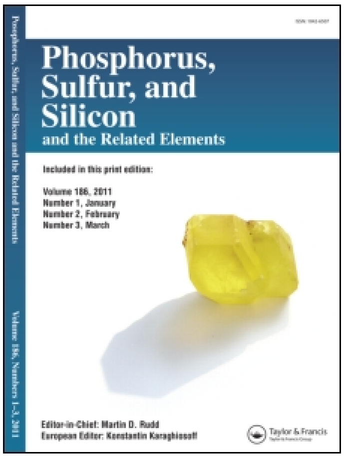

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Anchored Synthesis for Some Novel Mono and Disarylazo 1,2,4-Benzothiadiazine-Based Dyestuffs as Alternatives for Benzidine-Based Dyes

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Anchored Synthesis for Some Novel Mono and Disarylazo 1,2,4-Benzothiadiazine-Based Dyestuffs as Alternatives for Benzidine-Based Dyes

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A one mono and two disarylazo series of 1,2,4-benzothiadiazine-based dyestuffs has been synthesized with a view that these products, with their new all-round tinctorial properties, might find an application as new categories of direct dyes that satisfactorily replace prohibited benzidine-based dyes.

The assigned structures for the hitherto 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 1,2,4-Benzothiadiazine-based dyes; benzidine-based dyes alternatives; mono and disarylhydrazono dyes; predominant tautomeric structures

INTRODUCTION

The use of benzidine-based dyestuffs in the field of textile dyeing has been largely discontinued in view of the toxicological hazards associated with them. The problem of replacing benzidine dyes has not been fully resolved, although a number of approaches have been made based on two concepts. The first consists of the use of other classes of dye for dyeing purposes, and the second approach involves the use

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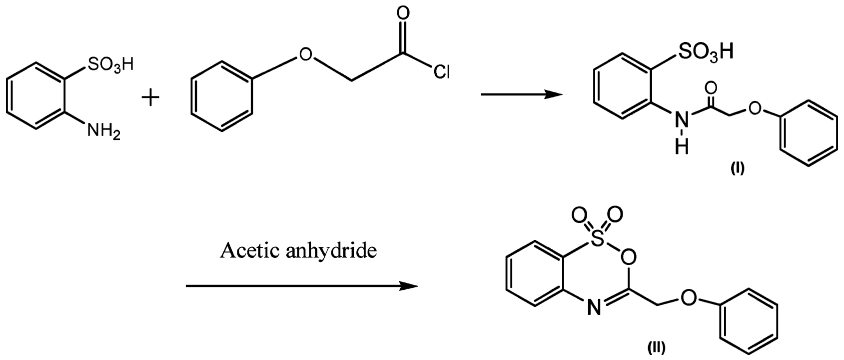
of other diamines, i.e., diaminostilbenedisulphonic acid[1] and diaminodiphenylaminesulphonic acid[2] in the dye synthesis. The first solution does not usually ensure obtaining all the hues possible from disarylazo benzidine-based dyestuffs; it is more expensive and often requires an alternative dyeing technology. Although the second concept is of great interest since it could yield new, harmless dyes having the same color and application properties as the benzidine dyes, it still faces a problem associated with the pollution of the environment. These diamine-based dyestuffs are designed to be chemically and photolytically stable; they exhibit a high resistance to microbial degradation and are highly persistent in a natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many of these disarylazo dyestuffs and their breakdown products are toxic and/or exhibit mutagenic effects.[3,4]

In continuation of our interest[5–8] in synthesizing new symmetric and/or asymmetric disaryl azo dyestuffs, we report herein on the synthesis of a novel group of mono and disarylazo dyestuffs that are based on the 1,2,4-benzothiadiazine 1,1-dioxide moiety. The produced dyes, being accommodating solublizing functions, are likely to undergo oxidation and/or hydrolysis to soluble metabolites, thus ensuring a lack of carcinogenicity[9] and in turn satisfying the basic requirements for a satisfactory replacement of prohibited benzidine-based dyes.

DISCUSSION

The synthesis of the previously mentioned dyestuffs involved different synthetic pathways. The multistep synthesis of the first series of these dyestuffs, as illustrated in Scheme 1, required the cyclization of the previously unreported 2-(2′-Phenoxyacetylamino)-benzenesulphonic acid I in the presence of acetic anhydride to the corresponding 3-phenoxymethyl-2,1,4-benzoxathiazine 1,1-dioxide II.



SCHEME 1

While compound I revealed intense absorption bands at 3430, 1350, 1140, and 1685 cm^{-1} corresponding to the sulphonic acid and primary amidic functions, compound II revealed its sulphonate ester and azomethine functions at 1360, 1155, and 1630 cm^{-1}, respectively. The ^{1}H NMR spectrum of this product exhibited a singlet signal at 4.05 ppm assignable to the methylene protons, respectively. Moreover, its ^{13}C NMR spectral pattern showed a characteristic sp^{3} triplet signal at $\delta = 79$ ppm (assignable to the methylene-carbon atom of the phenoxy methyl moiety). Beside the molecular ion peak, the mass spectral pattern of the same product revealed a group of characteristic signals that might be obtained as a result of α-cleavage fragmentation patterns. This is in accordance with the assigned structure of this product (cf. Experimental section).

The condensation of the later product with hydrazine hydrate in a 1:1 molar ratio afforded the 2-amino-3-phenoxymethyl-1,2,4-benzothiadiazine 1,1-dioxide III in a good yield. The assigned structure for this product was confirmed on the basis of its IR spectrum, which revealed the lack of a sulphonate ester function and the presence of stretching vibrations near 3340, 3330, 1350, and 1145 cm^{-1} that might be attributed to the N-amino and cyclic sulphonamido functions, respectively. Beside the aromatic proton signals, the ^{1}H-NMR spectrum of this compound showed a broad exchangeable hump centered at 4.90 ppm and a singlet signal at 4.05 ppm corresponding to the amino and methylene protons, respectively.

