those obtained for hetarylazoindoles in our previous work [26,27]. On the other hand, these results are in contrast with those for thiadiazolylazopyridones in previous work [17].

In contrast, absorption curves of triazolylazoindole dyes **7** and **8** are very sensitive to bases and acids. λ_{max} values of the dyes **7** and **8** showed generally small hypsochromic shifts and also a shoulder or second maximum at longest wavelength appeared when a small amount of piperidine was added to their DMSO, DMF and chloroform solutions and 0.1 M KOH was added to their methanolic solutions. Such a situation is consistent with the phenomenon of dissociation rather than azo–hydrazone tautomerism. This equilibrium is supported by the single isosbestic point in the visible spectra, for example dye **8** in basic solutions in DMSO and DMF (Fig. 8), and it could not be an acid–base equilibrium between azo or hydrazone tautomers and the corresponding common anion (Scheme 2) resulted by the acid dissociation of the azo or hydrazone tautomers. Because the similar results were observed in absorption spectra of their corresponding model compounds (**7a** and **8a**) which do not involve tautomeric hydrogen (Table 6). But

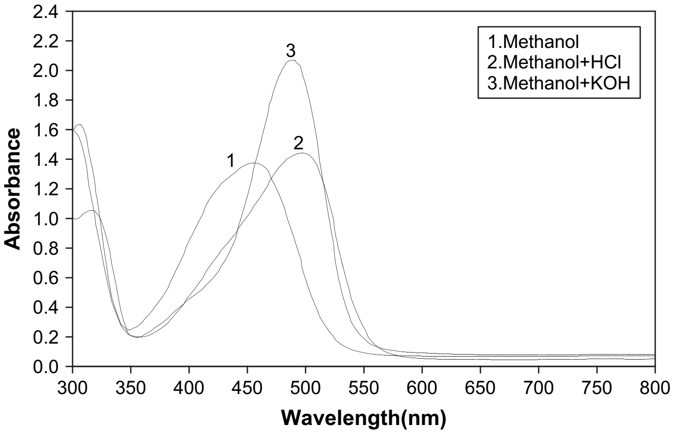


Fig. 6. Absorption spectra of dye **6** in acidic and basic solutions.

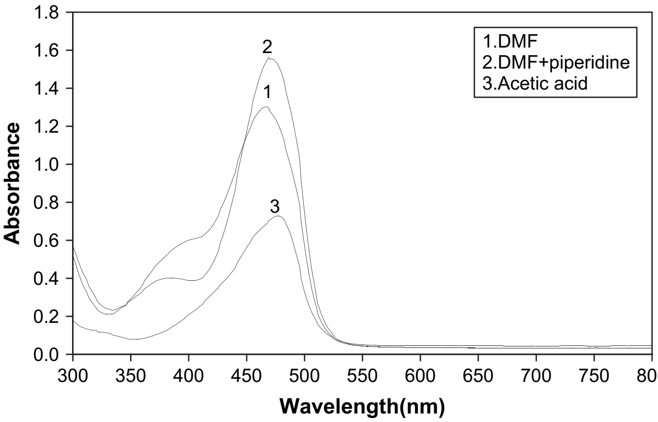


Fig. 7. Absorption spectra of dye **1** in acidic and basic solutions.

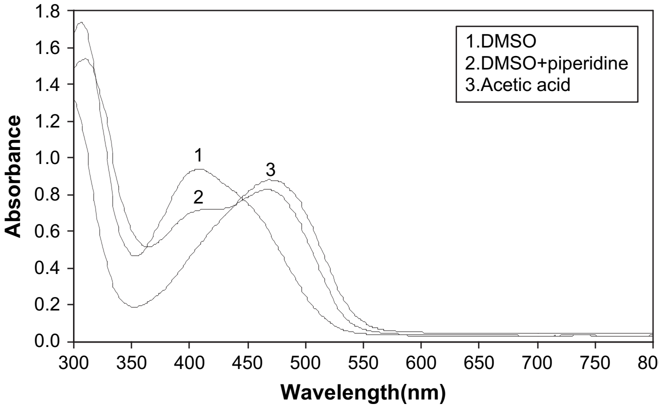


Fig. 8. Absorption spectra of dye **8** in acidic and basic solutions.

