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Synthesis, Characterization of Novel Bisheteroaryl Bisazo Dyes, and Their Dyeing and Solvatochromic Behavior

Visha P. Modi and Hasmukh S. Patel

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

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ABSTRACT: *4-Phenyl-2-aminothaizole was diazotized and coupled with N-(alkyl)-2-oxo-3-cyano-4-methyl-6-hydroxypyridine (2-pyridone). The resultant dyes were named as N-(alkyl)-6-hydroxy-4-methyl-2-oxo-5-((4-phenylthiazole-2-yl)diazenyl)-1,2-dihydro pyridine-3-carbonitrite and duly characterized. The diazotized aryl amines were then coupled to a moiety of above-mentioned dyes at 5-position of thiazole. The obtained bisheteroaryl azo dyes were characterized by elemental analysis and spectral studies. Solvent effects on the visible absorption spectra of the dyes were evaluated. The color of the dyes is discussed with respect to the nature of the heterocyclic ring, aromatic amines, and substituents present therein. All these dyes were applied as disperse dyes on to polyester fabrics, and their fastness properties were evaluated.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem 24:208–220, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21085

INTRODUCTION

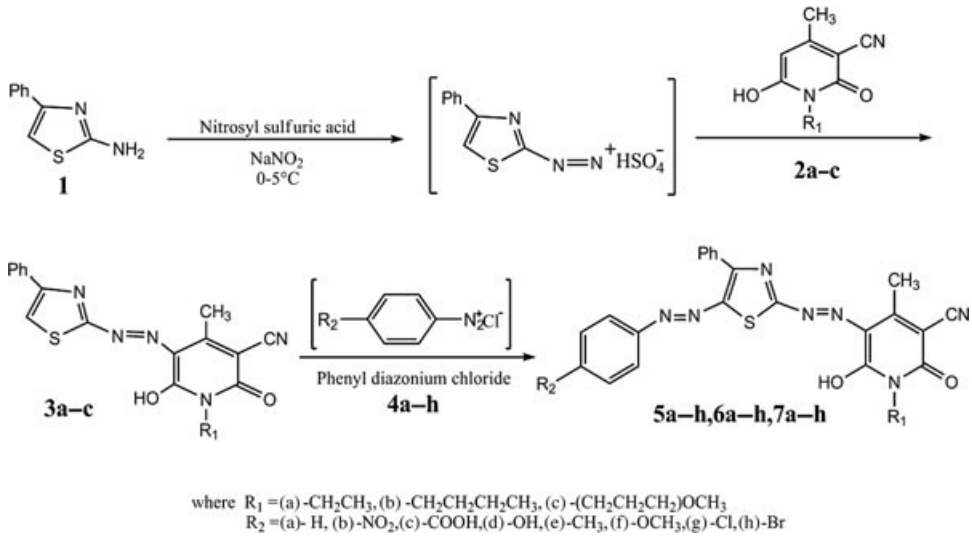
The synthetic azo compounds are very important in the fields of dyes, pigments, and advanced materials [1]. It has been known that azo compounds are widely used a class of dyes because of their adaptable application in various fields such as dyeing of textile fibers, coloring of different materials, colored plastics and polymers, biological-medical studies, and advanced applications in organic synthesis [2–4].

The heterocyclic compounds such as pyrazole, thaizole, oxadiazole, and thiadiazole and their derivatives have shown a wide spectrum of biological activities as well as formation of some dyes. The hetroaryl moieties like 2-aminothiazole derivatives were also reported with dyes characteristics.

For the synthesis of biologically active molecules, 2-aminothiazole derivatives have been used as precursors since long time [5–8]. A large number of 2-aminothiazoles substituted with different aryl and hetroaryl groups are already being prepared for pharmaceutical purposes (e.g., antispasmodic or antihistaminic activity [7]). Regarding this, the synthesis of disperse dyes based on 5-arylazothiazole derivatives and their applications as disperse dyes for dyeing polyester fabrics has been reported recently [9, 10]. It has also been reported that dyes made using 2-aminothiazole compounds, which possess different substituents in the 4-position of analogues derivatives as diazo components, tend to show bathochromic shifts when compared to analogous dyes derived from a benzenoid compound [11–14]. Thus, it was of great interest in several thiazolyl azo dyes substituted at the 4-position with phenyl and pyridones club molecules. The dyes having thiazole and pyridone heterocyclic moieties have received little interest academically as well as technically.

Although pyridones are widely used in textile industry for the preparation of azo and azamethine dyes [15–19], in the present study some new

Correspondence to: Hasmukh S. Patel; e-mail: drhspatel786@yahoo.com.



SCHEME 1 Proposed synthetic route for the synthesis of bisheteroaryl bisazo dyes: **5a–h**, **6a–h**, **7a–h**.

bishetroaryl azopyridone dyes are coupled with various diazotized aromatic amines at the 5-position of 2-amino-4-phenylthaizole and their solvatochromic behavior and fastness properties are studied and these dyes are applied to disperse dyes for dyeing of polyester fabrics.

RESULTS AND DISCUSSION

The synthetic route of these dyes is presented in Scheme 1.

Physical Properties of Dyes

All the dyes were obtained as an amorphous powders ranging in color from yellow to maroon to brown. The thin-layer chromatography (TLC) results showed that only a single spot was observed for each dye.

Structural Characterization

The produced bisheteroaryl bis-azo dyes **3a–c** have been prepared, which are shown in Scheme 1 followed by a reported method for 2-pyridone-based azo dyes [15, 20].

The elemental analysis is also in good agreement with the structural data. The physicochemical parameters and elemental analysis of bishetroaryl bisazo dyes **3a–c, 5a–h, 6a–h** and **7a–h** are described in the Experimental section.

IR Spectral Data

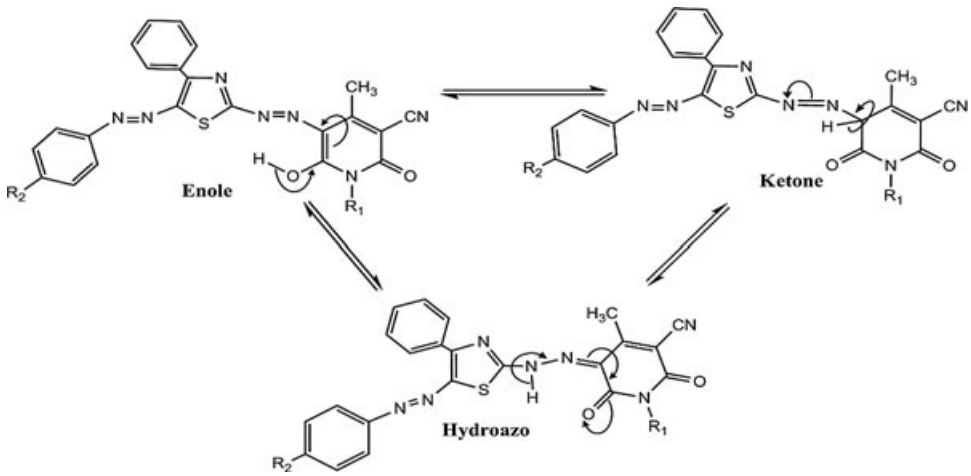
All the spectra exhibited a broad N–H hydrazone band in the region 3439–3457 cm^{-1}, which suggests that these compounds dominantly exist in the solid state in the hydrazone tautomeric form and was also confirmed by ^1H NMR. The infrared spectra of all synthesized dyes showed two intense carbonyl bands at about 1635 and 1695 cm^{-1}, which were assigned to the diketohydrazone form. The other ν_{max} values at 3095–3044 cm^{-1} (aromatic —CH) were also recorded.

1H NMR and ^{13}C NMR Spectral Data

The ^1H NMR spectrum analysis of the tris (heteroaryl) bisazo dyes **5a–h, 6a–h** and **7a–h** are summarized in the Experimental section, which reveals that the diazo coupling of the intermediates **3a–c** causes the —CH of dyes **5a–h, 6a–h** and **7a–h** to be replaced by an azo heteroaryl ring. The ^1H NMR spectra of all the dyes exhibited a signal near δ 14.13–14.19 ppm. This signal corresponds to the imine N–H proton resonance of the hydrazone form. These results are in agreement with the data obtained for the hydrazone form with N–H peaks in the range of δ 15.1–15.6 ppm [21]. The tautomerism is shown in Scheme 2. All of the aromatic protons are observed around δ 7.75 ppm, and aliphatic protons are observed around δ 1.2–3.5 ppm. The ^{13}C NMR spectral data of all the dyes are also summarized in the Experimental section, which are also in good agreement with their structures.

Mass Spectral Data

Besides, the structure of the compound was well confirmed by its mass spectral studies. The recorded direct analysis in real time-mass spectrometry



SCHEME 2 Enole–ketone–hydroazo tautomerism.