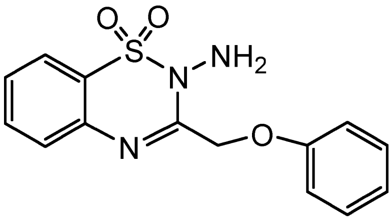
Subjecting the latter product to coupling reactions in basic a medium with different arene diazonium salt solutions gave rise to a novel series of the benzothiadiazine-based arylazo dyestuffs IVa–e.

The structure of these products was established on the basis of elemental as well as spectral data (c.f. Experimental section). Table I depicts the characteristic physical properties of these benzothiadiazine-based arylazo dyes.

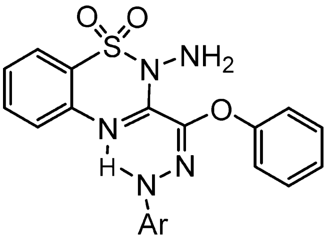
The latter coupling products might be represented by three possible tautomeric forms as illustrated in Scheme 2.

These structures are referred to as the azo-CH form (IV-A), the hydrazo form (IV-B), and the azo-NH form (IV-C). The available data indicated that the predominant tautomeric structure of $(\text{IV})_{\text{a}-\text{e}}$ derivatives is the chelated hydrazono form (IV-B).

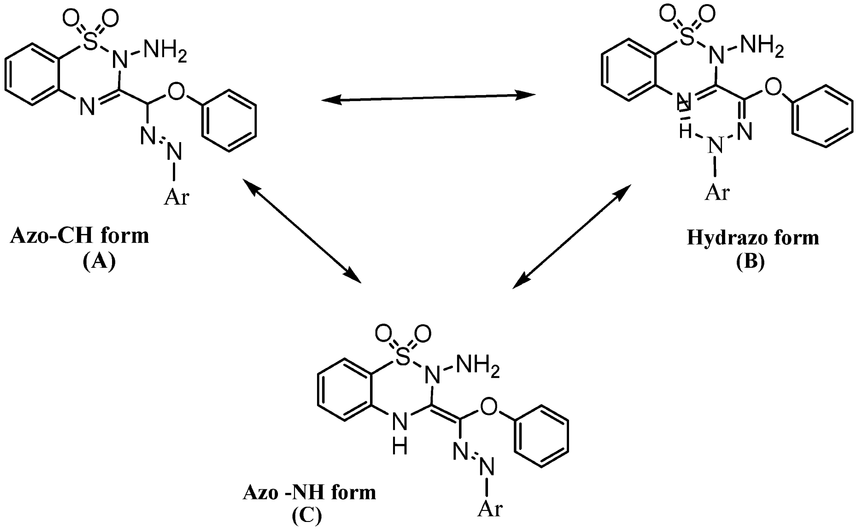
On the basis of the information obtained from the study of IR spectrum of 2-amino-3-phenoxymethyl-1, 2,4-benzothiadiazine 1,1-dioxide III, it is possible to assign absorption bands of the diazonium coupling products IVa–g with some confidence. Each of the compounds examined exhibits a strong band in the region of 1608–1605 cm^{-1}, which is assigned to the skeletal C=C in plane vibrations of phenyl rings.[10] The broad and strong absorptions near 1350 and 1140 cm^{-1} were ascribed



(III)



(IVa-g)



SCHEME 2 Tautotomeric structures of compounds IVa–g.

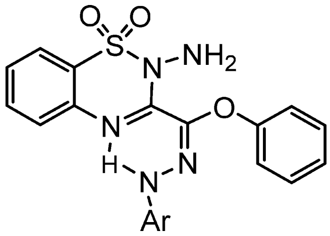


TABLE I 2-Amino-3-[α-(p-Arylhydrazono)phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide Derivatives $(IV)_{a-g}$

No. (IV)	Ar	Molecular formula (M.wt)	M.P. °C (yield %)	Calculated/found (%) C	H	N	S	Cl	Br
a	4-Nitrophenyl	$C_{20}H_{16}N_6O_5S$	246–248	53.09	3.56	18.57	7.09	—	—
		(452.44)	(61)	53.04	3.22	18.71	6.99	—	—
b	4-Methoxyphenyl	$C_{21}H_{19}N_5O_4S$	231–232	57.66	4.38	16.01	7.33	—	—
		(437.47)	(64)	57.70	4.18	16.05	7.21	—	—
c	4-Tolyl	$C_{21}H_{19}N_5O_3S$	202–204	59.84	4.54	16.62	7.61	—	—
		(421.47)	(62)	59.69	4.48	16.53	7.59	—	—
d	Phenyl	$C_{20}H_{17}N_5O_3S$	186–188	58.96	4.21	17.19	7.87	—	—
		(407.45)	(60)	59.01	4.16	17.18	7.49	—	—
e	3-Chlorophenyl	$C_{20}H_{16}ClN_5O_3S$	203–204	54.36	3.65	15.85	7.26	8.02	—
		(441.89)	(63)	54.60	3.41	15.91	7.28	8.14	—
f	4-Bromophenyl	$C_{20}H_{16}BrN_5O_3S$	193–194	49.39	3.32	14.40	6.59	—	16.43
		(486.34)	(61)	49.42	3.50	14.33	6.86	—	16.53
g	4-Carbethoxyphenyl	$C_{23}H_{21}N_5O_5S$	142–144	57.61	4.41	14.61	6.69	—	—
		(479.51)	(64)	57.70	4.29	14.67	6.52	—	—

to the asymmetric and symmetric stretching vibrations of the cyclic sulphonamide function.

