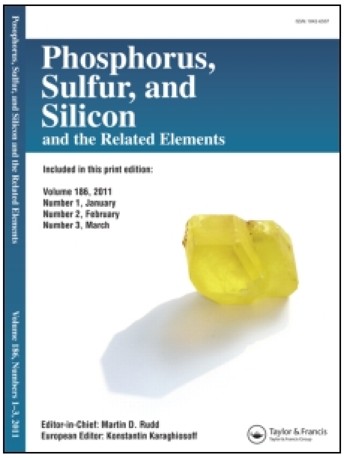

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Simple Approach to Some New Arylazo Spiro Indoline-Based Dyes as Alternatives for Benzidine-Based Dyestuffs

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Simple Approach to Some New Arylazo Spiro Indoline-Based Dyes as Alternatives for Benzidine-Based Dyestuffs

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Three categories of mono, dis- and tris arylazo dyestuffs, which are based on the spiro 2-oxoindole (3,2′) thiazolone moiety, have been synthesized. The assigned structures for the prepared dyes were confirmed on the basis of elemental analysis, as well as spectral data, and whenever possible, by alternative synthetic routes. Moreover, the predominant tautomeric structures for these highly colored products were tested and discussed on the basis of their spectral behavior.

Keywords Alternatives for benzidine-based dyestuffs; mono-, dis-, and tris arylazo; spiro Indole (3,2′)-1′,3′-thiazole-based dyes

INTRODUCTION

Wastewaters from the textile finishing industry commonly contain moderate concentrations (10–200 mg/l) of dyestuffs, contributing significantly to the pollution of aquatic ecosystems.[1] Isatin-bearing heterocycles,[2] thioindigoid,[3] as well as azo bis-isatin[4] dyestuffs represent a large class of dyes that are used in textile and other processing industries (Figure 1).

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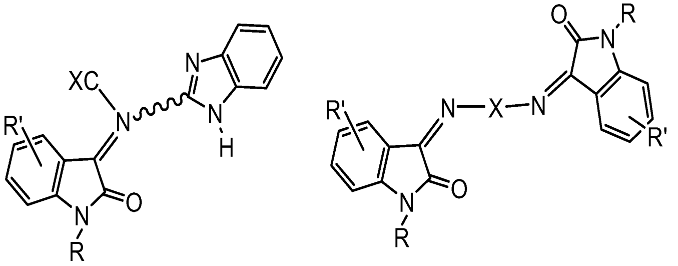


FIGURE 1 Illustrative examples for some isatin-based dyestuffs.

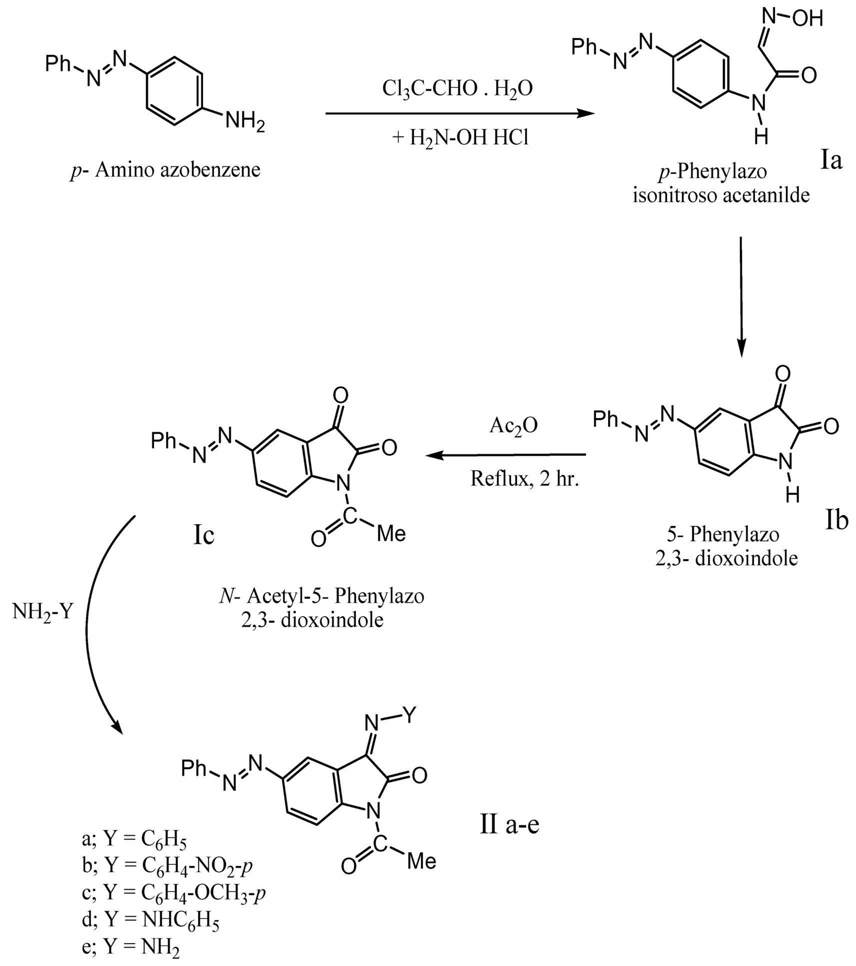
These dyes are designed to be chemically and photolytically stable, they exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many these dyes and their breakdown products are toxic and/or have mutagenic activity.[5–8]

In continuation of our interest[9–13] in synthesizing new symmetric and/or asymmetric aryl azo dyestuffs, we report herein on synthesis of a novel group of mono, dis- and tris arylazo dyestuffs that are based on the spiro 2-oxoindole(3,2)-1,3-thiazolone moiety. The produced dyes, being accommodating solublizing functions, are likely to undergo oxidation and/or hydrolysis to soluble metabolites thus ensure lack of carcinogenicity[6,7,14] and in turn satisfy the basic requirements for a satisfactory replacement of the already available isatin-based dyestuffs.

RESULTS AND DISCUSSION

Perusal in literature revealed that doubling of chromophoric moieties in molecular structure of arylazo dyestuffs highly enhances fastness properties of these dyes.[13–16] In view of these findings and in continuation of a research program directed for synthesis of new categories of mono, dis- and tris-aryl azo heterocyclic dyestuffs, that might overcome the disadvantages of the benzidine-based disaryl azo dyes, it becomes worthy to evaluate the synthetic potentiality of the parent *N*-acetyl-5-phenylazo-2,3-dioxo- indole (Ic) for preparation of such dyes.

Planning for synthesis of the above mentioned dyestuffs involved different synthetic pathways. The multistep synthesis of the first series of these dyestuffs required prior preparation of the previously unreported 5-phenylazo-2,3-dioxoindole derivative (Ib) and its *N*-acetyl derivative (Ic) and subsequent reaction of the later product with some nitrogen nucleophiles as illustrated in Scheme 1.



SCHEME 1

Besides, the characteristic stretching vibration of the azo function at 1525 cm^{-1}, compound Ib revealed its amidic, ketonic carbonyls and indolyl-NH functions at 1665, 1685, and 3110 cm^{-1}, respectively. Its ^1H-NMR spectrum exhibited a broad singlet signal and a multiplet at 9.05 and 7.40–6.76 ppm assignable to the amidic and aromatic protons, respectively.