(DART-MS) (Fig. 1) and the molecular ion peak for the dye compound **5a** was used to confirm the molecular formula. The proposed fragmentation pattern for compound **5a** is shown in Scheme 3. DART-MS mass spectra of compound **5a** gave a molecular ion peak with five decimal points at *m/z* 469.51387, corresponding to a molecular formula $C_{24}H_{19}N_7O_2S$. Scheme 3 demonstrates the possible degradation

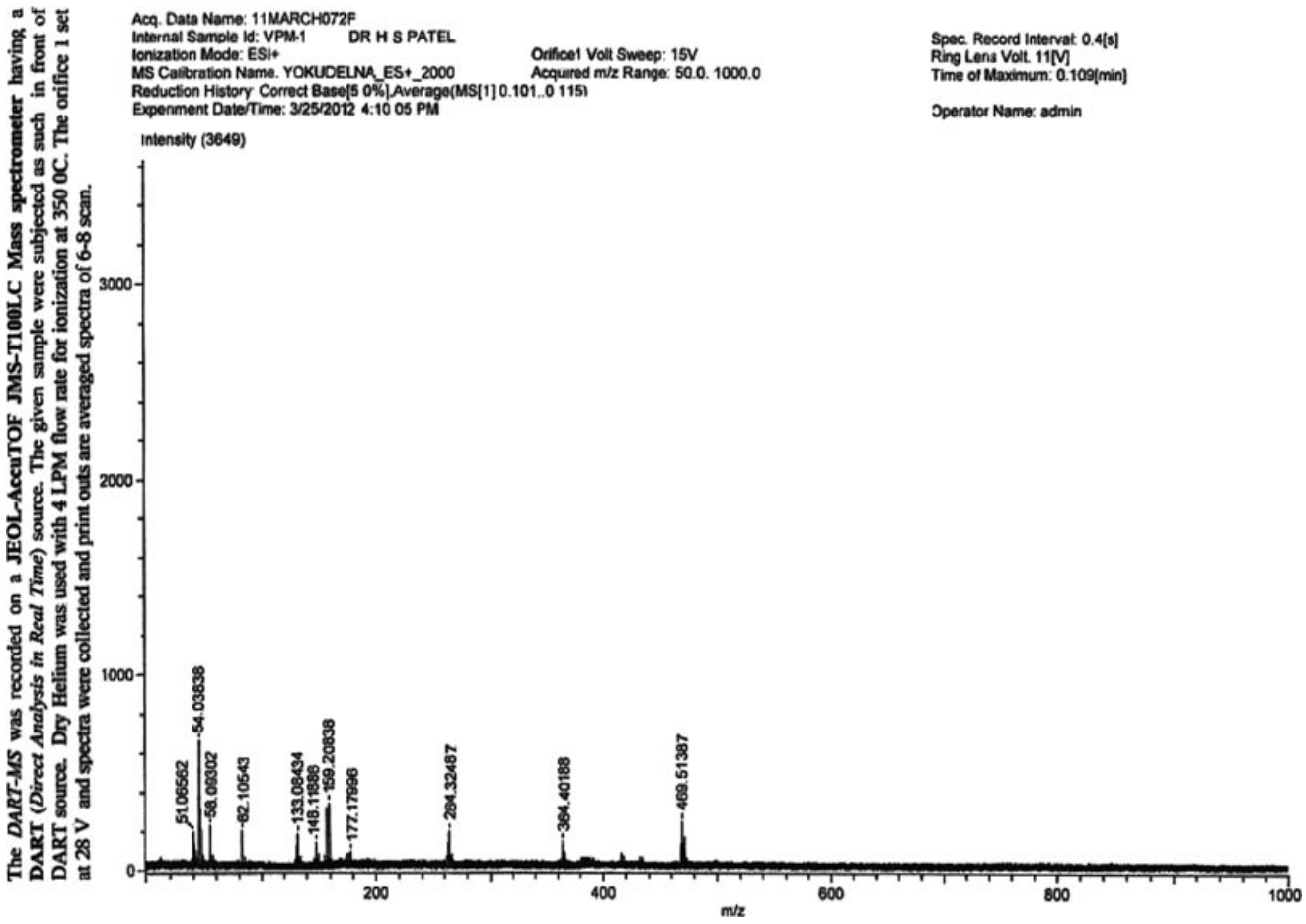
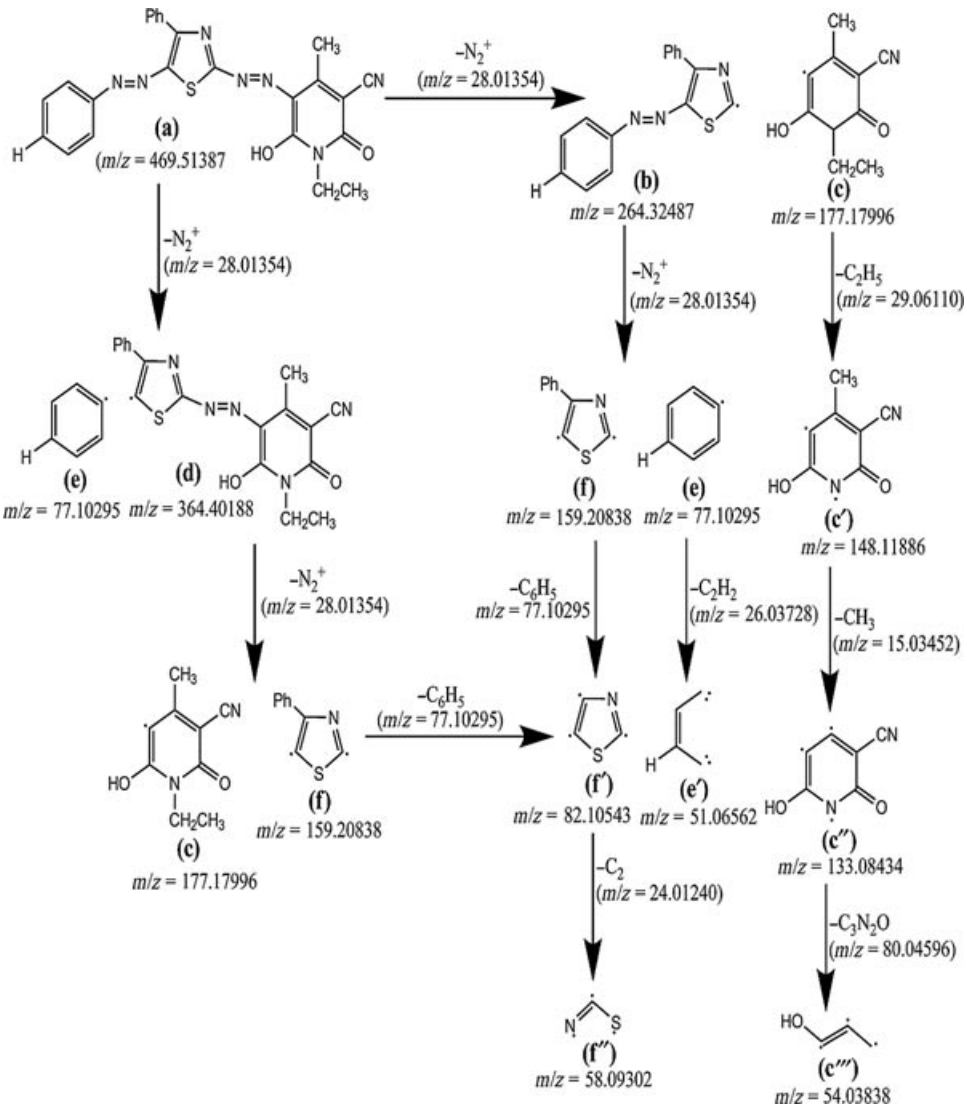


FIGURE 1 DART mass spectrum of compound **5a**.



SCHEME 3 Proposed fragmentation pattern for compound **5a** according to DAR-T mass spectrum.

pathway for the investigated dye molecule **5a**. The primary fragmentation of the dye molecule takes place due to the loss of one N_2 molecule from the species **a** to give species **b**, **c**, **d**, and **e** with the molecular ion peak at 264.32870, 177.17996, 364.40188 and 77.10295, respectively. Further degradation of species **b** and **d** takes place with the loss of one more N_2 molecule and yields species **f**, **e**, and **c** with the molecular ion peak 159.20838, 77.10295 and 177.17996, respectively. The species **c** further degrades with the loss of the ethyl group to give a species **c′** with molecular ion peak at 148.11886 and species **c′** also degrades with the loss of the $—CH_3$ group to give species **c″** with the molecular ion peak at 133.08434 and finally we get **c‴** from **c″** with the loss of the $—C_3N_2O$ moiety with the molecular ion peak at 54.03838. Meanwhile, we can see that more degradation in species **f** and **e** also occurred. From species **f**, we get species **f′** with the loss of one phenyl ring with the molecular ion peak at 82.10543 and from **f′** we get **f″** with the loss of C_2 with the molecular ion peak at 58.09302. Species **e** further degrades with the loss of the $—C_2H_2$ moiety with the molecular ion peak at 51.06562. The mass spectrum of compound **5a** is shown in Fig. 1. The measured molecular weights for all the suggested degradation steps were consistent with expected values.