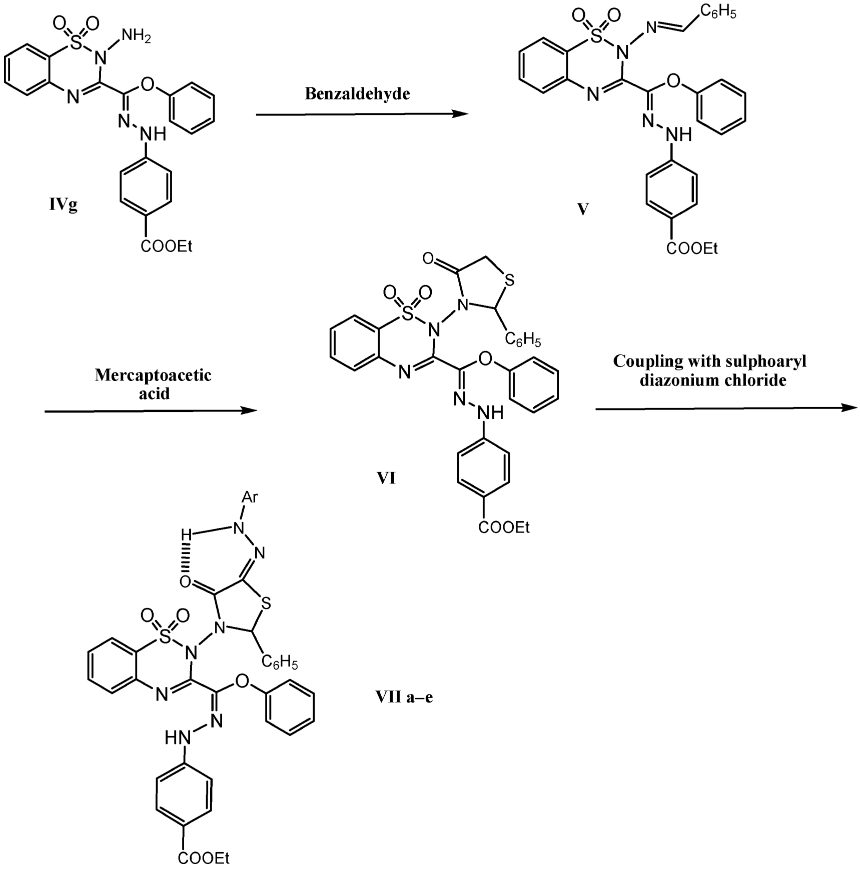
The parent amino thiadiazine derivative III was found to exhibit a moderate absorption near 1625 cm^{-1} corresponding to the endocyclic C=N stretching vibration. As to the coupling products IVa–g, each dye revealed two absorption bands of moderate intensity near 1625 and 1615 cm^{-1} that were assigned to the two C=N stretching vibrations.

Besides the asymmetric and symmetric stretching vibrations of the amino function, which were displayed in the range 3360–3340 cm^{-1} in IR spectra of these products, each spectrum revealed the presence of a very weak and broad band in the region between 3320 and 3310 cm^{-1}. This might be ascribed to the NH stretching vibration of the hydrazone moieties. The large shift and broadening of this band, as compared with those reported by Ramirz and Kerby[11] for simple hydrazones, can result only from strong intramolecular hydrogen bonding as in structure (B). The fact that compounds IVa–g show evidence for intramolecular hydrogen bonding at all is in favor of the hydrazone structure.

The lack of any stretching vibrations assignable to the —N=N— azo function in IR spectra of these products adds a further confirmation for the exclusion of A and C structures from the actual presentation of these coupling products.

^{1}H-NMR spectra of IV_g, as a typical example for this series of compounds, indicated its presence in the aryl hydrazono form rather than in the azo form. Thus, if the azo form (IV-A), which contains a CH group, was to represent the actual structure of these coupling products, the spectrum should exhibit a peak position at about 4.00 ppm that is similar to that of the methylene proton of the corresponding parent benzothiadiazine III. Such a peak is actually absent. Moreover, besides the triplet and quartet proton signals for the methylene and methyl protons of the ester function at $\delta = 3.92$ and 1.65 ppm respectively, the spectrum revealed a multiplet centered at 7.95–6.82 ppm and two other small, broad, and exchangeable humps near $\delta = 4.96$ and 12.95 ppm. These data are consistent with the amino hydrazone structure (IV-B). The multiplet absorption in the region 7.95–6.82 ppm is undoubtedly due to the aromatic protons. The peak at $\delta = 12.95$ ppm indicates the presence of a highly deshielded proton, which could be assigned to an intramolecularly hydrogen-bonded acidic proton. Since the shifts of the hydrogen-bonded NH proton usually occur near 13.0 ppm,[12] the peak can be reasonably assigned to the NH proton of the hydrazone moiety. On the basis of these visualizations, the broad signal at 4.96 ppm undoubtedly represents the two-proton signal of the amino function. The lack of any sp^3 doublet signal in the off-resonance ^{13}C NMR spectral pattern of this product adds further support for the exclusion of structure (IV-A) from the actual presentation of these coupling products. The presence of a characteristic signal for the p-carbethoxy anilinium cation in mass spectrum of this product (cf. Experimental section) highly confirms the exclusion of the azo-NH form (IV-C) and substantiates the presence of these products in the aryl hydrazono form (IV-B). These visualizations are in accordance with the assigned structure for these products.