Acetylation of the later product and subsequent condensation of the produced *N*-acetyl indole derivative Ic with aromatic amines or hydrazines, in equimolar quantities, and afforded the corresponding 3-substituted imino-2-oxo-5-phenylazo-indole derivatives (IIa–e) in good

TABLE I Physical Data of Compounds IIa–IIId

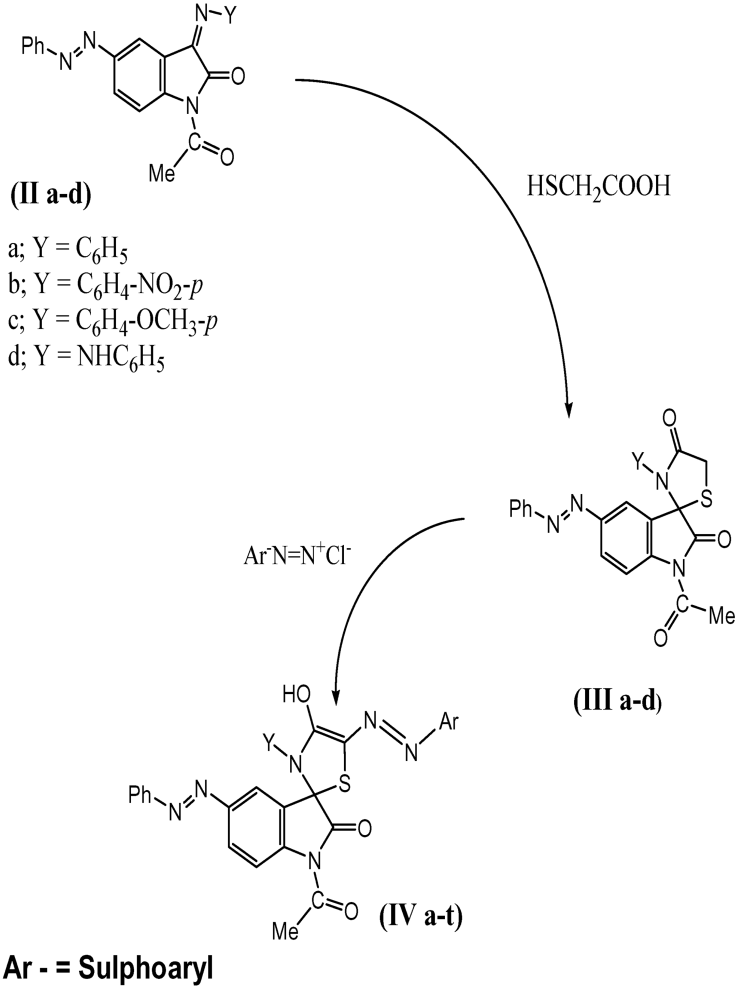
				(%) Calculated/ found			
No.	Y	Molecular formula (M. Wt)	M.P.°C (yield)	C	H	N	S
IIa	C_6H_{5-}	$C_{22}H_{16}N_4O_2$	146	71.73	4.38	15.21	—
		(368.27)	(72)	72.56	4.41	15.47	
IIb	C_6H_4-NO_2-*p*	$C_{22}H_{15}N_5O_4$	216	63.92	3.65	16.95	—
		(413.35)	(70)	64.06	3.79	17.12	
IIc	C_6H_4-OCH_3-*p*	$C_{23}H_{18}N_4O_3$	263	69.34	4.55	14.07	—
		(398.38)	(78)	70.02	4.23	13.85	
IId	NHC_6H_5-	$C_{22}H_{17}N_5O_2$	146	68.92	4.47	18.27	—
		(383.38)	(68)	69.00	4.76	18.41	
IIe	NH_2	$C_{16}H_{13}N_5O_2$	113	62.53	4.26	22.80	—
		(307.29)	(69)	62.80	4.52	23.00	
IIIa	C_6H_5-	$C_{24}H_{18}N_4SO_3$	208	65.15	4.10	12.67	7.25
		(442.45)	(72)	65.31	3.92	12.83	7.99
IIIb	C_6H_4-NO_2-*p*	$C_{24}H_{17}N_5SO_5$	198	59.13	3.52	14.37	6.58
		(487.44)	(73)	59.43	3.31	14.46	6.34
IIIc	C_6H_4-OCH_3-*p*	$C_{25}H_{20}N_4SO_4$	221	63.55	4.27	11.86	6.79
		(472.47)	(73)	63.80	4.15	12.03	7.05
IIId	—C_6H_5NH	$C_{24}H_{19}N_5SO_3$	236	63.01	4.19	15.31	7.01
		(457.47)	(70)	62.85	4.03	15.61	6.94

yield (Table I). The assigned structure for these products were confirmed on the basis of their IR spectrum, which revealed the lack of the cyclic ketonic carbonyl function, and the presence of a new stretching vibration near 1630 cm^{-1}. The later band might be attributed to the exocyclic C=N-functions. Besides the aromatic proton signals, ^{1}H-NMR spectrum of compound IIa showed the common acetyl-protons singlet signal near 1.82 ppm.

While compound IIa showed no evidence of the NH proton signal in its ^{1}H-NMR spectrum, its off resonance ^{13}C-NMR spectral pattern revealed a characteristic sp^3 triplet signal at $\delta = 20.25$ ppm assignable to the sp3 methyl-carbon atom of the acetylamino function. Besides the molecular ion peak, mass spectral pattern of the same product exhibited a group of characteristic signals that are consistent with the assigned structure for this product, (see EXPERIMENTAL).

Addition of mercapto acetic acid to the latent azo-methine function, in the later products IIa–d, resulted in the formation of the amino thiazolone derivatives IIIa–d, respectively (Table I). IR spectra of these products revealed the absence of any absorption corresponding to the previously mentioned azo-methine linkage (—C=N—) and displayed a new strong absorption bands near 1675 cm^{-1} that might be attributed to the new carbonyl function of the thiazolone moiety. Besides, the multiplet absorption at 7.95–6.75 ppm, ^{1}H-NMR spectrum of compound IIIa displayed a new singlet signal near 4.25 ppm corresponding to the methylene protons of the thiazolone moiety.

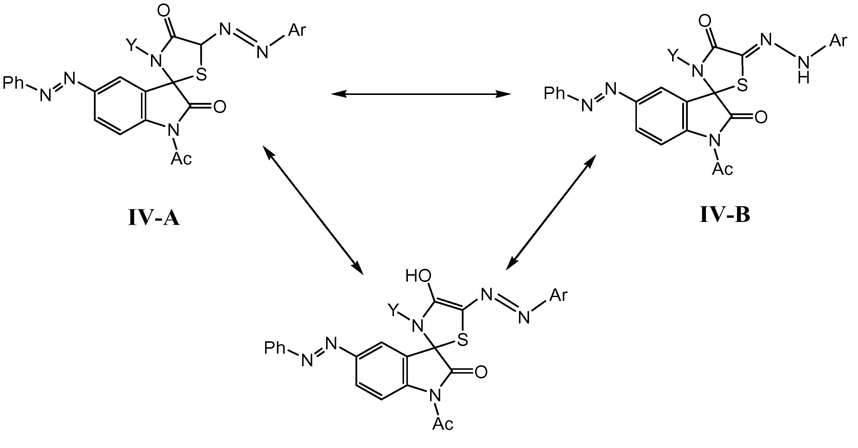
Ethanolic buffered solutions of the hitherto prepared thiazolone derivatives (IIIa–d) were subjected to coupling reactions with different sulphoaryl diazonium salt solutions with a view to get a novel group of the spiro 2-oxoindole(3,2)thiazolone-based disarylazo dyestuffs (IVa–t; Scheme 2).