the dyes **7** and **8** may also exhibit another acid–base equilibrium due to acid dissociation of the –SH group or the –NH group of triazolyl ring to their anions. On the other hand, λ_{max} values of the dyes **7** and **8**, and **7a** and **8a** in methanol showed large bathochromic shifts when 0.1 M HCl was added and being the same as those observed in acetic acid. This indicates that triazolylazoindole dyes exist in the azo form in acidic media.

2.2. Substituent effects on absorption spectra of the dyes in various solvents

Absorption maxima of the dyes prepared indicate that 1-methyl-2-phenyl substituted dyes (**2a**, **4a**, **6a** and **8a**) generally absorb bathochromically compared with the 1,2-dimethyl substituted dyes (**1a**, **3a**, **5a** and **7a**) in all solvents used with the exceptions of dye **8a** in chloroform, DMF and DMSO and dyes **2** and **4a** in acetonitrile (Table 7). The largest bathochromic shifts were observed in acetic acid. Thus, dye **1a** absorbs at 443 nm, whereas the analogous dye **2a** absorbs at 493 nm as shown in Table 5. On the other hand, λ_{max} values of the 1-methyl-2-phenyltriazolylazoindole dye **8a** show bathochromic shifts in acetic acid, methanol and acetonitrile whereas it produces hypsochromic shifts in chloroform, DMF and DMSO when compared with dye **7a**.

Although resultant values of $\Delta\lambda_{max}$ values can vary according to the solvent used, generally the dyes **2a**–**8a** absorb at longer wavelengths than the corresponding 1,2-dimethyl substituted derivatives. The greatest bathochromic differences in λ_{max} values appear in acetic acid as solvent. Presumably, the resonance effect enhanced by an electron-rich phenyl group is more favoured than the slightly stronger field effect of a methyl group. When $\Delta\lambda_{max}$ value between dyes **1** and **2**, **3** and **4**, **5** and **6**, and **7** and **8** was also compared with those between dyes **1a** and **2a**, **3a** and **4a**, **5a** and **6a**, and **7a** and **8a**, respectively, the resonance effect of phenyl group on the absorption maxima for dyes **1**–**8** is greater than their corresponding model compounds and resulted in larger bathochromic shifts (e.g. $\Delta\lambda_{max}$ value is 47 nm for dye **4** relative to dye **3** in DMSO, $\Delta\lambda_{max}$ value is 6 nm for dye **4a** relative to dye **3a** in DMSO). The similar results were also observed for dye **2** containing 2-phenyl group in the indole ring as compared with dye **1** containing 2-methyl group in the indole ring in all solvent used with the exception of DMF in which a very small hypsochromic shift was observed. Consequently, the effect of phenyl group at the 2-position of indole ring has a significant effect on colour in hetarylazoindole dyes. Comparison with $\Delta\lambda_{max}$ values of the dyes (**1** to **2**; **3** to **4**; **5** to **6**; and **7** to **8**) containing 2-methyl and 2-phenyl groups suggest that the resonance effect of phenyl group on the absorption maxima for dyes **2**, **4**, **6** and **8** is greater than that of their corresponding model compounds (**1a**–**2a**, **3a**–**4a**, **5a**–**6a** and **7a**–**8a**) and resulted in larger bathochromic shifts (Tables 8 and 9).

Absorption maxima obtained for thiadiazolylazoindole dyes indicated that electron-donating groups (ethyl and mercaptomethyl) in thiadiazole ring at 5-position generally absorb bathochromically when compared with the unsubstituted dyes (**1**, **1a**, **2** and **2a**) in all solvents used with the exception of ethylsubstitued derivatives in DMF (dye **5**) and in chloroform (dye **6a**) as shown in Tables 4 and 5.