The presence of a latent amino function in the structure of these arylhydrazono dyes prompted us to utilize these products as a precursor for synthesizing a new group of disarylazo dyestuffs, as illustrated in Scheme 5. Thus, the treatment of a base-catalyzed ethanolic solution of the hitherto synthesized dye IVg, as an example for the series of the parent compounds IV, with benzaldehyde furnished the corresponding benzylidine derivative V in a moderate yield (Scheme 3).



SCHEME 3

^{1}H NMR spectra of the latter product revealed the absence of the N-amino proton signal and the presence of a new singlet signal at 8.40 ppm assignable to the azo-methine proton.

The produced benzylidine derivative V reacted smoothly with mercapto acetic acid in the presence of a few drops of piperidine to afford the corresponding thiazolidinone derivative VI. The IR spectrum of the latter product exhibited characteristic absorptions that are in accordance with the assigned structure. Beside the ester and aromatic proton signals, the ^{1}H NMR spectrum of this product revealed two singlet signals at 5.65 and 3.10 ppm and a broad exchangeable hump at 12.90 ppm corresponding to the methine, methylene (of thiazolone moiety), and hydrazono NH protons, respectively. The relatively low chemical shift value for the C-5 mrthylene protons might be attributed to the anisotropic effect of the juxtaposed carbonyl function.

A coupling of an ethanolic buffered solution of the hitherto prepared thiazolone derivatives VI with different sulphoaryl diazonium salt solutions yielded the target disaryl azo dyestuffs $(\mathrm{VII})_{\mathrm{a-g}}$ in an average good yield (Scheme 3).

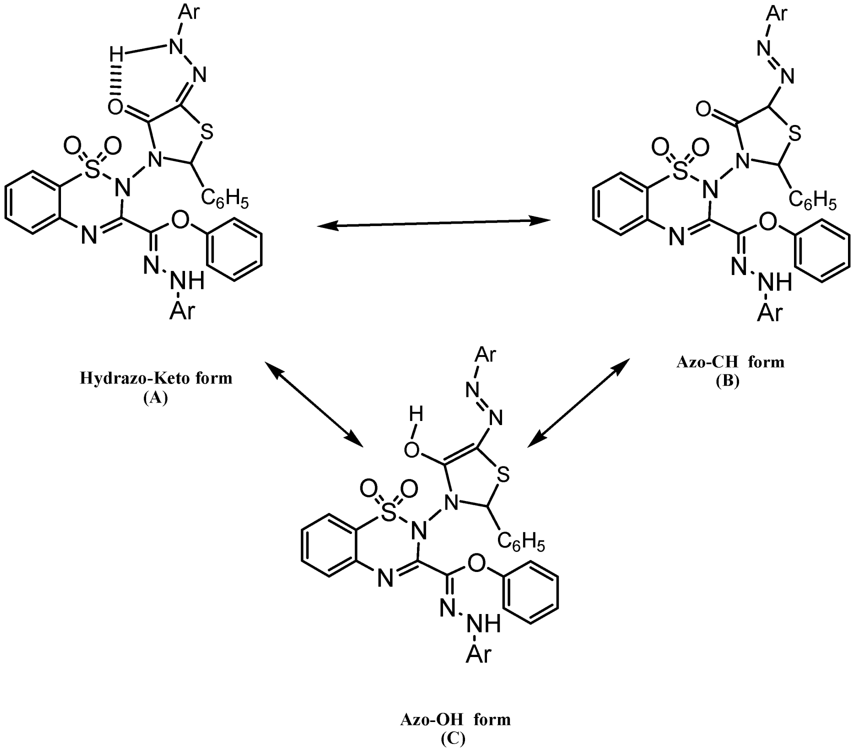
In a similar behavior to compounds $(\mathrm{IV})_{\mathrm{a-g}}$, the produced coupling products $(\mathrm{VII})_{\mathrm{a-g}}$ might be represented by three tautomeric forms as illustrated in Scheme 4.

IR spectra of these products revealed characteristic absorption bands at 3420 cm^{-1} (OH), 3320 cm^{-1} (NH), 1730 cm^{-1} (ester function), 1675 cm^{-1} (tertiary amidic carbonyl), and 1630 and 1625 cm^{-1}(exo and endo C=N functions). The ^{1}H-NMR spectrum of compound VIId, as a representative example for these products, revealed a singlet signal at 5.66 ppm (C-2 proton of the imino-thiazolone moiety) and two broad exchangeable humps near 13.55 and 12.90 ppm assignable to the NH protons of the two hydrazone moieties.

The lack of any characteristic absorption corresponding to the —N—N— azo linkage, as required by structures (B) & (C), in IR spectra of these products highly substantiates the exclusion of the latter two forms, and in turn, confirms the presence of these products in the disaryl hydrazono form (A). Further proof for the exclusion of structure (B) was drawn from ^{1}H-NMR of these coupling products that revealed the absence of any singlet signal corresponding to the C-5 proton, as required by this azo-CH tautomeric structure (B).

Judging from these spectral data, it is not unreasonable to assign the disaryl hydrazono form (A) for the actual structure of these coupling products. Physical properties of these coupling products are given in Table II.

An investigation was also extended in this study to explore the synthetic potentiality of the latent active functions in the parent



SCHEME 4 Tautotomeric structures of compounds IVa–g.

compounds $(IV)_{a-g}$. Thus, the treatment of an ethanolic solution of the hitherto synthesized dye IVc with phenyl isothiocyanate afforded the corresponding thiourea derivative VIII in a good yield. Aside from the correct elemental analysis, spectral patterns of the latter product came in accordance with the assigned structure (cf. Experimental section).