The visible absorption spectra of all the synthesized compounds were recorded in different solvent systems as shown in Figs. 2–4 such as dimethyl formamide (DMF), methanol, acetone, and chloroform, and their data are shown in Table 1. The solvatochromic properties of these dyes in different solvents with different polarities were systematically

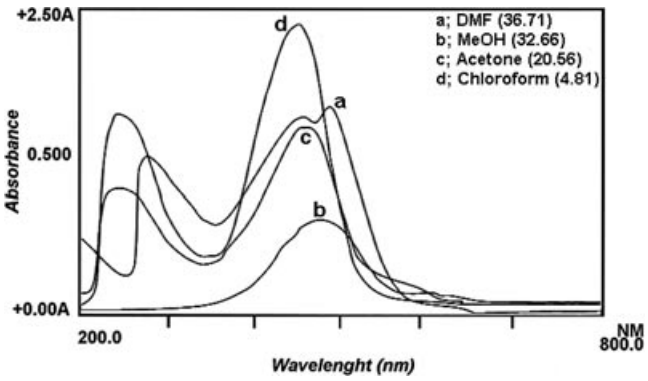


FIGURE 2 Absorption spectra of compound **5b** in different solvents.

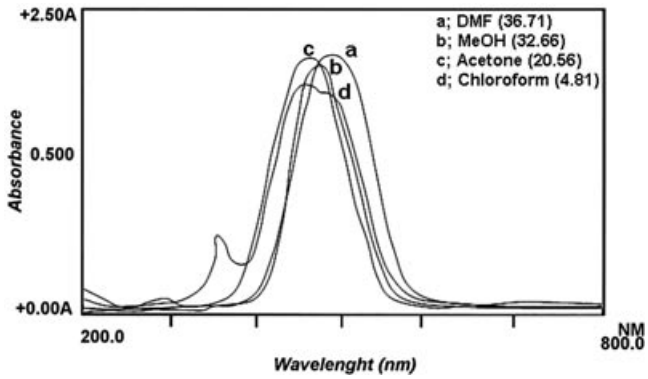


FIGURE 3 Absorption spectra of compound **6b** in different solvents.

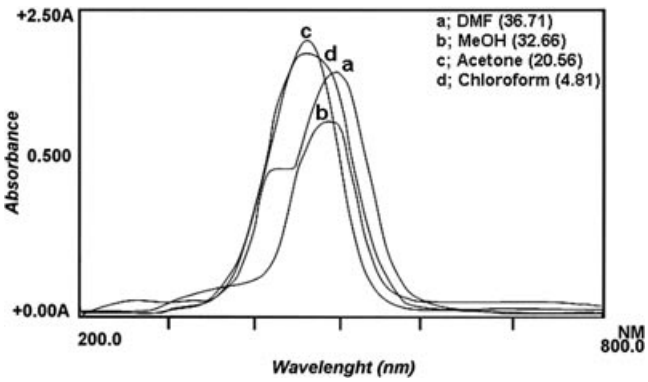


FIGURE 4 Absorption spectra of compound **7b** in different solvents.

investigated [22]. The visible absorption maxima of these dyes very clearly depends on the properties of solvents and increases with an increase in polarities of solvents in the following order: chloroform < acetone < methanol < DMF. The replacement of DMF by solvents of lower polarities, which are methanol (32.60), acetone (20.56), and chloroform (4.18) [23], led to a hypsochromic shift of absorption maxima. In methanol solvent system, the hydrogen bonding may be possible with dye molecules but from results as shown in Table 1 we can see that there is no significant effect of H bonding on the electronic spectra. The $\Delta\lambda_{max}$ values of these dyes shifted in the range of 3–27 nm in solvents with different polarities.

The effect of substitution in the phenyl ring of the diazo component and azo group of coupling component on the visible absorption spectrum and the color intensity was also investigated. The wavelength of maximum absorption (λ_{max}) of the dyes ranges from 441 to 476 nm in chloroform. A change in the λ_{max} value can be brought about by varying the substituent in the phenyl ring of the diazo component. As expected, the incorporation of an electron-withdrawing group at any carbon of the phenyl diazo component moiety was found to give rise in the bathochromic shift. Thus, the introduction of another azo group resulted in a shift of λ_{max} to a longer wavelength. As expected from the magnitude of the appropriate field and resonance components of the substituent effect [24, 25], other dyes followed a similar pattern. The introduction of another azo group at the 5-position of thiazole with a strong electron-withdrawing group provided the much more bathochromic effect; thus the most bathochromic dyes were prepared. The dyes **5b**, **6b**, and **7b** have a —NO_2 group, which is strongly an electron-withdrawing group, and it shows the good bathochromic shift. In the dye, **7f** has two methoxy (—OCH_3) group and the methoxy group is highly polar. So it shows the good bathochromic shift than **7a**, **7d**, and **7e** dyes. Dyes **5g**, **6g**, **7g** and **5h**, **6h**, **7h** also show the good bathochromic shift because —Cl and —Br are present in these dyes. So we can say that to bring the bathochromic shift, either an electropositive or -negative group is strategically to be placed in the diazo compound, which allows a greater electronic displacement. It has been suggested [26] that the increased diene character of the ring may be responsible for the observed large color shift. The bathochromicity of thiazolyl dyes is not attributed to the contribution of the 3d atomic orbital of the sulfur atom of the ring [27].

Dyeing Characterization on Polyester Fabric

All the dyes were applied on polyester fabric at 2% (w/w) shade as dispersed dyes. Their dyeing properties are summarized in Table 2. These dyes gave a wide range of shades varying from yellow to maroon to brown with excellent brightness, levelness, and depth of fabrics. Variation in the shades of the dyed fabric results from both the nature and position of the substituent present on the diazo component. The dyed fabrics have good to excellent sublimation

TABLE 1 Visible Absorption Spectra and Spectra Shifts in Various Solvents for Dyes **5a–h, 6a–h** and **7a–h**

		DMF (36.71)	*MeOH (32.66)*		*Acetone (20.56)*		*Chloroform (4.81)*	
Dyes	*Color on Polyester*	λ_{max}	λ_{max}	$\Delta\lambda_{max}$[a]	λ_{max}	$\Delta\lambda_{max}$	λ_{max}	$\Delta\lambda_{max}$
5a	Yellow	460	451	−09	443	−17	441	−19
5b	Reddish maroon	496	482	−14	476	−20	473	−23
5c	Yellow	463	458	−05	454	−09	447	−16
5d	Yellow	462	452	−10	448	−14	445	−17
5e	Yellow	459	454	−05	451	−08	450	−09
5f	Orange	473	464	−09	460	−13	458	−15
5g	Light red	480	473	−07	468	−12	465	−15
5h	Dark orange	476	468	−08	465	−11	462	−14
6a	Turmeric	465	458	−07	448	−17	447	−18
6b	Reddish Maroon	498	486	−12	479	−19	475	−23
6c	Orange	470	463	−07	457	−13	451	−19
6d	Turmeric	468	459	−09	453	−15	452	−16
6e	Turmeric	466	462	−04	455	−11	454	−12
6f	Light red	480	470	−10	462	−18	61	−19
6g	Red	487	476	−11	470	−17	468	−19
6h	Reddish orange	484	473	−11	467	−17	465	−19
7a	Orange	470	465	−05	454	−16	452	−18
7b	Maroon	503	491	−12	482	−21	476	−27
7c	Dark orange	477	468	−09	457	−20	455	−22
7d	Dark orange	475	466	−09	460	−15	459	−16
7e	Orange	472	469	−03	460	−12	458	−14
7f	Red	488	476	−12	464	−24	463	−25
7g	Bright red	494	480	−14	472	−22	470	−24
7h	Red	491	478	−13	468	−23	467	−24

[a] $\Delta\lambda_{max} = \lambda_{max(DMF)} - \lambda_{max(MeOH/acetone/chloroform)}$.

fastness. A remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of these dyes to the fabric.

Color Properties of the Dyes on Polyester Fabric

The dyes when applied to polyester fabric under the high-temperature dyeing condition furnished yellow to maroon to brown shades. There appears to be a general correlation between the hues of dyeing on polyester with the absorption characteristics in solution. Dyeing on the fabric is also affected by substitution of the phenyl ring. In contrast to the negligible effect of 4-substituents on the color than the azo group with the substituted phenyl ring at 5-position of the thaizole ring. These dyes have two azo groups with the strongly electron-withdrawing polar group. Therefore, it shows deep yellow to maroon to brown shades.

Fastness Properties of the Dyed Polyester Fabric

The fastness ratings are summarized in Table 2. They are good to excellent for fabrics that had been subjected to the reduction clearing stage. However when the reduction clearing was omitted, marginally worse staining was observed. This indicates that reduction clearing is important for these dyeing. As these dyes are characteristically hydroscopic and high fastness ratings.

Although in all the cases, light fastness was good as shown in Table 2, the dyes containing the strongly electron-withdrawing and highly polar group were marginally superior to the other, again emphasizing the importance of appropriate substituent. Attempts are in progress to improve the light fastness properties of these dyes.