As the electron-donating ability of the donor group increases from the ethyl to mercaptomethyl derivatives of the dyes, $\Delta\lambda_{max}$ values show bathochromic shifts (e.g. $\Delta\lambda_{max}$ value is 4 nm for dyes **2**–**6** and 18 nm for dyes **2**–**4** in methanol; $\Delta\lambda_{max}$ value is 1 nm for dyes **2a**–**6a** and 20 nm for dyes **2a**–**4a** in methanol). This bathochromic shift is attributed to the stronger electron-donating ability of the methylmercapto group with respect to the ethyl group at 5-position of thiadiazole ring, thus enhancing electron delocalization in the dye molecule. Moreover, such a substituent effect provided a strong evidence that the dyes prepared exist solely in one tautomeric form, namely azo form, in all solvents used.

Table 7
Comparison between dyes **1**–**8** and their corresponding model dyes **1a**–**8a**

Dye	λ_{max}					
	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
1–1a	+28	+30	−6	−5	+34	−10
2–2a	+44	+13	+6	+10	+10	+4
3–3a	+2	−1	−6	−4	+23	−9
4–4a	+43	+19	+8	+8	+11	+6
5–5a	+27	−2	−12	+6	+30	−3
6–6a	+49	+26	+2	+13	+10	+7
7–7a	−14	−9	−9	−4	+12	−17
8–8a	+17	+14	+3	+5	+5	+1

Values of λ_{max}: see Table 1.

Table 8
Comparison between dyes based on 1,2-dimethylindole and 1-methyl-2-phenylindole

Dye	λ_{max}					
	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
1a/2a	+11	+15	−3	+5	+50	+5
3a/4a	+6	+10	−8	+10	+42	+8
5a/6a	+8	+5	+6	+5	+46	−1
7a/8a	−8	−3	+7	+6	+46	−11

Values of λ_{max}: see Table 1.

Table 9
Comparison between dyes based on 2-methylindole and 2-phenylindole

Dye	λ_{max}					
	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
1/2	+27	−2	+9	+20	+26	+19
3/4	+47	+30	+22	+22	+30	+23
5/6	+30	+33	+20	+24	+26	+9
7/8	+23	+20	+19	+15	+39	+29

Values of λ_{max}: see Table 1.

It was also observed that λ_{max} values of thiadiazolylazoindole dyes **1–6** and **1a–6a** showed large bathochromic shifts in comparison with analogous triazolylazoindole dyes **7** and **8**, and **7a** and **8a** in all solvent used as shown in Table 5. These results show clearly that thiadiazole ring system act as a better electron donor than triazole ring system.

3. Experimental

3.1. General

The chemicals used in the synthesis of all dyes were obtained from Aldrich Chemical Company and were used without further purification. The solvents used were of spectroscopic grade.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr. ^{1}H NMR spectra were recorded on a Bruker-Spectrospin Avance DPX 400 MHz Ultra-Shield 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 on Analytikjena Specord 200 Spectrophotometer at the wavelength of maximum absorption (λ_{max}) in a range of solvents, i.e. dimethylsulphoxide (DMSO), dimethylformamide (DMF), acetonitrile, methanol, acetic acid and chloroform. Change of λ_{max} was investigated when 0.1 ml of piperidine was added to 1 ml of dye solutions in chloroform, DMSO and DMF, similarly, when 0.1 ml of base (potassium hydroxide, 0.1 M) or 0.1 ml of acid (hydrochloric acid, 0.1 M) was added to 1 ml dye solutions in methanol. Mass spectra were recorded on Agilent 5973 Network Mass Selective Detector, SIS (Direct Insertion Probe), electron impact 70, 100 or 150 eV and on AGILENT 1100 MSD and Elemental analyses were recorded on LECO CHNS 932 by Turkish Research Council Laboratories (Center of Science and Technology Research of Turkey). All melting points were uncorrected and in degree centigrade. The X-ray data were recorded in the Department of Chemistry, Atatürk University, Erzurum, Turkey.