Cyclization of the latter product with chloroacetic acid furnished the corresponding imino thiazolidinone derivative IX.

The formation of the imino-thiazolone derivative IX from the corresponding thiourea derivative VIII was established by elemental and spectral data where IR spectral data of the latter product IX revealed the presence of a new strong absorption band at 1680 cm^{-1} assignable to the tertiary amidic carbonyl function. Further confirmation for the structure of this product was obtained from its straightforward ^1H-NMR spectrum, which displayed a characteristic singlet signal at 3.16 ppm for the methylene protons of the thiazolone moiety.

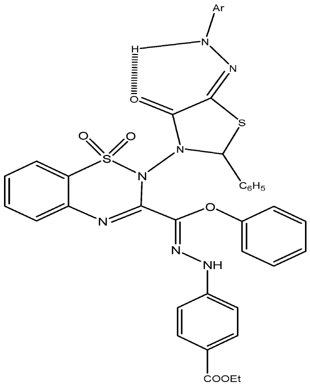


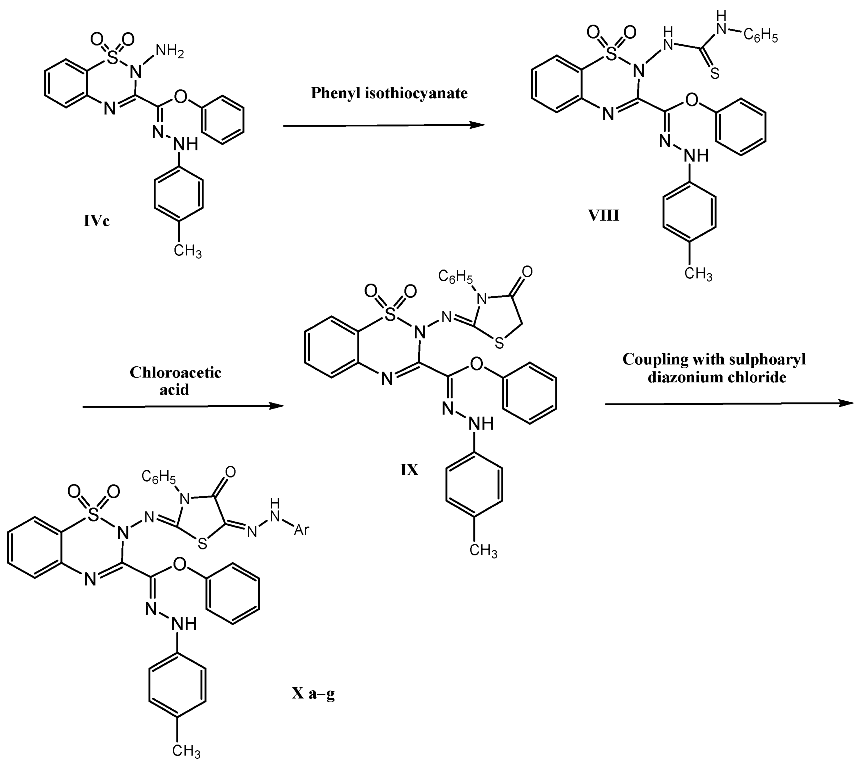
TABLE II 2-(4′-Oxo-3′-phenyl-5′-sulphoarylhydrazono-1′, 3′-thiazol-3′-yl)-3-[α-(p-carbethoxyphenylhydrazono)phenoxymethyl]- 1,2,4-benzothiadiazine 1,1-Dioxide Derivatives (VII)$_{a-e}$

	Ar	Molecular formula (M.wt)	M.P. °C (yield %)	Calculated/found (%) C	H	N	S	Cl
a	4-Sulphophenyl	$C_{38}H_{31}N_7O_9S_3$	179–180	55.26	3.78	11.87	11.65	—
		(825.89)	(73)	55.73	4.11	11.78	11.62	—
b	2-Carboxy-4-sulphophenyl	$C_{39}H_{31}N_7O_{11}S_3$	218	53.85	3.59	11.27	11.06	—
		(869.90)	(68)	54.11	3.82	11.18	10.95	—
c	2,5-Dichloro-4-sulphophenyl	$C_{38}H_{29}Cl_2N_7O_9S_3$	186–188	51.01	3.27	10.96	10.75	7.92
		(894.78)	(71)	50.91	3.16	11.08	10.91	7.81
d	6-Sulphonaphthyl	$C_{42}H_{33}N_7O_9S_3$	202–203	57.59	3.80	11.19	10.98	—
		(875.95)	(69)	57.93	4.14	11.30	10.82	
e	8-Sulphonaphthyl	$C_{42}H_{33}N_7O_9S_3$	226–227	57.96	3.80	11.16	10.91	—
		(875.95)	(72)	57.96	4.11	11.16	10.91	

The latter product was used, through coupling with a group of sulfur-containing arene diazonium salts, as a precursor for a second series of the disaryl azo dyestuffs (X). These coupling products were prepared by following the general procedure that was described for the preparation of sulphoaryl hydrazone derivatives $(IV)_{a-g}$.