SCHEME 2

Structure of these products was established on the basis of elemental as well as spectral data (experimental part). Table II depict the characteristic physical properties of spiro these 2-oxoindole (3,2) thiazolone-based arylazo dyestuffs.

The latter coupling products might be represented by three possible tautomeric forms as illustrated in Chart 1.



IV-C

CHART 1

These structures are referred to as the azo-methine form (IVa), the hydrazo form (IVb) and the azo-hydroxy form (IVc). The available data indicated that the predominant tautomeric structure of (IVa–j) derivatives is the chelated hydroxyl-azo form (IVc).

On the basis of the information obtained from the study of IR spectrum of the parent thiazolone derivatives IIIa–d, it is possible to assign the absorption bands of the diazonium coupling products IVa–j with some confidence. Each of the compounds examined, exhibits a strong band in the region of 1615–1605 cm,$^{-1}$ which is assigned to the skeletal C=C in plane vibrations of phenyl rings.[17] The broad and strong absorptions near 1655 cm^{-1} might be ascribed to the stretching vibrations of the acetyl amino CO function.

The parent thiazolone derivative III was found to exhibit strong absorption bands near 1675 cm^{-1} corresponding to the amidic carbonyl stretching vibrations. As to the coupling products IVa–t, each dye revealed a new absorption band of moderate intensity near 1550 ± 10 cm^{-1} that was assigned to the stretching vibration of the newly introduced —N=N— azo functions.

TABLE II Physical Data of Compounds IVa–IVt

				(%) Calculated/found				
No.	Ar	Molecular formula (M. Wt)	M.P.°C (yield)	C	H	N	S	Cl
IVa	4-sulphophenyl	$C_{30}H_{22}N_6O_6S_2$	186	57.50	3.54	13.42	10.23	—
		(626.60)	(69)	57.61	3.21	13.66	10.01	
IVb	2,5-dichloro-4-sulphophenyl	$C_{30}H_{20}N_6O_6S_2Cl_2$	127	51.81	2.90	12.09	9.22	10.19
		(695.48)	(73)	52.00	3.00	11.93	9.14	10.01
IVc	2-carboxy-4-sulphophenyl	$C_{31}H_{22}N_6O_8S_2$	166	55.52	3.31	12.54	9.56	—
		(670.59)	(73)	55.60	3.14	12.70	9.63	
IVd	6-sulphonaphthyl	$C_{34}H_{24}N_6O_6S_2$	210	60.35	3.58	12.42	9.48	—
		(676.65)	(70)	60.42	3.62	12.61	9.70	
IVe	8-sulphonaphthyl	$C_{34}H_{24}N_6O_6S_2$	233	60.35	3.58	12.42	9.48	—
		(676.65)	(68)	60.44	3.70	12.53	9.32	
IVf	4-sulphophenyl	$C_{30}H_{21}N_7S_2O_8$	218	53.65	3.15	14.60	9.55	—
		(671.48)	(66)	53.51	3.08	14.60	9.73	
IVg	2,5-dichloro-4-sulphophenyl	$C_{30}H_{19}N_7S_2O_8Cl_2$	183	48.66	2.59	13.24	8.66	9.58
		(740.46)	(72)	48.53	2.63	13.40	8.43	9.62
IVh	2-carboxy-4-sulphophenyl	$C_{31}H_{21}N_7S_2O_{10}$	233	52.03	2.96	13.71	8.96	—
		(715.57)	(73)	51.90	3.09	13.50	9.10	
IVi	6-sulphonaphthyl	$C_{34}H_{23}N_7S_2O_8$	219	56.59	3.21	13.59	8.89	—
		(721.62)	(70)	56.83	3.00	13.72	9.11	
IVj	8-sulphonaphthyl	$C_{34}H_{23}N_7S_2O_8$	276	56.59	3.21	13.59	8.89	—
		(721.62)	(68)	56.32	3.41	13.36	8.61	

(Continued on next page)

TABLE II Physical Data of Compounds IVa–IV *(Continued)*

No.	Ar	Molecular formula (M. Wt)	M.P.°C (yield)	(%) Calculated/found C	H	N	S	Cl
IVk	4-sulphophenyl	$C_{31}H_{24}N_6S_2O_7$	251	56.69	3.68	12.80	9.77	—
		(656.51)	(68)	56.48	3.71	13.11	9.96	
IVl	2,5-dichloro-4-sulphophenyl	$C_{31}H_{22}N_6S_2O_7Cl_2$	187	51.32	3.06	11.59	8.84	9.77
		(725.50)	(72)	51.42	2.89	11.754	9.16	9.44
IVm	2-carboxy-4-sulphophenyl	$C_{32}H_{24}N_6S_2O_9$	206	54.86	3.45	12.00	9.15	—
		(700.60)	(69)	55.05	3.61	12.14	9.33	
IVn	6-sulphonaphthyl	$C_{35}H_{26}N_6S_2O_7$	244	59.48	3.71	11.90	9.07	—
		(706.67)	(71)	59.21	3.92	12.06	8.83	
IVo	8-sulphonaphthyl	$C_{35}H_{26}N_6S_2O_7$	296	59.48	3.71	11.90	9.07	—
		(706.67)	(70)	59.20	3.59	12.20	8.14	
IVp	4-sulphophenyl	$C_{30}H_{23}N_7S_2O_6$	176	56.16	3.61	15.28	10.00	—
		(641.61)	(69)	55.90	3.73	15.06	10.12	
IVq	2,5-dichloro-4-sulphophenyl	$C_{30}H_{21}N_7S_2O_6Cl_2$	215	50.71	2.98	13.80	9.02	9.98
		(710.50)	(71)	51.66	3.12	14.00	8.91	10.06
IVr	2-carboxy-4-sulphophenyl	$C_{31}H_{23}N_7S_2O_8$	276	54.30	3.38	14.30	9.35	—
		(685.60)	(70)	54.14	3.60	14.11	9.41	
IVs	6-sulphonaphthyl	$C_{34}H_{25}N_7S_2O_6$	246	59.04	3.64	14.18	9.27	—
		(691.65)	(69)	58.89	3.75	14.36	9.51	
IVt	8-sulphonaphthyl	$C_{34}H_{25}N_7S_2O_6$	282	59.04	3.64	14.18	9.27	—
		(691.65)	(72)	58.91	3.42	14.41	9.32	