3.2. Crystallography

The X-ray diffraction data collection was performed on a Rigaku R-AXIS RAPID-S diffractometer equipped with Mo Kα ($\lambda = 0.71073$ Å) radiation using w scans. The intensity data were corrected for Lorentz polarization [55] and absorption [56] effects. The structure was analyzed using a combination of direct and difference Fourier methods provided by the SHELXS97 [57] and was refined as a full matrix least square against F^2 for all data by the SHELXL97 [57] computer programs; all non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically, with C–H = 0.97 and 0.96 Å, respectively, for methylene and methyl H atoms, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for methylene and $x = 1.5$ for methyl H atoms. The remaining H atoms were located in a difference map and refined isotopically [N–H = 0.80(3) and 0.87(3) Å, C–H = 0.89(3)–1.05(4) Å and $U_{iso}(H) = 0.057(7)$–0.120(13) Å^2]. Crystallographic data are summarized in Table 1, the CCDC reference number is CCDC 639701.

3.3. Preparation of hetarylazoindole dyes (*1–8* and *1a–8a*)

Diazotization of various heterocyclic amines was effected with H_2SO_4 and $NaNO_2$. A typical procedure used was that described below for 2-amino-1,3,4-thiadiazole, and all other dyes were prepared in a similar manner. The obtained compounds were purified by crystallization using ethanol and then analyzed.

3.3.1. Preparation of 2-methyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (*1*)

2-Amino-1,3,4-thiadiazole (0.202 g, 2.0 mmol) was dissolved in hot glacial acetic acid–propionic acid mixture (2:1, 8.0 ml) and was rapidly cooled in an salt/ice bath to −5 °C. The liquor was then 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 an additional 2 h at 0 °C. Excess nitrous acid was destroyed by the addition of urea. And then, the diazo liquor was slowly added to vigorously stirred solution of 2-methylindole (0.26 g, 2.0 mmol) which is solved in glacial acetic acid–propionic acid (3:1, 8.0 ml) and cooled. The solution was stirred at 0–5 °C for 2 h and pH of the reaction mixture was maintained at 4–6 by simultaneous addition of saturated sodium carbonate solution. The mixture was stirred for a further 1 h at 5 °C. The resulting product was filtered, washed with water, dried, and crystallized from ethanol. 2-Methyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole gave orange powder (yield: 0.40 g, 82%; mp: 243–244 °C). FT-IR (KBr) ν_{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): δ 12.78 (br, indole –NH), 9.38 (s, 1H), 8.28 (m, 1H), 7.46 (m, 1H), 7.31 (m, 2H), 2.75 (s, 3H). Anal. Calcd for $C_{11}H_9N_5S$: C, 54.32; H, 3.70; N, 28.81; S, 13.17. Found: C, 54.19; H, 3.69; N, 28.96; S, 13.22%. LC–MS (*m/z*, 100 eV): 244 (100%) (M$^+$), 158 (89.7%), 130 (32.9%).

3.3.2. 1,2-Dimethyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (*1a*)

This dye was obtained from 2-amino-1,3,4-thiadiazole and 1,2-dimethylindole as red crystals (yield: 0.39 g, 77%;

mp: 191−192 °C). FT-IR (KBr) ν_{max}: 3085, 3005 (aromatic C−H), 2884 (aliphatic C−H), 1508 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$): δ 9.38 (s, 1H), 8.30 (m, 1H), 7.68 (m, 1H), 7.39 (m, 2H), 3.83 (s, 3H, $-NCH_3$), 2.78 (s, 3H). Anal. Calcd for $C_{12}H_{11}N_5S$: C, 56.03; H, 4.28; N, 27.24; S, 12.45. Found: C, 55.88; H, 4.29; N, 27.33; S, 12.48%. MS (*m/z*, 70 eV): 257 (M^+).