The dry heat fastness property and rubbing fastness were determined and are shown in Table 2; generally fastness to heat was moderate to good, consistent with the presence of polar groups on the chromophores.

CONCLUSIONS

This article describes the synthesis of some novel heterocycle-based bisazo disperse dyes by using various aromatic amine derivatives as diazo components and 2-azopyridone-4-phenyl thaizole as a coupling component. The solvatochromic behavior and substituent effect 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

TABLE 2 Fastness Properties of the Dyes derivatives **5a–h**, **6a–h** and **7a–h**

						Sublimation Fastness			
		Perspiration		Rubbing			Staining		
Dye	*Washing*	*Acid*	*Alkali*	*Dry*	*Wet*	*Change in Tone*	*180° C*	*210° C*	*Light (40 h)*
5a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5
5b	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4	5
5c	4–5	4–5	4–5	3–4	4	4–5	4–5	4–5	5
5d	4–5	4	4–5	4–5	4–5	4–5	4–5	4–5	4
5e	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5
5f	4–5	4	4–5	4–5	4–5	4–5	4	4	4–5
5g	4–5	4–5	4–5	4	4–5	4–5	4	4–5	4
5h	4–5	4–5	4–5	3	3–4	4	3–4	4	4–5
6a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5
6b	4–5	4	4–5	4	4	4	4	3–4	4–5
6c	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4	5
6d	4–5	4–5	4–5	4	4	4–5	4–5	4–5	5
6e	4–5	4–5	4–5	3	4	4–5	4–5	4	4
6f	4–5	3	4	4–5	4	4–5	4–5	3–4	4–5
6g	4–5	4–5	4–5	4–5	4	4–5	4	4	4–5
6h	4–5	4–5	4–5	4	4	4–5	4–5	3	4
7a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5
7b	4–5	4	4–5	3–4	4	4–5	4–5	4	4–5
7c	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4
7d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
7e	4–5	4–5	4–5	3	4	4–5	4	3–4	4–5
7f	4–5	4	4–5	4	4	4–5	4–5	3–4	4–5
7g	4–5	4–5	4–5	3–4	4	4–5	4–5	3–4	3–4
7h	4–5	4	4–5	4–5	4	4–5	4–5	4–5	4–5

Grading: 1, poor; 2, fair; 3, moderate; 4, good; 5, very good to Excellent.

increased. The absorption maxima of dyes shifts bathochromically in the following sequence: DMF > methanol > acetone > chloroform. The washing fastness is good, whereas the light fastness property is poor, although in most cases incorporation of electron-withdrawing substituents results obtained in all samples in a correlation between the color strength of the dyes in solution and on polyester fabric.

EXPERIMENTAL

All the chemicals used throughout were of laboratory grade. The thiazole and pyridones were procured from Merck India(Mumbai, India).

Microanalysis data (C, H, N, and S) were recorded on a Perkin-Elmer 2400 CHN elemental analyzer (SICART, Vallabh Vidyanagar, India), and the results were within the accepted range (±0.50) of the calculated values. All melting points were determined on an electro-thermal IA 9100 apparatus (SICART, Vallabh Vidyanagar, India) and are uncorrected. IR spectra were recorded in KBr pellets on a Nicolet 760D spectrophotometer (Vaibhav Laboratory, Ahmedabad, India). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 spectrometer in DMSO-d_6 (Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India). Absorption spectra were recorded on a Shimadzu UV-1601 spectrophotometer (Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India) in various solvents. DART-MS of samples was carried out on a JEOL-AccuTOF JMC T100LC mass spectrometer instrument (CDRI, Lucknow, India).

Preparation of Bishetroaryl Monoazo Dyes **3a–c**

General Procedure: Diazotization and Coupling. 4-Phenyl-2-aminothiazole (1.76 g, 0.01 mol) **1** was dissolved in freshly prepared cool nitrosyl sulfuric acid (0.01) as per the reported method [27, 28] and was rapidly cooled in an ice bath to 0–5°C. Before the diazotization ends, sulfamic acid (0.5 mg) was added to the solution of the diazonium salt solution to remove excess nitrite ion.

In the beaker, 2-pyridone derivatives (0.01 mol) **2a–c** as a coupling component were dissolved in water and added solid sodium acetate until solution became clear. It was cooled at 0–5°C, and then the above-mentioned diazonium salt solution was added into the 2-pyridone solution by dropwise with

constant stirring under the 0–5°C temperature. The pH of the mixture was adjusted around 6–7 by adding 40% aqueous sodium hydroxide. The resultant dyes **3a–c** were filtered, washed with water, and air-dried.

Analytical and Spectral Data of the Bishetroaryl Monoazo Dyes **3a–c**.

*(E)-1-Ethyl-6-hydroxy-4-methyl-2-oxo-5-((4-phenylthiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonotrile (**3a**).* Yield: 85%. mp: 212°C. IR (KBr, cm^{-1}): 1619 (—C=C), 2217 (—CN), 1652 and 1682 (—CO), 3441 (—NH-hydrazo), 1621 (—N=N), 1542 (thiazole). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.11 (t, J = 7.2 Hz, 3H, CH_3), 2.52 (s, H, CH_3), 3.79 (q, J = 7.2 Hz, 2H, CH_2), 6.10 (s, 1H, thiazole), 7.58–7.87 (m, 5H, Ar-H), 15.13 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.20 (—CH_3), 13.34 (—CH_2), 35.70 (—CH_3), 117.76 (—CN), δ (Ar-C): 74.0, 110.4, 115.52, 127.43 (2C), 128.91 (2C), 128.70, 133.14, 146.72, 156.24, 159.37, 163.3, 166.4. Anal. Calcd. for $C_{18}H_{15}N_5O_2S$ (FW 365): C, 59.17; H, 4.54; N, 19.17; S, 8.76. Found: C, 59.18; H, 4.55; N, 19.18; S, 8.77.

*(E)-1-Butyl-6-hydroxy-4-methyl-2-oxo-5-((4-phenylthiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonotrile (**3b**).* Yield: 82%. mp: 211°C. IR (KBr, cm^{-1}): 1617 (—C=C), 2221 (—CN), 1650 and 1676 (—CO), 3452 (—NH-hydrazo), 1611 (—N=N), 1540 (thiazole). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.13 (t, J = 7.1 Hz, 3H, CH_3), 3.74 (t, J = 7.1 Hz, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 2.56 (s, H, CH_3), 6.12 (s, 1H, thiazole), 7.27–7.49 (m, 5H, Ar-H), 15.14 (s, 1H, N-H hydrazone). ^{13}C NMR: 9.18 (—CH_3), 13.37 (—CH_3), 20.23 (—CH_2), 30.63 (—CH_2), 41.52 (—CH_2), 117.84 (—CN), δ (Ar-C): 73.82, 111.03, 115.54, 127.53 (2C), 128.62, 129.20 (2C), 133.17, 152.5, 156.42, 163.17, 163.62, 166.24. Anal. Calcd. for $C_{20}H_{19}N_5O_2S$ (FW 393): C, 61.06; H, 4.83; N, 17.81; S, 8.14. Found: C, 61.08; H, 4.82; N, 17.82; S, 8.16.

*(E)-6-Hydroxy-1-(methoxymethyl)-4-methyl-2-oxo-5-((4-phenylthiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonotrile (**3C**).* Yield: 86%. mp: 222°C. IR (KBr, cm^{-1}): 1615 (—C=C), 2213 (—CN), 1648 and 1677 (—CO), 3451 (—NH-hydrazo), 1613 (—N=N), 1539 (thiazole). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.08 (m, 2H, CH_2), 3.77 (t, J = 7.0 Hz, 2H, CH_2), 4.89 (t, J = 7.0 Hz, 2H, CH_3), 3.42 (s, 3H, OCH_3), 2.57 (s, H, CH_3), 6.10 (s, 1H, thiazole), 7.33–7.57 (m, 5H, Ar-H), 15.11 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.23 (—CH_3), 56.31 (—OCH_3), 74.53 (—CH_3), 117.76 (—CN), 123.40 (2C, —CH_2), δ (Ar-C): 74.16, 110.76, 115.46, 127.58 (2C), 128.49, 129.34 (2C), 133.2, 152.43, 156.70, 163.26, 163.8, 166.32. Anal. Calcd. for $C_{20}H_{19}N_5O_3S$ (FW 409): C, 58.67; H, 4.64; N, 17.11; S, 7.82. Found: C, 58.69; H, 4.65; N, 17.12; S, 7.83.

Synthesis of Bisheteroaryl Bisazo Dyes **5a–h**, **6a–h** *and* **7a–h**

General Procedure: Diazotization and Coupling. Various aromatic amines **4a–h** were taken and diazotized by the conventional method. All the diazo salts were coupled with above-mentioned bishetroaryl dyes **3a–c** by the following process.