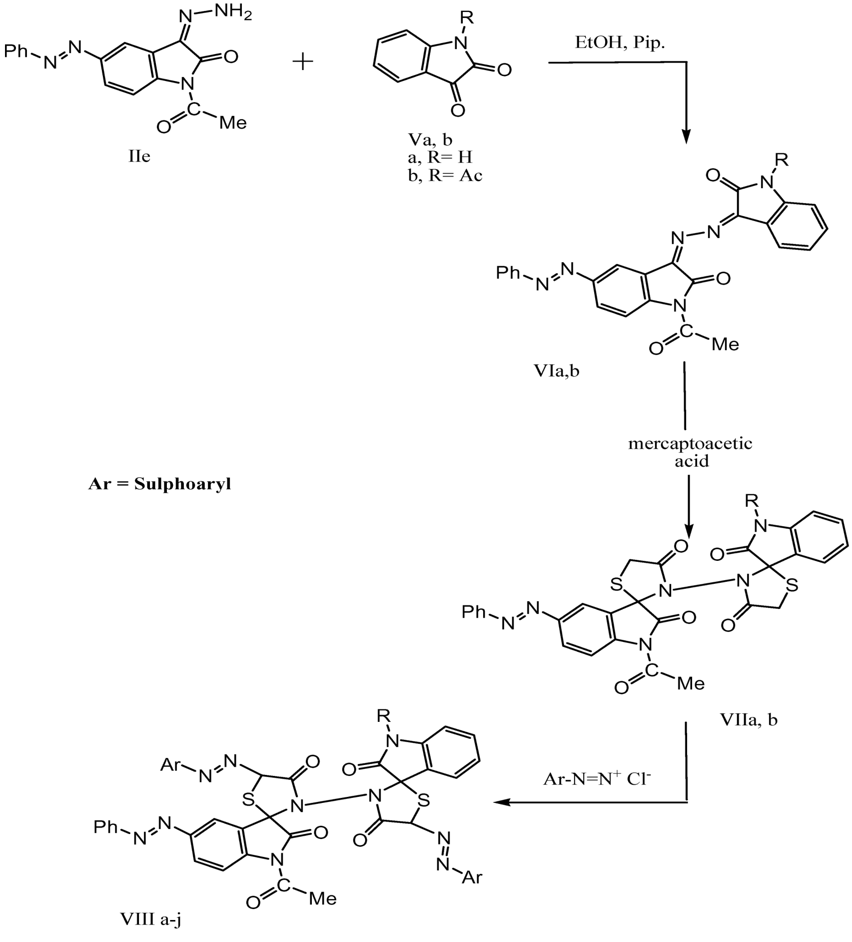
Besides the azo stretching vibrations, IR spectra of these products revealed the presence of a strong and broad band in the region between 3435 and 4350 cm^{-1}. This might be ascribed to the enolic OH stretching vibration of the hydroxy-azo moieties. The large shift and broadening of this band, as compared with normal hydroxyl functions, can result only from strong intramolecular hydrogen bonding as in structure (c). The fact that compounds IV a–t show evidence for intramolecular hydrogen bonding, at all, is in favor of the hydroxy-azo structure.

The lack of any stretching vibrations assignable to the -NH group—in IR spectra of these products—adds a further confirmation for the exclusion of the B structure from the actual presentation of these coupling products.

^{1}H-NMR spectra of IV f, as a typical example for this series of compounds, indicated its presence in the hydroxy-arylazo form rather than any other tautomeric structure. If the azo-methine form (IVa), which contains a CH group, was to represent the actual structure of these coupling products, the spectrum should exhibit a peak position at about 4.25–4.00 ppm similar to that of the methylene proton of the corresponding parent thiazolone III b. Such a peak is actually absent. Moreover, besides the singlet proton signal for the acetyl protons at $\delta = 1.80$ ppm, the spectrum revealed a multiplet centered at 8.12–16.70 ppm and two other small, broad and exchangeable humps near $\delta = 10.45$ and 11.15 ppm. These data are consistent with the hydroxy-azo structure (IVa). The multiplet absorption in the region 8.12–6.70 ppm is undoubtedly due to the aromatic protons. The later two peaks indicate the presence of deshielded protons, which could be assigned to the sulphonic hydroxyl proton and the highly deshielded intramolecular hydrogen bonded acidic proton, respectively. On the basis of these visualizations, the later broad signal is undoubtedly represents the proton signal of the hydroxy-azo function.

The lack of any sp^3 doublet signal in the off-resonance ^{13}C-NMR spectral pattern of this product adds a further support for the exclusion of structure (IVa) from the actual presentation of these coupling products. The presence of a characteristic signal for the *p*-sulphophenyl azo cation at m/e 185 (57%), in mass spectral pattern of compound IVk (experimental part), highly confirms the exclusion of the hydrazo-NH form (IVb), and substantiates the presence of these products in the aryl azo form (IV-C). These visualizations are in accordance with the assigned structure for these products.

In another attempt to prepare a second novel group of spiro indole (3,2)-1,3-thiazole-based arylazo dyestuffs, it was planned to shed more light on the synthetic potentiality of the *N*-amino function of the already available starting compound IIe. Doubling of chromophoric functions in molecular structure of the target compounds (VIII–a–j; Scheme 3) might enhance their tinctorial properties.



SCHEME 3

Thus, refluxing equimolar quantities of IIe and 2,3-dioxo indole (Va) or its *N*-acetyl derivative (Vb), in a basic medium afforded the corresponding *N*-(1-acetyl-5-phenylazo-2,3-dioxoindole) *N′*-(2,3-dioxoindole 3,3-dihydrazone derivatives) (VIa, b). Reaction of the later products with mercapto-acetic acid, in ethanolic-buffered solution, gave the corresponding 3,3-Bis [substituted spiro 2-oxoindole(3,2)-1,3-thiazol-4-one] derivatives (VIIa, b).

Structure of these products was confirmed on the basis of elemental analysis, as well as spectral behavior. Table III depicts the physical

TABLE III Physical Data of Compounds Ia,b and VIIab

No.	Molecular formula (M. Wt)	M.P.°C (yield)	(%) Calculated/ found C	H	N	S
VIa	$C_{24}H_{16}N_6O_3$	271	66.05	3.79	19.29	—
	(436.40)	(68)	65.81	3.86	18.97	
VIb	$C_{26}H_{18}N_6O_4$	253	56.27	3.79	17.57	—
	(478.42)	(66)	65.98	3.43	17.40	
VIIa	$C_{28}H_{20}N_6S_2O_5$	182	57.53	3.45	14.38	10.97
	(584.57)	(63)	57.73	3.61	14.46	10.61
VIIb	$C_{30}H_{22}N_6S_2O_6$	214	57.50	3.54	13.42	10.23
	(626.60)	(68)	57.36	3.22	13.11	10.59

properties of the isolated compounds. Subsequent coupling of the later products with ice-cold solutions of sulphoaryl diazonium salt solutions afforded the target compounds (VIIIa–j), as highly colored solid materials, in moderate yield. Table IV accommodates the characteristic physical data of these dyestuffs.

IR and ^{1}H-NMR spectra of these products revealed no evidence for their presence in the hydrazo or the azo-methine forms. The later conclusion was based not only on the absence of any characteristic stretching for the NH group in IR spectra of these products, but also on the basis of disappearance of any singlet signal, corresponding to the methylene function of thiazolone moiety, in there ^{1}H-NMR spectra.

On the basis of these observations, along with the other spectral data (experimental part), it would not be unreasonable to confirm the exclusion of structures (A) and (B) from presenting the actual structure of such coupling products (Chart 2). This elimination is compatible with the absence of absorption for the cyclic tertiary amidic carbonyl function of thiazolone moieties.

Formation of these bis spiro arylazo dyes has been further confirmed by mass spectral patterns. In the mass spectra of compound VIIIa, the molecular ion peak was observed at m/e 952 (79%) corresponding to its molecular weight.

Judging from these results it could be concluded that the diazonium coupling products (VIIIa–j) exist predominantly in the hydroxy-azo form (C).