*3.3.3. 2-Phenyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**2**)*

This dye was obtained from 2-amino-1,3,4-thiadiazole and 2-phenylindole as red crystals (yield: 0.52 g, 85%; mp: 304−305 °C). FT-IR (KBr) ν_{max}: 3223 (indole −NH), 3070 (aromatic C−H), 1484 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 13.21 (br, indole −NH), 9.43 (s, 1H), 8.42 (m, 1H), 8.09 (m, 2H), 7.62 (m, 4H), 7.41 (m, 2H). Anal. Calcd for $C_{16}H_{11}N_5S$: C, 62.95; H, 3.61; N, 22.95; S, 10.49. Found: C, 63.00; H, 3.69; N, 22.96; S, 10.48%. LC−MS (*m/z*, 100 eV): 306 (100%) (M^+), 220.1 (44.3%), 192.1 (21.9%).

*3.3.4. 1-Methyl-2-phenyl-3-(1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**2a**)*

This dye was obtained from 2-amino-1,3,4-thiadiazole and 1-methyl-2-phenylindole as orange crystals (yield: 0.50 g, 79%; mp: 185−186 °C). FT-IR (KBr) ν_{max}: 3056 (aromatic C−H), 2940 (aliphatic C−H), 1478 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): 9.38 (s, 1H), 8.43 (m, 1H), 7.78 (m, 3H), 7.66 (m, 3H), 7.51 (m, 2H), 3.89 (s, 3H, $-NCH_3$). Anal. Calcd for $C_{17}H_{13}N_5S$: C, 63.95; H, 4.08; N, 21.94; S, 10.03. Found: C, 63.78; H, 4.02; N, 21.86; S, 10.08%. LC−MS (*m/z*, 100 eV): 320 (100%) (M^+), 234.1 (22.2%), 206.1 (10%).

*3.3.5. 2-Methyl-3-(5-methylthio-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**3**)*

This dye was obtained from 2-amino-5-methylthio-1,3,4-thiadiazole and 2-methylindole as red crystals (yield: 0.42 g, 83%; mp: 264−265 °C). FT-IR (KBr) ν_{max}: 3448 (indole −NH), 3064, 3031 (aromatic C−H), 2928, 2877 (aliphatic C−H), 1490 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.77 (br, indole −NH), 8.24 (m, 1H), 7.48 (m, 1H), 7.31 (m, 2H), 2.79 (s, 3H, $-SCH_3$), 2.73 (s, 3H). Anal. Calcd for $C_{12}H_{11}N_5S$: C, 49.32; H, 3.81; N, 24.22; S, 22.15. Found: C, 49.11; H, 3.89; N, 24.26; S, 22.18%. LC−MS (*m/z*, 100 eV): 290 (31.4%) (M^+), 158.1 (100%), 130.1 (29.1%).

*3.3.6. 1,2-Dimethyl-3-(5-methylthio-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**3a**)*

This dye was obtained from 2-amino-5-methylthio-1,3,4-thiadiazole and 1,2-dimethylindole as orange crystals (yield: 0.51 g, 84%; mp: 246−247 °C). FT-IR (KBr) ν_{max}: 3043 (aromatic C−H), 2920 (aliphatic C−H), 1523 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.30 (m, 1H), 7.53 (m, 1H), 7.30 (m, 2H), 3.83 (s, 3H, $-NCH_3$), 2.78 (s, 3H, $-SCH_3$), 2.73 (s, 3H). Anal. Calcd for $C_{13}H_{13}N_5S_2$: C, 51.49; H, 4.29; N, 23.10; S, 21.12. Found: C, 51.38; H, 4.29; N, 23.06; S, 21.18%. MS (*m/z*, 70 eV): 303 (M^+).