Bishetroaryl monoazo dyes were dissolved in aqueous sodium hydroxide (aq. NaOH) (0.01 M) and cooled at 0–5°C. The previously prepared diazonium solution was then added into it dropwise with constant stirring. After completion of the coupling reaction, the resultant solution was made neutral by addition of aqueous ammonium solution and the precipitate of dye was obtained. The precipitated dye **5a–h, 6a–h** and **7a–h** were filtered, washed with water, and air-dried. The progress of the reaction was monitored by TLC using a DMSO:water mixture (5:2 by volume) as a developing solvent and silica gel TLC plates as the stationary phase.

Analytical and Spectral Data of the Bisheteroaryl Bisazo Dyes **5a–h, 6a–h** *and* **7a–h**.

*1-Ethyl-6-hydroxy-4-methyl-2-oxo-((E)-(4-phenyl-5-((E)-phenyldiazenyl)thiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonitrile (**5a**).* Yield: 76%. mp: 226°C. IR (KBr, cm^{-1}): 1612 (—C=C), 2230 (—CN), 1648 and 1689 (—CO), 3447 (—NH-hydrazo), 1638 (—N=N), 3057 (—C—H), 843 (*p*-sub. Ph). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.09 (t, J = 7.4 Hz, 3H, CH_3), 2.56 (s, 3H, CH_3), 3.95 (q, J = 7.2 Hz, 2H, CH_2), 7.37–8.28 (m, 10H, Ar-H), 15.15 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.25 (—CH_3), 13.38 (—CH_2), 35.73 (—CH_3), 117.79 (—CN), δ (Ar-C): 74.08, 115.50, 127.48 (2C), 127.97 (3C), 128.38 (2C), 128.72 (2C), 128.97, 129.0, 133.18, 146.76, 156.27, 159.33, 163.16, 163.38, 166.48. Anal. Calcd. for $C_{24}H_{19}N_7O_2S$ (FW 469): C, 60.88; H, 4.01; N, 20.71; S, 6.76. Found: C, 60.85; H, 4.02; N, 20.69; S, 6.74.

*1-Ethyl-6-hydroxy-4-methyl-5-((E)-(5-((E)-(4-nitrophenyl) diazenyl)-4-phenyl thiazol-2-yl)diazenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**5b**).* Yield: 83%. mp: 225°C. IR (KBr, cm^{-1}): 1616 (—C=C), 2217 (—CN), 1652 and 1693 (—CO), 3449 (—NH-hydrazo), 1646 (—N=N), 3060 (—C—H), 842 (*p*-sub.Ph), 1565 (s, —NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm):

1.08 (t, J = 7.4 Hz, 3H, CH_3), 2.60 (s, H, CH_3), 3.98 (q, J = 7.2 Hz, 2H, CH_2), 7.33–8.10 (m, 9H, Ar-H), 15.17 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.20 (—CH_3), 13.39 (—CH_2), 35.78 (—CH_3), 117.79 (—CN), δ (Ar-C): 74.00, 115.53, 123.81 (2C), 126.35 (2C), 127.47 (2C), 128.70, 128.93 (2C), 133.19, 134.62, 146.74, 147.61, 156.28, 159.37, 163.19, 163.70, 166.43. Anal. Calcd. for $C_{24}H_{18}N_8O_4S$ (FW 514): C, 56.03; H, 3.50; N, 21.78; S, 6.22. Found: C, 56.04; H, 3.49; N, 21.80; S, 6.20.

*4-((E)-(2-((E)-(5-Cyano-1-ethyl-2-hydroxy-4-methyl-6-oxo-1,6-dihydro pyridin-3-yl)diazenyl)-4-phenylthiazol-5-yl)diazenyl) benzoic acid (***5c***)*. Yield: 87%. mp: 228°C. IR (KBr, cm^{-1}): 1614 (—C=C), 2215 (—CN), 1656 and 1685 (—CO), 3452 (—NH-hydrazo), 1640 (—N=N), 3058 (—C—H), 848 (p-sub.Ph), 1697 (s, —COOH). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.10 (t, J = 7.4 Hz, 3H, CH_3), 2.59 (s, H, CH_3), 3.96 (q, J = 7.4 Hz, 2H, CH_2), 7.32–7.96 (m, 9H, Ar-H), 15.15 (s, 1H, N-H hydrazone), 11.78 (1H, s, —COOH). ^{13}C NMR: 9.24 (—CH_3), 13.37 (—CH_2), 35.74 (—CH_3), 117.78 (—CN), δ (Ar-C): 74.09, 115.52, 127.49 (2C), 128.60 (2C), 128.91 (2C), 128.76, 130.42 (2C), 130.62, 133.17, 133.83, 146.78, 156.29, 159.32, 163.17, 163.39, 166.44, 166.98. Anal. Calcd. for $C_{25}H_{19}N_7O_4S$ (FW 513): C, 58.47; H, 3.70; N, 19.10; S, 6.23. Found: C, 58.46; H, 3.71; N, 19.08; S, 6.24.

*1-Ethyl-6-hydroxy-5-((E)-(5-((E)-(4-hydroxyphenyl)diazenyl)-4-phenyl thiazol-2-yl) daizenyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***5d***)*. Yield: 77%. mp: 247°C. IR (KBr, cm^{-1}): 1617 (—C=C), 2212 (—CN), 1650 and 1687 (—CO), 3450 (—NH-hydrazo), 1648 (—N=N), 3055 (—C—H), 838 (p-sub.Ph), 3452–3460 (br, —OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.12 (t, J = 7.4 Hz, 3H, CH_3), 2.58 (s, H, CH_3), 3.97 (q, J = 7.2 Hz, 2H, CH_2), 7.35–8.13 (m, 9H, Ar-H), 15.16 (s, 1H, N—H hydrazone), 10.58 (s, 1H, —OH). ^{13}C NMR: 9.27 (—CH_3), 13.36 (—CH_2), 35.76 (—CH_3), 117.77 (—CN), δ (Ar-C): 74.04, 115.54, 116.12 (2C), 121.48, 127.46 (2C), 128.93 (2C), 128.73, 130.14 (2C), 133.14, 146.72, 156.30, 158.60, 159.35, 163.14, 163.34, 166.42. Anal. Calcd. for $C_{24}H_{19}N_7O_3S$ (FW 485): C, 59.38; H, 3.91; N, 20.02; S, 6.59. Found: C, 59.41; H, 3.92; N, 20.04; S, 6.60.

*1-Ethyl-6-hydroxy-4-methyl-2-oxo-5-((E)-(4-phenyl-5-((E)-p-totyldiazenyl)thiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonitrile (***5e***)*. Yield: 90%. mp: 225°C. IR (KBr, cm^{-1}): 1608 (—C=C), 2211 (—CN), 1646 and 1683 (—CO), 3442 (—NH-hydrazo), 1636 (—N=N), 3057 (—C—H), 842 (p-sub.Ph), 1465 (—CH_3). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.12 (t, J = 7.4 Hz, 3H, CH_3), 2.57 (s, H, CH_3), 3.93 (q, J = 7.2 Hz, 2H, CH_2), 7.28–8.02 (m, 9H, Ar-H), 15.17 (s, 1H, N—H hydrazone), 2.27 (s, 3H, CH_3). ^{13}C NMR: 9.23 (—CH_3), 13.39 (—CH_2), 21.32 (—CH_3), 35.71 (—CH_3), 117.73 (—CN), δ (Ar-C): 74.02, 115.52, 125.62, 127.46 (2C), 128.51 (2C), 128.90 (2C), 129.07, 129.36 (2C), 133.16, 138.50, 146.74, 156.25, 159.33, 163.18, 163.37, 166.87. Anal. Calcd. for $C_{25}H_{21}N_7O_2S$ (FW 483): C, 62.11; H, 4.34; N, 20.28; S, 6.62. Found: C, 62.10; H, 4.35; N, 20.30; S, 6.60.

*1-Ethyl-6-hydroxy-5-((E)-(4-methoxyphenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***5f***)*. Yield: 79%. mp: 227°C. IR (KBr, cm^{-1}): 1615 (—C=C), 2220 (—CN), 1644 and 1687 (—CO), 3443 (—NH-hydrazo), 1633 (—N=N), 3059 (—C—H), 839 (p-sub.Ph), 1253 (—OCH_3). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.13 (t, J = 7.4 Hz, 3H, CH_3), 2.60 (s, H, CH_3), 3.94 (q, J = 7.2 Hz, 2H, CH_2), 7.40–8.04 (m, 9H, Ar-H), 15.15 (1H, s, N—H hydrazone), 3.85 (s, 3H, OCH_3). ^{13}C NMR: 9.26 (—CH_3), 13.36 (—CH_2), 35.72 (—CH_3), 55.54 (—OCH_3), 117.70 (—CN), δ (Ar-C): 74.08, 114.36 (2C), 115.52, 121.09, 127.42 (2C), 128.91 (2C), 128.76, 129.79 (2C), 133.17, 146.70, 156.25, 159.36, 160.31, 163.17, 163.37, 166.58. Anal. Calcd. for $C_{25}H_{21}N_7O_3S$ (FW 499): C, 60.12; H, 4.20; N, 19.63; S, 6.41. Found: C, 60.13; H, 4.21; N, 19.61; S, 6.42.