Further confirmation for the chemical structure of compounds VIIIa–j was obtained via alternative synthetic pathway (Scheme 4). Plan for this synthetic route was based on prior preparation of *N*-amino spiro indole thiazole derivative IX and subsequent coupling with

TABLE IV Physical Data of Compounds VIIIa–VIIIj

No.	Ar	Molecular formula (M. Wt)	M.P.°C (yield)	Calculated/ found (%) C	H	N	S	Cl
VIIIa	4-sulphophenyl	$C_{40}H_{28}N_{10}S_4O_{11}$	141	50.42	2.96	14.70	13.46	—
		(952.85)	(60)	50.65	3.11	14.98	13.26	
VIIIb	2,5-dichloro-4-sulphophenyl	$C_{40}H_{24}N_{10}S_4O_{11}Cl_4$	209	44.05	2.22	12.85	11.76	13.00
		(1090.62)	(59)	44.20	2.39	13.05	11.52	13.19
VIIIc	2-carboxy-4-sulphophenyl	$C_{42}H_{28}N_{10}S_4O_{15}$	169	48.46	2.71	13.46	12.32	—
		(1040.83)	(52)	48.31	2.98	13.52	12.00	
VIIId	6-sulphonaphthyl	$C_{48}H_{32}N_{10}S_4O_{11}$	209	54.75	3.06	13.31	12.18	—
		(1052.97)	(53)	54.90	2.89	13.12	12.39	
VIIIe	8-sulphonaphthyl	$C_{48}H_{32}N_{10}S_4O_{11}$	196	54.75	3.06	13.31	12.18	—
		(1052.97)	(53)	54.50	3.11	13.49	12.00	
VIIIf	4-sulphophenyl	$C_{42}H_{30}N_{10}S_4O_{12}$	226	50.70	3.04	14.08	12.89	—
		(994.88)	(62)	50.49	2.96	13.80	13.62	
VIIIg	2,5-dichloro-4-sulphophenyl	$C_{42}H_{26}N_{10}S_4O_{12}Cl_4$	169	44.53	2.31	12.37	11.32	12.52
		(1132.65)	(48)	44.63	2.12	12.53	11.16	12.38
VIIIh	2-carboxy-4-sulphophenyl	$C_{44}H_{30}N_{10}S_4O_{16}$	245	48.80	2.79	12.94	11.84	—
		(1082.86)	(59)	49.02	2.89	13.12	11.93	
VIIIi	6-sulphonaphthyl	$C_{50}H_{34}N_{10}S_4O_{12}$	290	54.84	3.13	12.79	11.71	—
		(1094.99)	(60)	54.96	3.00	12.90	11.96	
VIIIj	8-sulphonaphthyl	$C_{50}H_{34}N_{10}S_4O_{12}$	281	54.84	3.13	12.79	11.71	—
		(1094.99)	(51)	55.02	3.36	12.58	11.58	

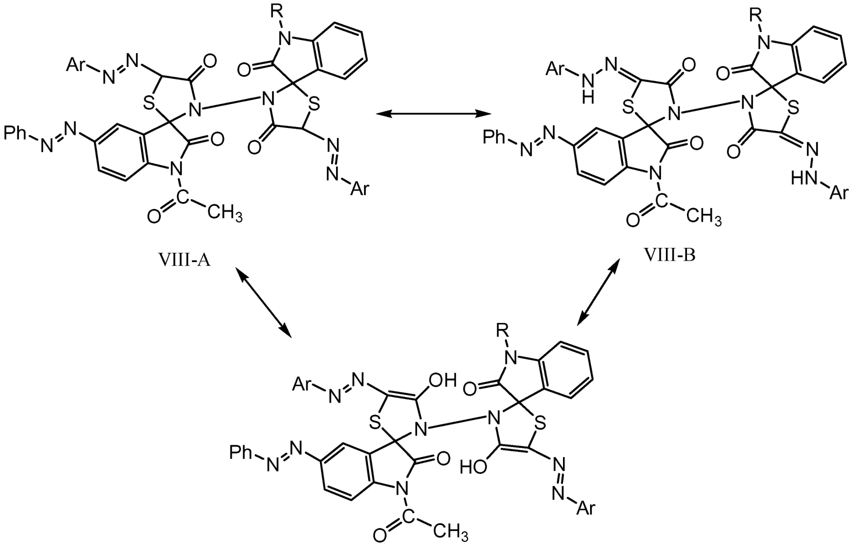


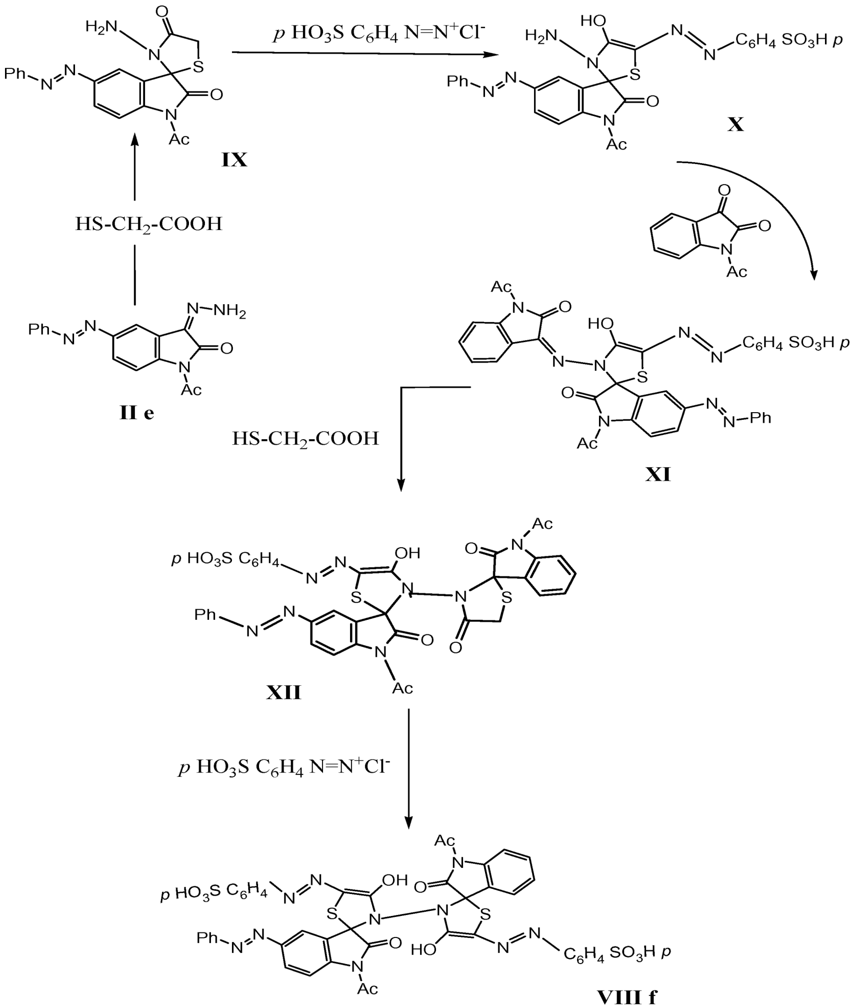
CHART 2 Tautomeric structures of the bis arylazo coupling products (VIIIa–j).

p-sulphophenyl diazonium chloride to give the hydroxy sulphoarylazo derivative X. Condensation of the later product with *N*-acetyl-2,3-dioxo indole derivative VIb afforded the corresponding indol-3-ylidine amino spiro indole thiazole derivative XI in good yield. Refluxing the later key intermediate product with mercapto acetic acid, followed by coupling of the produced compound XII with *p*-sulphophenyl diazonium chloride, afforded the original dye VIIIf with no depression in m.p. or mixed m.p.