*3.3.7. 2-Phenyl-3-(5-methylthio-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**4**)*

This dye was obtained from 2-amino-5-methylthio-1,3,4-thiadiazole and 2-phenylindole as orange crystals (yield: 0.54 g, 85%; mp: 266−267 °C). FT-IR (KBr) ν_{max}: 3462 (indole −NH), 3056 (aromatic C−H), 2986, 2864 (aliphatic C−H), 1490 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 13.01 (br, indole −NH), 8.38 (m, 1H), 8.08 (m, 2H), 7.61 (m, 4H), 7.38 (m, 2H), 2.78 (s, 3H, $-SCH_3$). Anal. Calcd for $C_{17}H_{13}N_5S_2$: C, 58.12; H, 3.70; N, 19.94; S, 18.23. Found: C, 58.01; H, 3.66; N, 19.88; S, 18.12%. LC−MS (*m/z*, 150 eV): 352 (19.5%) (M^+), 220.1 (70.8%), 165.1 (48.5%).

*3.3.8. 1-Methyl-2-phenyl-3-(5-methylthio-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**4a**)*

This dye was obtained from 2-amino-5-methylthio-1,3,4-thiadiazole and 1-methyl-2-phenylindole as orange crystals (yield: 0.58 g, 88%; mp: 269−271 °C). FT-IR (KBr) ν_{max}: 3063 (aromatic C−H), 2949, 2864 (aliphatic C−H), 1496 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.41 (m, 1H), 7.76 (m, 3H), 7.67 (m, 2H), 7.51 (m, 2H), 3.91 (s, 3H, $-NCH_3$), 2.78 (s, 3H, $-SCH_3$). Anal. Calcd for $C_{18}H_{15}N_5S_2$: C, 59.18; H, 4.11; N, 19.18; S, 17.53. Found: C, 59.11; H, 4.09; N, 19.06; S, 17.58%. LC−MS (*m/z*, 150 eV): 366 (33.0%) (M^+), 234.1 (69.1%), 206.1 (100%).

*3.3.9. 2-Methyl-3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**5**)*

This dye was obtained from 2-amino-5-ethyl-1,3,4-thiadiazole and 2-methylindole as yellow crystals (yield: 0.44 g, 80%; mp: 271−273 °C). FT-IR (KBr) ν_{max}: 3442 (indole −NH), 3064 (aromatic C−H), 2985, 2877 (aliphatic C−H), 1510 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.75 (br, indole −NH), 8.24 (m, 1H), 7.48 (m, 1H), 7.31 (m, 2H), 3.08 (q, 2H, $-CH_2CH_3$), 2.75 (s, 3H), 1.33 (t, 3H, $-CH_2CH_3$). Anal. Calcd for $C_{13}H_{13}N_5S$: C, 57.56; H, 4.80; N, 25.83; S, 11.81; found: C, 57.44; H, 4.67; N, 25.88; S, 11.73%. LC−MS (*m/z*, 100 eV): 272.1 (50.8%) $(M+1)^+$, 158.1 (100%), 130.1 (52.7%).

*3.3.10. 1,2-Dimethyl-3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**5a**)*

This dye was obtained from 2-amino-5-ethyl-1,3,4-thiadiazole and 1,2-dimethylindole as red crystals (yield: 0.44 g, 83%; mp: 200−202 °C). FT-IR (KBr) ν_{max}: 3015 (aromatic C−H), 2939 (aliphatic C−H), 1526 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.29 (m, 1H), 7.66 (m, 1H), 7.36 (m, 2H), 3.84 (s, 3H, $-NCH_3$), 3.07 (q, 2H, $-CH_2CH_3$), 2.75 (s, 3H), 1.33 (t, 3H, $-CH_2CH_3$). Anal. Calcd for $C_{14}H_5N_5S$: C, 58.95; H, 5.26; N, 24.56; S, 11.23. Found: C, 58.71; H, 5.25; N, 24.38; S, 11.21%. MS (*m/z*, 70 eV): 285 (M^+).