*5-((E)-(5-((E)-(4-Chlorophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***5g***)*. Yield: 86%. mp: 232°C. IR (KBr, cm^{-1}): 1617 (—C=C), 2216 (—CN), 1652 and 1687 (—CO), 3440 (—NH-hydrazo), 1642 (—N=N), 3061 (—C—H), 835 (p-sub.Ph), 1086 (s, C—Cl stre.). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.10 (t, J = 7.4 Hz, 3H, CH_3), 2.61 (s, H, CH_3), 3.97 (q, J = 7.2 Hz, 2H, CH_2), 7.23–8.99 (m, 9H, Ar-H), 15.18 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.20 (—CH_3), 13.32 (—CH_2), 35.78 (—CH_3), 117.72 (—CN), δ (Ar-C): 74.09, 115.57, 126.71, 127.46 (2C), 128.14 (2C), 128.93 (2C), 128.76, 130.20 (2C), 133.19, 134.38, 146.70, 156.23, 159.30, 163.17, 163.32, 166.92. Anal. Calcd. for $C_{24}H_{18}ClN_7O_2S$ (FW 503.5): C, 57.20; H, 3.57; N, 19.46; S, 6.35. Found: C, 57.23; H, 3.55; N, 19.48; S, 6.32.

*5-((E)-(5-((E)-(4-Bromophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***5h***)*. Yield: 81%. mp: 228°C. IR (KBr, cm^{-1}): 1613 (—C=C), 2217 (—CN), 1642 and 1687 (—CO), 3446 (—NH-hydrazo), 1637 (—N=N), 3066 (—C—H), 840 (p-sub.Ph), 1075

(s, C-Br stre.). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.12 (t, J = 7.4 Hz, 3H, CH_3), 2.54 (s, H, CH_3), 3.95 (q, J = 7.2 Hz, 2H, CH_2), 7.34–8.16 (m, 9H, Ar-H), 15.14 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.21 (—CH_3), 13.33 (—CH_3), 35.77 (—CH_3), 117.73 (—CN), δ (Ar-C): 74.07, 115.56, 123.10, 127.05, 127.46 (2C), 128.90 (2C), 128.73, 131.12 (2C), 131.84 (2C), 133.16, 146.72, 156.26, 159.38, 163.14, 163.39, 166.64. Anal. Calcd. for $C_{24}H_{18}BrN_7O_2S$ (FW 548): C, 52.55; H, 3.28; N, 17.88; S, 5.83. Found: C, 52.56; H, 3.27; N, 17.90; S, 5.84.

*1-Butyl-6-hydroxy-4-methyl-2-oxo-5-((E)-(4-phenyl-5-((E)-phenyldiazenyl)thiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonitrile (***6a***)*. Yield: 82%. mp: 227°C. IR (KBr, cm^{-1}): 1612 (—C=C), 2220 (—CN), 1638 and 1686 (—CO), 3439 (—NH-hydrazo), 1646 (—N=N), 3069 (—C—H), 828 (p-sub.Ph). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.09 (t, J = 7.2 Hz, 3H, CH_3), 3.73 (t, J = 7.2 Hz, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 2.60 (s, H, CH_3), 7.42–8.12 (m, 10H, Ar-H), 15.16 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.19 (—CH_3), 13.64 (—CH_2), 20.13 (—CH_2), 30.81 (—CH_2), 41.52 (—CH_3), 117.87 (—CN), δ (Ar-C): 73.80, 115.54, 127.50 (2C), 128.59, 128.73 (3C), 128.89 (2C), 128.97, 129.13 (2C), 133.20, 146.49, 156.40, 159.42, 163.32, 163.84, 166.92. Anal. Calcd. for $C_{26}H_{23}N_7O_2S$ (Fw 497): C, 62.27; H, 4.62; N, 19.71; S, 6.43. Found: C, 62.28; H, 4.64; N, 19.72; S, 6.45.

*1-Butyl-6-hydroxy-4-methyl-5-((E)-(5-((E)-(4-nitrophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (***6b***)*. Yield: 78%. mp: 224°C. IR (KBr, cm^{-1}): 1607 (—C=C), 2212 (—CN), 1645 and 1682 (—CO), 3440 (—NH-Hydrazo), 1637 (—N=N), 3062 (—C—H), 840 (p-sub.Ph), 1563 (s, —NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.11 (t, J = 7.2 Hz, 3H, CH_3), 3.76 (t, J = 7.2 Hz, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 2.57 (s, H, CH_3), 7.63–8.10 (m, 9H, Ar-H), 15.17 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.21 (—CH_3), 13.70 (—CH_2), 20.15 (—CH_2), 30.82 (—CH_2), 41.53 (—CH_3), 117.90 (—CN), δ (Ar-C): 73.82, 115.52, 123.72 (2C), 126.63 (2C), 127.52 (2C), 128.58, 129.10 (2C), 133.21, 134.82, 146.48, 147.82, 156.42, 159.39, 163.34, 163.82, 166.87. Anal. Calcd. for $C_{26}H_{22}N_8O_4S$ (Fw 542): C, 57.56; H, 4.05; N, 20.66; S, 5.90. Found: C, 57.57; H, 4.08; N, 20.67; S, 5.92.

*4-((E)-(2-((E)-(1-Butyl-5-cyano-2-hydroxy-4-methyl-6-oxo-1,6-dihydropyridine-3-yl)diazenyl)-4-phenylthiazol-5-yl)diazenyl) benzoic acid (***6c***)*. Yield: 76%. mp: 229°C. IR (KBr, cm^{-1}): 1614 (—C=C), 2218 (—CN), 1646 and 1690 (—CO), 3447 (—NH-hydrazo), 1642 (—N=N), 3055 (—C—H), 850 (p-sub.Ph), 1699 (s, —COOH). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.12 (t, J = 7.2 Hz, 3H, CH_3), 3.81 (t, J = 7.2 Hz, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.36 (m, 2H, CH_2), 2.56 (s, H, CH_3), 7.33–8.05 (m, 9H, Ar-H), 15.13 (s, 1H, N—H hydrazone), 11.74 (s, 1H, —COOH). ^{13}C NMR: 9.23 (—CH_3), 13.71 (—CH_2), 20.14 (—CH_2), 30.80 (—CH_2), 41.54 (—CH_3), 117.93 (—CN), δ (Ar-C): 73.83, 115.54, 127.53 (2C), 128.32 (2C), 128.57, 129.12 (2C), 130.12 (2C), 130.40, 133.22, 133.78, 146.47, 156.44, 159.37, 163.33, 163.80, 166.86, 166.95. Anal. Calcd. for $C_{27}H_{23}N_7O_4S$ (Fw 541): C, 59.88; H, 4.25; N, 18.11; S, 5.91. Found: C, 59.89; H, 4.23; N, 18.12; S, 5.92.

*1-Butyl-6-hydroxy-5-((E)-(5-((E)-(4-hydroxyphenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***6d***)*. Yield: 84%. mp: 250°C. IR (KBr, cm^{-1}): 1615 (—C=C), 2219 (—CN), 1653 and 1694 (—CO), 3443 (—NH-hydrazo), 1647 (—N=N), 3053 (—C—H), 839 (p-sub.Ph), 3451–3456 (br, —OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.10 (t, J = 7.2 Hz, 3H, CH_3), 3.79 (t, J = 7.2 Hz, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.37 (m, 2H, CH_2), 2.53 (s, H, CH_3), 7.39–8.13 (m, 9H, Ar-H), 15.12 (s, 1H, N—H hydrazone), 10.65 (s, 1H, —OH). ^{13}C NMR: 9.24 (—CH_3), 13.72 (—CH_2), 20.12 (—CH_2), 30.83 (—CH_2), 41.51 (—CH_3), 117.92 (—CN), δ (Ar-C): 73.84, 115.56, 116.19 (2C), 121.44, 127.54 (2C), 128.58, 129.14 (2C), 130.51 (2C), 133.21, 146.49, 156.43, 158.38, 159.38, 163.18, 163.84, 166.58. Anal. Calcd. for $C_{26}H_{23}N_7O_3S$ (Fw 513): C, 60.81; H, 4.48; N, 19.10; S, 6.23. Found: C, 60.83; H, 4.50; N, 19.11; S, 6.25.

*1-Butyl-6-hydroxy-4-methyl-2-oxo-5-((E)-(4-phenyl-5-((E)-p-totyldiazenyl)thiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonitrile (***6e***)*. Yield: 77%. mp: 235°C. IR (KBr, cm^{-1}): 1609 (—C=C), 2212 (—CN), 1642 and 1689 (—CO), 3442 (—NH-hydrazo), 1639 (—N=N), 3059 (—C—H), 840 (p-sub.Ph), 1467(—CH_3). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.08 (t, J = 7.2 Hz, 3H, CH_3), 3.75 (t, J = 7.2 Hz, 2H, CH_2), 1.60 (m, 2H, CH_2), 1.33 (m, 2H, CH_2), 2.59 (s, H, CH_3), 2.23 (s, 3H, CH_3), 7.28–7.96 (m, 9H, Ar-H), 15.16 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.22 (—CH_3), 13.70 (—CH_2), 20.15 (—CH_2), 21.43 (—CH_3), 30.83 (—CH_2), 41.55 (—CH_3), 117.93 (—CN), δ (Ar-C): 73.82, 115.51, 125.36, 127.56 (2C), 128.54, 128.92 (2C), 129.16 (2C), 129.72 (2C), 133.26, 138.76, 146.46, 156.43, 159.38, 163.32, 163.83, 166.87. Anal. Calcd. for $C_{27}H_{25}N_7O_2S$ (Fw

511): C, 63.40; H, 4.89; N, 19.17; S, 6.26. Found: C, 63.42; H, 4.87; N, 19.19; S, 6.25.