In consequence the tautomeric structure (C) of the dyes, under investigation, is the only one which accommodates these spectral observations.

Unlike other dyes that accommodate additional *o*-, sulphonic group and suffer lower substantivity behavior, as a result of deformation of the dye molecules due to the vicinity of the previous group to an azo function,[14] the hitherto synthesized highly colored products, being substituted with additional *p*-sulphonic acid groups, exhibited high substantivity and preliminary good light and washing fastness and thus might fully satisfy all the requirements for a satisfactory use as environmentally safe arylazo dyestuffs.

The general strategy of this article was based not only on a plan for synthesis of the previously mentioned series of arylazo heterocyclic dyestuffs that might find valuable industrial application, but also to use these highly colored products for dyeing purposes and subsequent evaluation of the possibility of application of adsorption technology for removal of the color of their residuals from effluents of dyeing baths. The used dyes revealed good affinity to cellulosic fibers and showed good all-round fastness properties. The results of dyeing performance and application of adsorption technology to remove the color of their residuals from dyeing baths, on different types of carbon, will be the subject of our forthcoming communication.



SCHEME 4 Alternative synthetic route for preparation of compound VIIIf.

CONCLUSION

The produced dyes, with their new all-round tinctorial properties and being accommodating solublizing functions, are likely to undergo oxidation and/or hydrolysis to soluble metabolites. Thus, these products ensure lack of carcinogenicity and in turn, might find application, in the field of textile and dyeing industry, as new categories of direct dyes that satisfactory replace the prohibited benzidine-based dyes.

EXPERIMENTAL

All melting points are uncorrected and measured on a Griffin & George MBF 010T apparatus. Recorded yields correspond to the pure products. IR (KBr) spectra were recorded on a Perkin Elmer model 1750 FTIR. H^1NMR and ^{13}C-NMR spectra were measured on a Varian 270 MHz spectrometer and a Bruker AM360, respectively, using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard (Chemical shifts are given as δ in ppm). Mass spectra (70 eV) were recorded on a Varian VG 7035 mass spectrometer. Microanalysis was carried out in the Microanalytical Data Unit at Cairo University and the National Research Center (NRC), Cairo, Egypt. Nomenclature of the hitherto prepared compounds is in line with the IUPAC rules for nomenclature of organic compounds.

Synthesis of *p*-Phenylazo Isonitrosoacetanitide (Ia)

It was prepared as white crystals of m.p. 175°C in 73% yield using *p*-amino azobenzene and following a previously reported procedure.[1]

For $C_{14}H_{12}N_4O_2$ (268.26); Calcd: C, 62.68%; H, 4.51%; N, 20.89% found: C, 62.31%; H, 4.58%; N, 21.00%.

Synthesis of 5-Phenylazo-2,3-dioxoindole (Ib)

60 g. (326 ml.) of concentrated sulfuric acid (sp. gr. 1.84) was warmed to 50°C in a 1-1. round-bottomed flask fitted with an efficient mechanical stirrer, and, to this, 7.5 g (46 mmol) of dry iso nitrosoacetanilide is added at such a rate as to keep the temperature between 60°C and 70°C but not higher. External cooling should be applied at this stage so that the reaction can be carried out more rapidly. After the addition of the isonitroso compound is finished, the solution is heated to 80°C and kept at this temperature for about 10 min to complete the reaction. Then the reaction mixture is cooled to room temperature and poured

upon 10 to 12 times its volume of crushed ice. After standing for about one-half hour, the indole derivative is filtered with suction, washed several times with cold water to remove the sulfuric acid, and then dried in the air and recrystallized from glacial acetic acid to give the pure product of m.p. 196°C in 73% yield.

For $C_{14}H_9N_3O_2$ (251.22); Calcd: C, 66.93%; H, 3.61%; N, 16.73%; found: C, 67.14%; H, 3.49%; N, 16.92%. IR (v^-/cm^{-1}): 3110 (NH), 1685 (ketonic CO), 1680 (cyclic sec. amidic CO), 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): 7.40–6.76 (m, 8H, Ar-H) and 9.05 (br. exchangeable singlet, 1H, amidic NH-).

Synthesis of N-Acetyl-2,3-dioxo-5-phenylazoindole (I c)

A mixture of Ib (10 mmol, 2.51 g), acetyl chloride (10 mmole, 0.78 ml) and piperidine (0.3 ml) in dilute sodium hydroxide (20 ml) was refluxed under anhydrous conditions for 3 h and left to cool to room temperature. The resulting solid that formed after cooling was filtered off and recrystallized from acetic acid to give the pure product of m.p. 208°C in 71% yield.

For $C_{16}H_{11}N_3O_3$ (293.25); Calcd: C, 65.53%; H, 3.78%; N, 14.33%; found: C, 65.41%; H, 3.93%; N, 14.46%. IR (v^-/cm^{-1}): 1685 (ketonic CO), 1665 (cyclic sec. amidic CO), 1655 (acetyl C=O) and 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): 7.12–6.75 (m, 8H, Ar-H) and 1.85 (s, 3H, acetyl protons). ^{13}C-NMR: 191 (C-3), 174.9 (acetyl $\underline{C}$=O), 159.1 (C-2), 149.4 (C-7a), 115.6 (C-3a) and 19.4 (acetyl $\underline{C}H_3$).

Synthesis of *N*-Acetyl-2-oxo-5-phenylazo 3-Substituted Imino Indole Derivatives (IIa–e)

A mixture of Ic (10 mmol, 2.93 g), aromatic amine or hydrazine (0.01 mol) for preparation of IIc, phenyl hydrazine (10 mmol, 1.8 ml), and piperidine (3 drops) in absolute ethanol (10 ml) was refluxed for 4 h and left to cool to room temperature. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure products of 68–78% yield. The prepared products together with their physical data are depicted in Table I.

For compound IIa: IR (v^-/cm^{-1}): 1665 (cyclic amidic CO), 1655 (acetyl CO), 1630 (exocyclic C=N-), 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): 7.60–6.62 (m, 13H, Ar-H) and 1.82 (s, 3H, acetyl protons). Mass spectra (m/e): 368 (M^+) 69%, 263 (M^+-$C_6H_5N_2$) 100%, 188 (M^+-$C_{12}H_8N_2$) 37%, 145 (188-C_2H_3O) 81%, 103 (188-$C_3H_3NO_2$) 52% and 60 (M^+-$C_{20}H_{12}N_4$) 46%.^{13} C-NMR: for compound IIb: 174.9 (acetyl C=O), 161.4 (C-3), 160.8 (C-1 of 4-nitrophenyl moiety), 160.1 (C-2), 149 (C-7a), 144.8 ($\underline{C}$-NO_2), 115.1 (C-3a), and 19.4 (acetyl $\underline{C}H_3$).

Synthesis of 1-Acetyl-3-aryl-5-phenylazo spiro 2-oxoindole(3,2′)-1′, 3—thiazol-4′ -one derivatives (IIIa–c) and 1-Acetyl-3-phenylamino-5-phenylazo spiro 2-oxoindole(3,2′)-1′, 3—thiazol-4′-one derivative (IIId)

A mixture of IIa–d (10 mmol in each case), mercapto acetic acid (0.01 mol, 0.9 ml) and piperidine (0.3 ml) in absolute ethanol (10 ml) was refluxed under anhydrous conditions for 4 h and left to cool to room temperture. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure products (Table II).