*3.3.11. 2-Phenyl-3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**6**)*

This dye was obtained from 2-amino-5-ethyl-1,3,4-thiadiazole and 2-phenylindole as red crystals (yield: 0.57 g, 85%; mp: 172−174 °C). FT-IR (KBr) ν_{max}: 3442 (indole −NH), 3050 (aromatic C–H), 2935, 2900 (aliphatic C–H), 1490 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 13.01 (br, indole –NH), 8.41 (m, 1H), 8.09 (m, 2H), 7.62 (m, 4H), 7.41 (m, 2H), 3.08 (q, 2H, $-CH_2CH_3$), 1.36 (t, 3H, $-CH_2CH_3$). Anal. Calcd for $C_{18}H_{15}N_5S$: C, 64.86; H, 4.50; N, 21.02; S, 9.61. Found: C, 64.77; H, 4.44; N, 21.06; S, 9.58%. LC–MS (*m/z*, 150 eV): 334.1 (18.8%) (M^+), 220.1 (68.6%), 192.1 (100%).

*3.3.12. 1-Methyl-2-phenyl-3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1H-indole (**6a**)*

This dye was obtained from 2-amino-5-ethyl-1,3,4-thiadiazole and 1-methyl-2-phenylindole as red crystals (yield: 0.61 g, 88%; mp: 220–222 °C). FT-IR (KBr) $\nu_{\max}$: 3056 (aromatic C–H), 2940, 2870 (aliphatic C–H), 1498 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): 8.42 (m, 1H), 7.76–7.44 (m, 8H), 3.88 (s, 3H, $-NCH_3$), 3.01 (q, 2H, $-CH_2CH_3$), 1.3 (t, 3H, $-CH_2CH_3$). Anal. Calcd for $C_{19}H_{17}N_5S$: C, 65.71; H, 4.90; N, 20.17; S, 9.22. Found: C, 65.56; H, 4.78; N, 20.10; S, 9.09%. LC–MS (*m/z*, 100 eV): 348.1 (100%) (M^+), 234.1 (17.7%), 206.1 (6.1%).

*3.3.13. 2-Methyl-3-(5-mercapto-1,2,4-triazol-3-yldiazenyl)-1H-indole (**7**)*

This dye was obtained from 3-amino-5-mercapto-1,2,4-triazole and 2-methylindole as dark yellow powder (yield: 0.45 g, 88%; mp: 228–229 °C). FT-IR (KBr) $\nu_{\max}$: 3403–3191 (indole, triazole –NH and thiol –SH), 3035 (aromatic C–H), 2915, 2870 (aliphatic C–H), 1458 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 14.33 (br, triazole –NH), 12.49 (br, indole –NH), 8.27 (m, 1H), 7.43 (m, 1H), 7.24 (m, 2H), 2.78 (s, 3H). Anal. Calcd for $C_{11}H_{10}N_6S$: C, 51.16; H, 3.88; N, 32.56; S, 12.40. Found: C, 51.11; H, 3.89; N, 32.48; S, 12.33%. LC–MS (*m/z*, 100 eV): 259.0 (64.6%) $(M+1)^+$, 158.1 (100%), 130.2 (41.4%).

*3.3.14. 1,2-Dimethyl-3-(5-mercapto-1,2,4-triazol-3-yldiazenyl)-1H-indole (**7a**)*

This dye was obtained from 3-amino-5-mercapto-1,2,4-triazole and 1,2-dimethylindole as yellow powder (yield: 0.45 g, 91%; mp: 239 °C dec.). FT-IR (KBr) $\nu_{\max}$: 3418–3264 (triazole –NH and thiol –SH), 3018 (aromatic C–H), 2920 (aliphatic C–H), 1589 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6/$CDCl_3$): δ 14.11 (br, triazole –NH), 13.13 (br, –SH), 8.21 (m, 1H), 7.38 (m, 1H), 7.20 (m, 2H), 3.88 (s, 3H, $-NCH_3$), 2.72 (s, 3H). Anal. Calcd for $C_{12}H_{12}N_6S$: C, 52.94; H, 4.41; N, 30.88; S, 11.76. Found: C, 52.77; H, 4.33; N, 30.96; S, 11.68%. LC–MS (*m/z*, 100 eV): 273.0 (100%) $(M+1)^+$, 172.0 (95%), 144.1 (52.4%).