*1-Butyl-6-hydroxy-5-((E)-(5-((E)-(4-methoxyphenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***6f***).* Yield: 86%. mp: 225°C. IR (KBr, cm^{-1}): 1615 (—C=C), 2218 (—CN), 1639 and 1687 (—CO), 3448 (—NH-hydrazo), 1643 (—N=N), 3057 (—C—H), 838 (p-sub.Ph), 1256 (—OCH_3). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.10 (t, J = 7.2 Hz, 3H, CH_3), 3.79 (t, J = 7.2 Hz, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 2.57 (s, H, CH_3), 3.85 (s, 3H, OCH_3), 7.48–8.17 (m, 9H, Ar-H), 15.19 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.21 (—CH_3), 13.73 (—CH_2), 20.13 (—CH_2), 30.81 (—CH_2), 41.52 (—CH_3), 55.74 (—OCH_3), 117.91 (—CN), δ (Ar-C): 73.80, 114.43 (2C), 115.53, 121.23, 127.53 (2C), 128.51, 129.15 (2C), 129.82 (2C), 133.36, 146.46, 156.40, 159.38, 160.55, 163.34, 163.84, 166.62. Anal. Calcd. for $C_{27}H_{25}N_7O_3S$ (Fw 527): C, 61.48; H, 4.74; N, 18.59; S, 6.07. Found: C, 61.47; H, 4.75; N, 18.57; S, 6.05.

*1-Butyl-5-((E)-(5-((E)-(4-chlorophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***6g***).* Yield: 89%. mp: 230°C. IR (KBr, cm^{-1}): 1611 (—C=C), 2213 (—CN), 1650 and 1686 (—CO), 3450 (—NH-hydrazo), 1642 (—N=N), 3063 (—C—), 834 (p-sub.Ph), 1081 (s, C—Cl strc.). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.11 (t, J = 7.2 Hz, 3H, CH_3), 3.81 (t, J = 7.2 Hz, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 2.54 (s, H, CH_3), 7.35–8.00 (m, 9H, Ar-H), 15.16 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.23 (—CH_3), 13.71 (—CH_2), 20.15 (—CH_2), 30.63 (—CH_2), 41.56 (—CH_3), 117.09 (—CN), δ (Ar-C): 73.84, 115.54, 126.34, 127.51 (2C), 128.55, 128.90 (2C), 129.14 (2C), 130.53 (2C), 133.24, 134.56, 146.47, 156.42, 159.34, 163.35, 163.82, 166.92. Anal. Calcd. for $C_{26}H_{22}ClN_7O_2S$ (Fw 531.5): C, 58.70; H, 4.13; N, 18.43; S, 6.02. Found: C, 58.72; H, 4.14; N, 18.45; S, 6.03.

*5-((E)-(5-((E)-(4-Bromophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-1-butyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***6h***).* Yield: 79%. mp: 233°C. IR (KBr, cm^{-1}): 1619 (—C=C), 2212 (—CN), 1646 and 1696 (—CO), 3446 (—NH-hydrazo), 1644 (—N=N), 3064 (—C—H), 842 (p-sub.Ph), 1078 (s, C—Br strc.). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 1.09 (t, J = 7.2 Hz, 3H, CH_3), 3.80 (t, J = 7.2 Hz, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.37 (m, 2H, CH_2), 2.58 (s, H, CH_3), 7.36–8.08 (m, 9H, Ar-H), 15.14 (s, 1H, N—H hydrazone). ^{13}C NMR: 9.22 (—CH_3), 13.74 (—CH_2), 20.16 (—CH_2), 30.62 (—CH_2), 41.53 (—CH_3), 117.91 (—CN), δ (Ar-C): 73.82, 115.51, 123.33, 127.09, 127.52 (2C), 128.54, 129.17 (2C), 131.07 (2C), 131.63 (2C), 133.26, 146.44, 156.45, 159.34, 163.37, 163.81, 166.82. Anal. Calcd. for $C_{26}H_{22}BrN_7O_2S$ (Fw 576): C, 54.16; H, 3.81; N, 17.01; S, 5.55. Found: C, 54.18; H, 3.79; N, 17.00; S, 5.56.

*6-Hydroxy-1-(methoxymethyl)-4-methyl-2-oxo-5-((E)-(4-phenyl-5-((E)-phenyldiazenyl)thiazol-2-yl)diazenyl)-1,2-dihydropyridine-3-carbonitrile (***7a***).* Yield: 84%. mp: 228°C. IR (KBr, cm^{-1}): 1612 (—C=C), 2213 (—CN), 1637 and 1685 (—CO), 3439 (—NH-hydrazo), 1642 (—N=N), 3068 (—C—H), 830 (p-sub.Ph). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 3.76 (t, J = 7.3 Hz, 2H, CH_2), 2.07 (m, 2H, CH_2), 4.87 (t, J = 7.3 Hz, 2H, CH_2), 3.48 (s, 3H, OCH_3), 2.56 (s, 3H, CH_3), 7.31–7.93 (m, 10H, Ar-H), 15.15 (s, 1H, N—H hydrazone form). ^{13}C NMR: 9.33 (—CH_3), 56.37 (—OCH_3), 74.52 (—CH_2), 117.54 (—CN), 123.43 (—CH_2, 2C), δ (Ar-C): 74.19, 115.34, 127.60 (2C), 128.38, 128.72 (4C), 128.93 (2C), 129.32 (2C), 133.28, 146.52, 156.76, 159.28, 163.24, 163.82, 166.64. Anal. Calcd. for $C_{26}H_{23}N_7O_3S$ (Fw 513): C, 60.18; H, 4.48; N, 19.01; S, 6.23. Found: C, 60.19; H, 4.50; N, 19.03; S, 6.24.

*6-Hydroxy-1-(methoxymethyl)-4-methyl-5-((E)-(5-((E)-(4-nitrophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***7b***).* Yield: 85%. mp: 229°C. IR (KBr, cm^{-1}): 1613 (—C=C), 2217 (—CN), 1642 and 1686 (—CO), 3440 (—NH-hydrazo), 1638 (—N=N), 3060 (—C—H), 837 (p-sub.Ph), 1566 (s, —NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.52 (s, 3H, CH_3), 3.79 (t, J = 7.3 Hz, 2H, CH_2), 2.12 (m, 2H, CH_2), 4.89 (t, J = 7.3 Hz, 2H, CH_2), 3.45 (s, 3H, OCH_3), 7.45–8.10 (m, 9H, Ar-H), 15.17 (s, 1H, N—H hydrazone form). ^{13}C NMR: 9.31 (—CH_3), 56.36 (—OCH_3), 74.53 (—CH_2), 117.54 (—CN), 123.42 (—CH_2, 2C), δ (Ar-C): 74.17, 115.36, 124.13 (2C), 126.52 (2C), 127.62 (2C), 128.40, 129.30 (2C), 133.32, 135.08, 146.53, 148.07, 156.76, 159.27, 163.25, 163.83, 166.82. Anal. Calcd. for $C_{26}H_{22}N_8O_5S$ (Fw 558): C, 55.91; H, 3.94; N, 20.07; S, 5.73. Found: C, 55.92; H, 3.93; N, 20.09; S, 5.75.

*4-((E)-(2-((E)-(5-Cyano-2-hydroxy-1-(methoxymethyl)-4-methyl-6-oxo-1,6-dihydro pyridine-3-yl)diazenyl)-4-phenylthiazol-5-yl) diazenyl) benzoic acid (***7c***).* Yield: 88%. mp: 230°C. IR (KBr, cm^{-1}): 1619 (—C=C), 2217 (—CN), 1651 and 1691 (—CO), 3439 (—NH-hydrazo), 1643 (—N=N), 3059 (—C—H), 848 (p-sub.Ph), 1697 (s, —COOH). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.57 (s, 3H, CH_3), 3.72 (t, J =

7.3 Hz, 2H, CH_2), 2.09 (m, 2H, CH_2), 4.86 (t, J = 7.3 Hz, 2H, CH_2), 3.43 (s, 3H, OCH_3), 7.40–8.15 (m, 9H, Ar-H), 11.82 (s, 1H, COOH), 15.17 (s, 1H, N—H hydrazone form). ^{13}C NMR: 9.32 (—CH_3), 56.35 (—OCH_3), 74.52 (—CH_2), 117.53 (—CN), 123.43 (—CH_2, 2C), δ (Ar-C): 74.18, 115.37, 127.63 (2C), 128.42, 128.60 (2C), 129.32 (2C), 130.30 (2C), 130.82, 133.38, 134.08, 146.54, 156.77, 159.28, 163.28, 163.82, 166.32, 169.98. Anal. Calcd. for $C_{27}H_{23}N_7O_5S$ (Fw 557): C, 58.16; H, 4.12; N, 17.59; S, 5.74. Found: C, 58.18; H, 4.11; N, 17.60; S, 5.76.