For compound IIIa: IR (v^{-}/cm^{-1}): 1675 (thiazolyl CO), 1665 (indolyl cyclic amidic CO), 1665 (acetyl CO), 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): 7.95–6.75 (m, 13H, Ar-H) and 4.25 (s, 2H, thiazolyl $C\underline{H}_2$) 1.80 (s, 3H, acetyl protons).^{13} C-NMR: 174 (acetyl $\underline{C}$=O), 173.0 (thiazolyl $\underline{C}$=O), 160 (C-2), 149 (C-7a), 146.2 (C-5), 126 (C-6), 125.2 (C-7), 124.5 (C-3a), 119.6 (C-4), 34.1 (thiazolyl methylene carbon atom), and 19.4 (acetyl $\underline{C}H_3$).

Synthesis of 1-Acetyl-3′-aryl-5′-hydroxy-2-oxo-5-phenylazo-4′-sulphoarylazo Spiro Indole (3,2′)-1′,3-thiazol-4′-one Derivatives (IVa–o) and 1-Acetyl-3′-phenylamino-5′-hydroxy-2-oxo-5-phenylazo-4′-sulphoarylazo Spiro Indole (3,2′)-1′,3-thiazol-4′-one derivatives (IVp–t)—General Procedure

In a 250 ml conical flask, 5 mmol of the sulphoaryl amine was mixed with anhydrous sodium carbonate (2.6 g) and water (100 ml), and the whole mixture was warmed until a clear solution was obtained then cooled to about 15°C. Next, a solution of sodium nitrite (5.2 mmol, 3.6 g) in water (10 ml) was added. The resulting solution was slowly added—while stirring—to a 600 ml beaker containing hydrochloric acid (12 ml, 30%) and crushed ice (100 g). The solution was tested for the presence of slight excess nitrous acid and we continued stirring 15 min, where the fine crystals of diazo component soon separated. The suspension was kept in an ice bath for a further 10 min and poured, while stirring, into a solution of IIIa (5 mmol, 2.21 g) in cold 10% sodium hydroxide solution (50 ml), and the whole mixture was cooled to 0–3°C. Coupling readily takes place and the dyestuff separates as a paste. The whole mixture was stirred well for 10 min and warmed until the paste has dissolved completly; concentrated sodium chloride solution (20 ml) was added to the mixture. The solution was allowed to cool spontaneously for 1 h in air and then cooled in an ice bath until complete precipitation of the product. The produced salt was collected by filtration, washed with a little saturated sodium chloride solution and dried at 80°C. Acidification of aqueous solution of the produced salt, with diluted acetic acid, afforded the crude product, which was recrystallized from acetic acid to give highly colored crystals of the pure derivatives (IV) in an average yield 68–73%. The prepared dyestuffs together with their physical data are depicated in Table II.

For compound IVf, IR (v^{-}/cm^{-1}): 3470 (OH), 1665 (indolyl cyclic amidic CO), 1655 (acetyl CO), 1545 & 1340 (asym. and sym. stret. vibrations of NO_2 group), 1320 & 1185 (asym. and sym. stretching vibration of sulphonic acid moiety), 1555& 1525 (—N=N—), 1610 (C=C). ^{1}H-NMR spectrum (δ in ppm):11.15 (br. exchangeable hump, 1H, enolic O$\underline{H}$), 10.45 br. exchangeable hump, 1H, $SO_3\underline{H}$), (8.12-6.70 (m, 16H, Ar-H) and 1.80 (s, 3H, acetyl proton).

For compound IV K, ^{13}C-NMR: 181.5 ($\underline{C}$-4), 174.2 (acetyl $\underline{C}$=O), 163.8 ($\underline{C}$-5), 160.4 ($\underline{C}$-2), 152.1 ($\underline{C}$-SO_3H), 147.8 ($\underline{C}$-OCH_3), 147.6 ($\underline{C}$-7a), 145.8 ($\underline{C}$-5), 125.5 ($\underline{C}$-7), 124.7 ($\underline{C}$-6), 124.5 ($\underline{C}$-3a), 67.5 (spiro $\underline{C}$-3), 54.6 ($O\underline{C}H_3$) and 19.4 (acetyl $\underline{C}H_3$). Mass spectra for the same product (m/e): 656 (M^+) 33%, 613 (M^+-C_2H_3O) 100%, 549 (M^+-C_7H_7O) 36%, 465 (M^+-$C_6H_5N_2O_3S$) 76%, 419 (M^+-$C_{14}H_{11}N_3O$) 55%, 258 (419-$C_9H_7NO_2$), 43%, 185 ($C_6H_5N_2SO_3$) 57%.

Synthesis of N-(1-Acetyl-5-phenylazo-2,3-dioxoindole) N′-(2′,3′-Dioxoindole 3,3′-dihydrazone Derivatives (VIa, b)

A mixture of IIe (10 mmol, 3.07 g), V (10 mmol), and piperidine (0.3 ml) in absolute ethanol (10 ml) was refluxed under anhydrous conditions for 4 h and left to cool to room temperature. The resulting solid that formed after cooling was filtered off and recrystallized from acetic acid to give the pure products together with their physical data are depicted in Table III.

For compound VIb: IR (v^{-}/cm^{-1}): 1665 (cyclic sec. amidic CO), 1630 (C=N-), 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): 7.62–6.45 (m, 12H, Ar-H), and 1.85 (s, 6H, acetyl protons).

Synthesis of 3,3′-Bis[Substituted Spiro 2-Oxoindole(3.2′)-1′,3′-thiazol-4′-one] Derivatives (VIIa, b)

These dyes were prepared by mixing 1:2 molar ratios of reactants and following the same procedure given in preparation of compounds IIIa–d. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure products. The synthesized dyes together with their physical data are depicted in Table III.

For compound VIIb, IR (v^{-}/cm^{-1}): 1675 (thiazolyl CO), 1665 (indolyl cyclic amidic CO), 1655 (acetyl CO), 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): 7.65–6.45 (m, 12H, Ar-H), 4.30 (s, 4H, thiazolyl $C\underline{H}_2$ groups) and 1.85 (s, 3H, —N-$COC\underline{H}_3$).

Synthesis of 3,3′-Bis[5′-arylazo-4′-hydroxy Substituted Spiro 2-Oxoindole(3.2′)-1′,3′-thiazole] Derivatives (VIIIa–j)

These dyes were prepared by mixing 1:2 molar ratios of reactants and following the same procedure that was described for the preparation of compounds IVa–t. The resulting solid that formed after cooling was filtered off and recrystallized from acetic acid to give highly colored crystals of the pure derivatives (VIIIa–j) in an average 48–63% yield. The prepared dyestuffs together with their physical data are listed in Table IV.