*3.3.15. 2-Phenyl-3-(5-mercapto-1,2,4-triazol-3-yldiazenyl)-1H-indole (**8**)*

This dye was obtained from 3-amino-5-mercapto-1,2,4-triazole and 2-phenylindole as dark yellow powder (yield: 0.54 g, 85%; mp: 265–267 °C). FT-IR (KBr) $\nu_{\max}$: 3404–3180 (indole, triazole –NH and thiol –SH), 3064, 3020 (aromatic C–H), 1450 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ14.51 (br, triazole –NH), 13.82 (br, –SH), 12.58 (br, indole –NH), 8.22 (m, 1H), 8.08 (m, 3H), 7.88–7.61 (m, 5H). Anal. Calcd for $C_{16}H_{12}N_6S$: C, 60.00; H, 3.75; N, 26.25; S, 10.00. Found: C, 59.79; H, 3.66; N, 26.26; S, 9.87%. LC–MS (*m/z*, 100 eV): 321.0 (7.6%) $(M+1)^+$, 308.1 (45.6%), 220.1 (10.6%), 193.1 (100%).

*3.3.16. 1-Methyl-2-phenyl-3-(5-mercapto-1,2,4-triazol-3-yldiazenyl)-1H-indole (**8a**)*

This dye was obtained from 3-amino-5-mercapto-1,2,4-triazole and 1-methyl-2-phenylindole as orange crystals (yield: 0.59 g, 89%; mp: 218–219 °C). FT-IR (KBr) $\nu_{\max}$: 3404 (triazole –NH and thiol –SH), 3056 (aromatic C–H), 2928 (aliphatic C–H), 1471 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 14.48 (br, triazole –NH), 13.77 (br, –SH), 8.47 (m, 1H), 8.38 (m, 1H), 7.72–7.21 (m, 7H), 3.82 (s, 3H, $-NCH_3$). Anal. Calcd for $C_{17}H_{14}N_6S$: C, 61.08; H, 4.19; N, 25.15; S, 9.58. Found: C, 59.95; H, 4.19; N, 25.16; S, 9.44%. LC–MS (*m/z*, 100 eV): 335.1 (7.2%) $(M+1)^+$, 322.1 (12.2%), 234.1 (15%), 207.1 (28.4%).

4. Conclusions

A series of bis-hetarylazoindole dyes were obtained by the coupling of 2-methyl, 2-phenyl, 1,2-dimethyl and 1-methyl-2-phenylindoles with diazotized 2-amino-1,3,4-thiadiazoles and 3-amino-5-mercapto-1,2,4-triazole in nitrosylsulphuric acid. The solvatochromic behaviours and substituent effects in various solvents were evaluated. The results indicated that these dyes were strongly dependent on solvents and show generally bathochromic shifts as the polarity of solvents was increased. The absorption maxima of dyes shifted bathochromically in the sequence acetic acid > DMSO > DMF > acetonitrile ∼ methanol > chloroform.

The results of solvent effects on the absorption spectra of the dyes indicated that the azo structure is predominant in solution. X-ray crystallographic data showed that the bis-hetarylazoindole dyes exist in the azo form too. As a results of the introduction of electron-donating substituents into the thiadiazole ring $\lambda_{\max}$ shifts bathochromically in all solvent used. Also, the thiadiazolylazoindoles absorb bathochromically compared with their triazolyl analogues.

To determine the azo–hydrazone tautomerism of the dyes in solid state, the structure of 2-phenyl-3-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)-1*H*-indole (dye **6**) was determined by the X-ray diffraction analysis. It was shown that the dye exists in azo form. The asymmetric unit of the dye contains two crystallographically independent molecules; in each molecule, all of the rings are planar and the indole ring systems are also nearly planar. The crystal packing is stabilized by intra- and intermolecular N–H···N hydrogen bonds, linking the molecules to form infinite chains along the [001] directions.

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