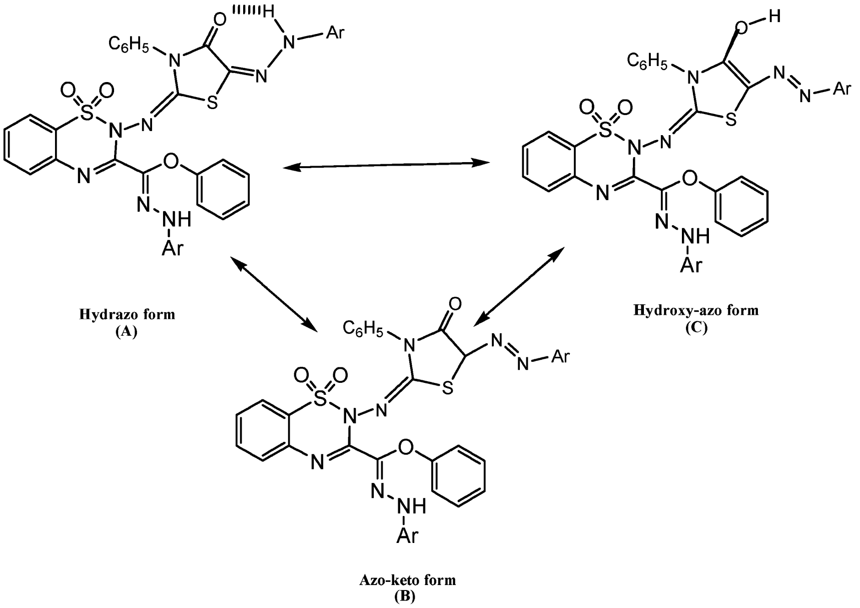
The crude products that were recrystallized from acetic acid yielded highly colored crystals of the pure dyestuffs $(VII)_{a-e}$ in an average yield of 68–73%. The prepared dyestuffs together with their physical data are given in Table II.

Thus, the treatment of the parent imino-thiazolone derivative IX with sulphoaryl diazonium salt in alkaline medium afforded the corresponding 5-sulphoarylazo derivatives $(X)_{a-e}$ (Scheme 5).



SCHEME 5

As in the case of aryl hydrazono derivatives $(VII)_{a-g}$, the produced coupling products $(X)_{a-g}$ might be represented by three tautomeric forms, as illustrated in Scheme 6. These tautomeric structures are



SCHEME 6 Tautotomeric structures of compounds Xa–g.

referred to as the keto-hydrazo form (A), the azo-keto form (B), and the hydroxyl-azo form (C).

In the present study, the predominant tautomeric structure of these compounds has been found to be the hydrazo form (A). The spectral evidence, upon which such a conclusion is based, is discussed in view of their spectral behavior.

In IR spectrum of each of the prepared dyestuffs $(X)_{a-e}$, a sharp and well-defined peak was found near 1670 ± 5 cm^{-1} assignable to the tert. amidic-carbonyl stretching vibrations. If the hydroxy-azo form was to represent the actual structure of these coupling products, one would expect the lack of such a strong absorption band. The presence of strong absorption in the range 1675–1665 cm^{1}, in their IR spectra, thus excludes the possibility of the hydroxy-azo structure of type (C).

Moreover, in the spectrum of each of the hitherto examined iminothiazolone dyestuffs, two other absorption bands were noted near 1630 and 1620 cm^{-1}. As these bands were observed in spectra of both of the N-phenyl N′-benzothiadiazinyl thiourea derivative (VIII) and the corresponding cyclized product (IX), it was plausible not to assign any of these two bands to an —N=N— azo stretching vibration but to the exo and endo azo-methine stretching vibrations, which are common in all the three series of compounds.

The great intensity of such two peaks might result from the azomethine being superimposed in a peak due to vibration. It is reasonable to conclude, therefore, that the hitherto prepared 4-sulphoaryl azo imino-thiazolidinone dyestuffs (Xa–e) predominantly exist in the keto-hydrazo form (A).

In view of the strong evidence against the presence of an absorption for the azo function (IR spectra) and C-5 proton signal of the imino-thiazolone moiety (^{1}H-NMR spectra), it would not be unreasonable to confirm the exclusion of structures (B) and (C) from presenting the actual structure of such coupling products. This elimination is compatible with the presence of absorption for the cyclic tert. amidic carbonyl function. In consequence, the tautomeric structure (A) of the hitherto prepared 5-sulphoaryl azo derivatives $(X)_{a-g}$, under investigation, is the only one that accommodates these IR spectral observations.

^{1}H-NMR spectra of compound X_a, as a representative example for these dyestuffs (in $CDCl_3$), showed the usual phenyl and methyl patterns at 8.05–6.85 and 2.41 ppm; three other broad peaks at 10.35, 12.90, and 13.50 ppm assignable to the acidic protons of the sulphonic acid; and the two intramolecularly hydrogen bonded NH protons, respectively. Judging from these results, it could be concluded that the diazonium coupling products (Xa–e) exist predominantly in keto-hydrazo form (A.) Table III depicts the physical data for these disaryl hydrazono dyestuffs.

Unlike other dyes that accommodate additional *o*-, sulphonic or carboxylic groups 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,[9] the hitherto synthesized highly colored products, being substituted with additional *p*-sulphonic acid groups, exhibited high substantivity, preliminary good light, and washing fastness and thus might fully satisfy all requirements for a satisfactory replacement of harmful benzidine-based dyes. A detailed study for the dyeing performance, all-round fastness properties, and evaluation of applying Fenton oxidation process (as an advanced oxidation technology) for decomposition and removal of the residual of these dyes from dyeing baths are, for the time being, under investigation and will be the subject of the forthcoming communication.