For compound VIIIf, IR (v^{-}/cm^{-1}): 3430 (OH), 1665 (indolyl cyclic amidic CO), 1655 (acetyl CO), 1355 & 1140 (asym. and sym. stretching vibration of sulphonic acid moiety), 1545 & 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): ^{1}H-NMR spectrum, (δ in ppm): 11.46 (br. exchangeable humps, 2H, enolic O$\underline{H}$ protons) and 10.51 (br. exchangeable humps, 2H, $SO_3\underline{H}$ protons) 8.10–6.65 (m, 20H, Ar-H), and 1.85 (s, 6H, two —N—$COC\underline{H}_3$ protons). ^{13}C-NMR: 181.0 ($\underline{C}$-4), 174.7 (acetyl $\underline{C}$=O), 163.8 ($\underline{C}$-5), 160.2 ($\underline{C}$-2), 152.0 ($\underline{C}$-SO_3H), 147.4 ($\underline{C}$-7a), 145.8 ($\underline{C}$-5), 125.3 ($\underline{C}$-7), 124.9 ($\underline{C}$-6), 124.5 ($\underline{C}$-3a), 67.2 (spiro $\underline{C}$-3) and 19.4 (acetyl $\underline{C}H_3$).

For compound VIIIa, mass spectra (m/e): 952 (M^+) 79%, 892 (M^+-$C_2H_4O_2$), 93%, 699 (M^+-$C_{16}H_{11}N_3O_2$) 100%, 582 (M^+-$C_{12}H_{10}N_4S_2O_6$) 38%, 582 (M^+-$C_{12}H_{10}N_4S_2O_6$) 65%, 549 (M^+-$C_{16}H_{11}N_4S_2O_5$) 43%.

Synthesis of 1-Acetyl-3′-amino-2,4′-dioxo-5-phenylazo Spiro Indole (3,2′)-1′,3′-Thiazole (IX)

This dye was prepared by mixing molar ratio of reactants and following the same procedure that was given for the preparation of compounds IIIa–d. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure product, of m.p. 168°C, in 65% yield.

For $C_{18}H_{15}N_5SO_3$ (381.38); Calcd.: C, 56.68%; H, 3.96%; N, 18.37%; S, 8.41; found: C, 56.99%; H, 3.78%; N, 18.11%; S, 8.79%.

IR (v^{-}/cm^{-1}): 3380 & 3365 (amino group), 1675 (thiazolyl CO), 1665 (indolyl cyclic amidic CO), 1655 (acetyl CO), 1525 (—N=N—). ^{1}H-NMR spectrum, (δ in ppm): 7.45–6.55 (m, 8H, Ar-H), 5.30 (br. exchangeable hump, 2H, N$\underline{H}_2$), and 4.15 (s, 2H, thiazolyl C$\underline{H}_2$) and 1.85 (s, 3H, —N-COC$\underline{H}_3$).

Synthesis of 1-Acetyl-3′-amino-4′-hydroxy-2-oxo-5-phenylazo-5′-sulphophenylazo Spiro Indole (3,2′)-1′,3′-Thiazole Derivative (X)

This product was prepared by following the previously mentioned procedure for the preparation of compounds IVa–t. The resulting solid that formed after cooling was filtered off and recrystallized from acetic acid to give the pure disarylazo dye X, of m. p. 236°C, % in 63% yield.

For $C_{24}H_{19}N_7S_2O_6$ (565.58); Calcd.: C, 50.97%; H, 3.39%; N, 17.34%; S, 11.34; found: C, 51.20%; H, 3.48%; N, 17.11%; S, 11.14%.

IR (v^-/cm^{-1}): 3375 & 3360 (amino group), 3465 (enolic OH), 1665 (indolyl cyclic amidic CO), 1655 (acetyl CO), 1555 & 1525 (—N=N—), 1320 & 1185 (asym. and sym. stretching vibration of sulphonic acid moiety) ^{1}H-NMR spectrum, (δ in ppm): 11.12 (br. exchangeable hump, 1H, enolic O$\underline{H}$), 10.50 br. exchangeable hump, 1H, $SO_3\underline{H}$), 8.08–6.50 (m, 12H, Ar-H), 5.25 (br. exchangeable hump, 2H, N$\underline{H}_2$) and 1.82 (s, 3H, —N-COC$\underline{H}_3$).

Synthesis of 1-Acetyl-3′-amino-4′-hydroxy-2-oxo-5-phenylazo-5′-sulphophenylazo-3′- [1-acetyl-2-oxoindol-3′-ylimino] Spiro Indole (3,2′)-1′,3′-thiazole Derivative (XI)

This dis arylazo dye was prepared by following the same procedure that was mentioned for the preparation of compounds IIa–d. The resulting solid that formed after cooling was filtered off and recrystallized from acetic acid to give the pure product XI, of m.p. 184°C, in 48% yield.

For $C_{34}H_{24}N_8S_2O_8$ (736.12); Calcd.: C, 55.43%; H, 3.28%; N, 15.21%; S, 8.70; found: C, 55.69%; H, 3.08%; N, 15.11%; S, 8.83%.

IR (v^-/cm^{-1}): 3465 (enolic OH), 1665 (indolyl cyclic amidic CO), 1655 (acetyl CO), 1625 (exocyclic C=N), 1555 & 1525 (—N=N—), 1320 & 1185 (asym. and sym. stretching vibration of sulphonic acid moiety). ^{1}H-NMR spectrum, (δ in ppm): 11.12 (br. exchangeable hump, 1H, enolic O$\underline{H}$), 10.50 br. exchangeable hump, 1H, $SO_3\underline{H}$), 8.12–6.55 (m, 16H, Ar-H), and 1.82 (s, 6H, —N—COC$\underline{H}_3$).

Synthesis of 1-Acetyl-3′-amino-4′-hydroxy-2-oxo-5-phenylazo-5′-sulphophenylazo-3′-[spiro 1-acetyl-2,4′-dioxo indol-3′-ylimino] Spiro Indole (3,2′)-1′,3′-Thiazole Derivative (XII)

This product was prepared by following the previously mentioned procedure for the preparation of compounds IIIa–d. The resulting solid that formed after cooling was filtered off and recrystallized from acetic acid to give the pure dye XI, of m.p. 219°C, in 57% yield.

For $C_{36}H_{26}N_8S_3O_9$ (810.10); Calcd: C, 53.33%; H, 3.23%; N, 13.82%; S, 11.86; found: C, 53.49%; H, 3.38%; N, 14.01%; S, 11.79%.

IR (v^{-}/cm^{-1}): 3465 (enolic OH), 1670 (thiazolyl CO), 1665 (indolyl cyclic amidic CO), 1655 (acetyl CO), 1555 & 1525 (—N=N—), 1320 & 1185 (asym. and sym. stretching vibration of sulphonic acid moiety). ^{1}H-NMR spectrum, (δ in ppm): 11.15 (br. exchangeable hump, 1H, enolic O$\underline{H}$), 10.50 br. exchangeable hump, 1H, $SO_3\underline{H}$), 8.12–6.55 (m, 16H, Ar-H), 4.20 (s, 2H, thiazolyl $C\underline{H}_2$), and 1.82 (s, 6H, —N—$COC\underline{H}_3$).

^{13}C-NMR: 181.5 ($\underline{C}$-4), 174.2 (acetyl $\underline{C}$=O), 173.0 (thiazolyl $\underline{C}$=O), 163.8 ($\underline{C}$-5), 160.4 ($\underline{C}$-2), 152.1 ($\underline{C}$-SO_3H), 147.6 ($\underline{C}$-7a), 145.8 ($\underline{C}$-5), 125.5 ($\underline{C}$-7), 124.7 ($\underline{C}$-6), 124.5 ($\underline{C}$-3a), 119.6 ($\underline{C}$-4), 67.5 (spiro $\underline{C}$-3), 33.9 (thiazolyl methylene carbon atom), and 19.4 (acetyl $\underline{C}H_3$).

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