*6-Hydroxy-5-((E)-(5-((E)-(4-hydroxyphenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-1-(methoxymethyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***7d***).* Yield: 89%. mp: 243°C. IR (KBr, cm^{-1}): 1613 (—C=C), 2223 (—CN), 1649 and 1694 (—CO), 3446 (—NH-hydrazo), 1637 (—N=N), 3056 (—C—H), 841 (p-sub.Ph), 3455–3458 (br, —OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.59 (s, 3H, CH_3), 3.73 (t, J = 7.3 Hz, 2H, CH_2), 2.07 (m, 2H, CH_2), 4.78 (t, J = 7.3 Hz, 2H, CH_2), 3.41 (s, 3H, OCH_3), 7.38–8.03 (m, 9H, Ar-H), 10.72 (s, 1H, OH), 15.17 (1H, s, N—H hydrazone form). ^{13}C NMR: 9.34 (—CH_3), 56.37 (—OCH_3), 74.53 (—CH_2), 117.52 (—CN), 123.44 (—CH_2, 2C), δ (Ar-C): 74.19, 115.36, 115.60 (2C), 121.18, 127.62 (2C), 128.44, 129.33 (2C), 130.32 (2C), 133.27, 146.55, 156.76, 158.38, 159.29, 163.29, 163.84, 166.34. Anal. Calcd. for $C_{26}H_{23}N_7O_4S$ (Fw 529): C, 58.97; H, 4.34; N, 18.52; S, 6.04. Found: C, 58.95; H, 4.35; N, 18.51; S, 6.02.

*6-Hydroxy-1-(methoxymethyl)-4-methyl-2-oxo-5-((E)-(4-phenyl-5-((E)-p-totyldiazenyl)thiazol-2-yl) diazenyl)-1,2-dihydropyridine-3-carbonitrile (***7e***).* Yield: 78%. mp: 235°C. IR (KBr, cm^{-1}): 1614 (—C=C), 2221 (—CN), 1639 and 1686 (—CO), 3442 (—NH-hydrazo), 1648 (—N=N), 3060 (—C—H), 834 (p-sub.Ph), 1461 (s, —CH_3). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.53 (s, 3H, CH_3), 3.76 (t, J = 7.3 Hz, 2H, CH_2), 2.06 (m, 2H, CH_2), 4.74 (t, J = 7.3 Hz, 2H, CH_2), 3.40 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3) 7.28–8.10 (m, 9H, Ar-H), 15.13 (s, 1H, N—H hydrazone form). ^{13}C NMR: 9.30 (—CH_3), 21.24 (—CH_3), 56.38 (—OCH_3), 74.55 (—CH_2), 117.53 (—CN), 123.45 (—CH_2, 2C), δ (Ar-C): 74.17, 115.37, 125.58, 127.63 (2C), 128.42, 128.82 (2C), 129.19 (2C), 129.34 (2C), 133.36, 138.40, 146.53, 156.74, 159.28, 163.28, 163.83, 166.97. Anal. Calcd. for $C_{27}H_{25}N_7O_3S$ (Fw 527): C, 61.48; H, 4.74; N, 18.59; S, 6.07. Found: C, 61.49; H, 4.75; N, 18.60; S, 6.09.

*6-Hydroxy-1-(methoxymethyl)-5-((E)-(4-methoxyphenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***7f***).* Yield: 78%. mp: 226°C. IR (KBr, cm^{-1}): 1609 (—C=C), 2215 (—CN), 1647 and 1693 (—CO), 3444 (—NH-hydrazo), 1640 (—N=N), 3058 (—C—H), 836 (p-sub.Ph), 1255 (s, —OCH_3). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.52 (s, 3H, CH_3), 3.80 (t, J = 7.3 Hz, 2H, CH_2), 2.09 (m, 2H, CH_2), 4.77 (t, J = 7.3 Hz, 2H, CH_2), 3.42 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 7.39–8.12 (m, 9H, Ar-H), 15.16 (s, 1H, N—H hydrazone form). ^{13}C NMR: 9.32 (—CH_3), 55.88 (—OCH_3), 56.3 (—OCH_3), 74.56 (—CH_2), 117.50 (—CN), 123.42 (—CH_2, 2C), δ (Ar-C): 74.18, 114.28 (2C), 115.34, 121.37, 127.62 (2C), 128.43, 129.32 (2C), 129.72 (2C), 133.29, 146.53, 156.70, 159.24, 160.32, 163.24, 163.83, 166.78. Anal. Calcd. for $C_{27}H_{25}N_7O_4S$ (Fw 543): C, 59.66; H, 4.60; N, 18.03; S, 5.89. Found: C, 59.68; H, 4.58; N, 18.01; S, 5.86.

*5-((E)-(5-((E)-(4-Chlorophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-6-hydroxy-1-(methoxymethyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***7g***).* Yield: 79%. mp: 231°C. IR (KBr, cm^{-1}): 1610 (—C=C), 2214 (—CN), 1637 and 1687 (—CO), 3449 (—NH-hydrazo), 1643 (—N=N), 3064 (—C—H), 838 (p-sub.Ph), 1080 (s, C—Cl strc.). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.56 (s, 3H, CH_3), 3.81 (t, J = 7.3 Hz, 2H, CH_2), 2.10 (m, 2H, CH_2), 4.81 (t, J = 7.3 Hz, 2H, CH_2), 3.44 (s, 3H, OCH_3), 7.40–8.06 (m, 9H, Ar-H), 15.19 (s, 1H, N—H hydrazone form). ^{13}C NMR: 9.35 (—CH_3), 56.37 (—OCH_3), 74.52 (—CH_2), 117.52 (—CN), 123.46 (—CH_2, 2C), δ (Ar-C): 74.18, 115.34, 126.82, 127.64 (2C), 128.46, 129.08 (2C), 129.32 (2C), 130.37 (2C), 133.32, 134.52, 146.59, 156.71, 159.27, 163.22, 163.80, 166.32. Anal. Calcd. for $C_{26}H_{22}ClN_7O_3S$ (Fw 547.5): C, 56.98; H, 4.01; N, 17.89; S, 5.84. Found: C, 56.97; H, 4.03; N, 17.90; S, 5.85.

*5-((E)-(5-((E)-(4-Bromophenyl)diazenyl)-4-phenylthiazol-2-yl)diazenyl)-6-hydroxy-1-(methoxymethyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (***7h***).* Yield: 84%. mp: 234°C. IR (KBr, cm^{-1}): 1616 (—C=C), 2217 (—CN), 1640 and 1691 (—CO), 3440 (—NH-hydrazo), 1649 (—N=N), 3069 (—C—H), 838 (p-sub.Ph), 1074 (s, C—Br strc.). ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 2.60 (s, 3H, CH_3), 3.79 (t, J = 7.3 Hz, 2H, CH_2), 2.09 (m, 2H, CH_2), 4.83 (t, J = 7.3 Hz, 2H, CH_2), 3.45 (s, 3H, OCH_3), 7.42–8.04 (m, 9H, Ar-H), 15.15 (s, 1H, N—H hydrazone form). ^{13}C NMR: 9.31 (—CH_3), 56.38 (—OCH_3), 74.53 (—CH_2), 117.50 (—CN), 123.42 (—CH_2, 2C), δ (Ar-C): 74.17, 115.32, 122.98, 127.03, 127.62 (2C), 128.44, 129.34 (2C), 131.34 (2C), 131.98 (2C), 133.27, 146.56, 156.70, 159.28, 163.23, 163.82, 166.78. Anal. Calcd. for $C_{26}H_{22}BrN_7O_3S$ (Fw 592): C, 52.70; H, 3.71; N,

16.55; S, 5.40. Found: C, 52.69; H, 3.69; N, 16.56; S, 5.42.

Dyeing of Polyester Fabric and Dying Properties

Dyeing Procedure. 1% (Avolan IS; Atul Ltd., Vapi, India) dispersing agent was kept at a liquor ratio of 20:1. The process was started at 60°C; the temperature was then raised to 130°C over 30 min and maintained for 1 h. Fabric was taken out after cooling, and treated with 2% sodium bisulfate, 2% sodium hydroxide, and 0.1% dispersing agent (Avolan IS) at 70°C for 30 min. Finally, the fabric was rinsed and dried at 60°C.

Fastness Properties. The fastness to light, sublimation and perspiration was assessed in accordance with BS: 1006-1978. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness test in accordance with IS:765-1979. The details of various fastness tests are mentioned in the literature [29]. The fastness test and dyeing facilities was provided by Atul Ltd. (India).

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