EXPERIMENTAL

All melting points are uncorrected and are measured on a Griffin & George MBF 010T apparatus. Recorded yields correspond to the pure

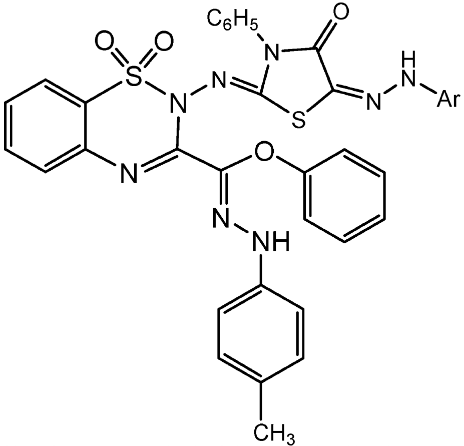


TABLE III 2-(4′-Oxo-3′-phenyl-5′-arylhydrazono-1′,3′-thiazol-2′-ylimino)-3-[α-(*p*-tolylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-Dioxide Derivatives $(\mathbf{X})_{\mathbf{a-e}}$

No. (X)	Ar	Molecular formula (M.wt)	M.P. °C (yield %)	Calculated/found (%)				
				C	H	N	S	Cl
a	4-Sulphophenyl	$C_{36}H_{28}N_8O_7S_3$	189–190	55.37	3.61	14.35	12.32	—
		780.85	(72)	54.98	3.81	13.99	11.86	
b	2-Carboxy-4-sulphophenyl	$C_{37}H_{28}N_8O_9S_3$	215–216	53.88	3.42	13.58	11.66	—
		824.86	(69)	53.52	3.76	13.97	11.46	
c	2,5-Dichloro-4-sulphophenyl	$C_{36}H_{26}Cl_2N_8O_7S_3$	241	50.88	3.08	13.19	11.32	8.34
		849.74	(70)	50.60	3.32	12.69	10.91	8.11
d	6-Sulphonaphthyl	$C_{40}H_{30}N_8O_7S_3$	213–214	57.82	3.64	13.49	11.58	—
		830.91	(61)	57.90	3.12	13.40	11.50	
e	8-Sulphonaphthyl	$C_{40}H_{30}N_8O_7S_3$	276	57.82	3.64	13.49	11.58	—
		830.91	(79)	58.12	3.91	13.12	11.31	

products. IR (KBr) spectra were recorded on a Perkin Elmer model 1750 FTIR. ^{1}H NMR 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 Units at Cairo University and National Research Center (NRC), Cairo, Egypt. Nomenclature of the hitherto prepared compounds are in line with the IUPAC rules for nomenclature of organic compounds.

Synthesis of 2-(2′-Phenoxyacetylamino)-benzenesulphonic Acid (I)

A mixture of phenoxychloroacetic acid (0.01 mol, 1.7 g) and phosphorous pentachloride (0.01 mol, 2.1 g) was triturated with orthanilic acid (0.01 mol, 3.1 g), and the whole mixture was allowed to be set aside at r.t. for 3 h; water was added to the reaction mixture, and concentrated sodium chloride solution (20 mL) was added to that mixture. The solution was allowed to cool spontaneously for 1 h in air and then was cooled in an ice bath until complete precipitation of the product. The produced solid was collected by filtration, washed with a little saturated sodium chloride solution, and dried at 80°C. Acidification of an aqueous solution of the produced salt afforded the free acid, which was filtered off, washed well with water, and recrystallized from ethanol to give the pure product of m.p. 218°C in a 65% yield.

For $C_{14}H_{13}NO_5S$ (307.32) calcd.: C, 54.71; H, 4.26; N, 4.56; S, 10.43%. Found: C, 54.22; H, 4.43; N, 4.85; S,10.74%. IR (ν/cm^{-1}): 3430 (OH), 3325 (NH), 1685 (CO), 1350 and 1140 (asym. and sym. stretching vibration of sulphonic acid moiety), and 1065 (ether linkage).

Synthesis of 3-Phenoxymethyl-2,1,4-benzoxathiazine 1,1-Dioxide (II)

A mixture of I (0.01 mol, 3.1 g) and acetic anhydride (0.05 mol, 5.1 mL) was refluxed under anhydrous conditions for 8 h. The excess acetic anhydride was distilled off under reduced pressure, and the whole mixture was cooled to r.t. Trituration of the residual material with water afforded a solid product that was filtered off and recrystallized from ethanol to give the pure product of m. p. 231°C in a 59% yield.

For $C_{14}H_{11}NO_4S$ (289.31) calcd.: C, 58.12; H, 3.83; N, 4.84; S, 11.08%; Found: C, 58.39; H, 3.96; N, 4.50; S, 11.32%. IR (ν/cm^{-1}) 1360 and 1155 (asym. and sym. stretching vibration of sulphonate ester function), 1630 (C=N), and 1065 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 8.10–6.80 (m, 9H, Ar-H) and 4.05 (s, 2H, $C\underline{H}_2$-O); ^{13}C-NMR spectrum (δ in ppm): 163.1 (C-3 of benzothiadiazine moiety), 159.2 (ipso-carbon of phenoxy function), 136.4 (C-8_a of benzothiadiazine moiety), 121.9 (C-4_a of benzothiadiazine moiety), and 79 (methylene-carbon of phenoxymethyl function), m/e (%): 289 (M^+, 78), 212 (33), 93 (80), and 77 (85).

Synthesis of 2-Amino-3-phenoxymethyl-1,2,4-benzothiadiazine 1,1-Dioxide (III)

A mixture of II (0.01 mol, 2.9 g), hydrazine hydrate (0.01 mol, 0.5 mL), and piperidine (0.3 mL) in absolute ethanol (10 mL) was refluxed for 4 h and left to cool to r.t. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure product of m. p. 189°C in a 43% yield.

For $C_{14}H_{13}N_3O_3S$ (303.34) calcd.: C, 55.43; H, 4.32; N, 13.85; S, 10.57%. Found: C,55.60; H, 4.21; N, 14.07; S, 10.18%. IR (ν/cm^{-1}): 3340, 3330 (NH_2), 1625 (C=N), 1350, 1145 (cyclic sulphonamide function), and 1065 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 8.10–6.80 (m, 9H, Ar-H), 4.90 (br., 2H, Amino function), and 4.05 (s, 2H, oxymethyl moiety).

Synthesis of 2-Amino-3-[(α-arylhydrazono)phenoxymethyl]-1,2,4-benzothiadiazine 1,1-Dioxide $(IV)_{a\text{-}g}$

General Procedure

The aromatic amine (0.005 mol) was dissolved in 3 mL of 6 M hydrochloric acid, and the whole solution was cooled below 5°C. To the resulting cold solution, 10 mL of 0.6 M sodium nitrite solution was added while keeping the temperature of the reaction mixture below 5°C. After the addition was complete, the solution was stirred for an additional 10 min. In a separate 250-mL beaker, the solution of the coupling component was prepared by stirring compound III (0.005 mol, 1.5 g) with 50 mL of 0.3 N aqueous sodium hydroxide solution, to which 2 g of sodium acetate trihydrate was added. A few drops of ethanol were added to ensure complete dissolution of the entire coupling component. The resulting solution was cooled in an ice-salt bath and mechanically stirred. To the cold solution of (III), the diazonium salt solution was added dropwise while stirring and keeping the temperature below 5°C during the addition, which took about 15 min. The reaction mixture was left overnight in a refrigerator, and the precipitated colored product was filtered off, washed three times with water, and recrystallized from glacial acetic acid. Physical data of the synthesized arylazo dyestuffs are listed in Table I.

IR (ν/cm^{-1}) for (IVg): 3355 and 3340 (NH_2), 3320 (NH of hydrazone moiety), 1735 (ester function), 1605 (C=C), 1625 and 1615 (C=N), 1350 and 1140 (cyclic sulphonamide function), and 1065 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 12.95 (br., 1H, hydrazone moiety), 7.95–6.82 (m, 13H, Ar-H), 4.96 (br, 2H, amino protons), 3.92 (q, 2H, O-C$\underline{H}_2$-CH3), and 1.65 (t, 3H, O-CH_2-C$\underline{H}_3$); ^{13}C-NMR spectrum (δ in ppm): 168.3 (carbonyl-carbon of ester function), 161.8 (C-3 of benzothiadiazine moiety), 154.2 (ipso carbon of phenoxy function), 152.8 (oxymethyl-carbon), 137.3 (C-8_a of benzothiadiazine moiety), 124.9 (C-4_a of benzothiadiazine moiety), 61.4 (methylene-carbon in ester function), and 16.7 (methyl-carbon in ester function). M/e (%): 479 (M^+, 86), 402 (46), 164 (93), 93 (79), and 77 (42).

Synthesis of 2-Benzylidinamino-3-[α-(p-carbethoxyphenylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-Dioxide (V)

A mixture of IVg (0.01 mol, 4.8 g), benzaldehyde (0.01 mol, 1 mL), and piperidine (0.3 mL) in absolute ethanol (10 mL) was refluxed under anhydrous conditions for 4 h and left to cool to r.t. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure product of m. p. 173°C in a 70% yield.

For $C_{30}H_{25}N_5O_5S$ (567.62) calcd.: C, 63.48; H, 4.44; N, 12.34; S, 5.65%. Found: C, 63.79; H, 4.84; N, 12.78; S, 5.98%. IR (ν/cm^{-1}): 3310 (NH), 1735 (ester function), 1630–1625 (C=N functions), 1350 and 1160 (cyclic sulphonamide function), and 1060 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 12.90 (br., 1H, hydrazone moiety), 8.40 CH=N—), 7.92–6.80 (18H, Ar-H) and 3.92 (q, 2H, O-C$\underline{H}_2$-CH_3), and 1.65 (t, 3H, O-CH_2-C$\underline{H}_3$).

Synthesis of 2-(4′-Oxo-2′-phenyl-1′, 3′-thiazol-3′-yl)-3-[α-(p-carbethoxy-phenylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-Dioxide (VI)

A mixture of V (0.01 mol, 5.7 g), mercaptoacetic 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 r.t. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure product of m. p. 166°C in a 61% yield.

For $C_{32}H_{27}N_5O_6S_2$ (641.72) calcd.: C, 59.89; H, 4.24; N, 10.91; S, 9.99%. Found: C, 59.80; H, 4.03; N, 10.70; S, 9.89%. IR (ν/cm^{-1}) for (IV): 3315 (NH), 1735 (ester function), 1630 and 1625 (C=N functions), 1350 and 1160 (cyclic sulphonamide function), and 1060 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 12.90 (br., 1H, hydrazone moiety), 7.95–6.75 (m, 18H, Ar-H), 5.65 (s, 1H, C-2 proton of thiazolone moiety), 3.92 (q, 2H, $O\text{-}C\underline{H}_2\text{-}CH_3$), 1.70 (t, 3H, $O\text{-}CH_2\text{-}C\underline{H}_3$))and 3.10 (s, 2H, methylene protons of thiazolone moiety).

Synthesis of 2-(4′-Oxo-2′-phenyl-5′-sulphoarylhydrazono-1′,3′-thiazol-3′-yl)-3-[α-(p-carbethoxyphenylhydrazono)-phenoxymethyl]-1,2,4-benzo-thiadiazine 1,1-Dioxide (VII)$_{a-e}$

General Procedure

In a 250-mL conical flask, 0.005 mol 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, a solution of sodium nitrite (0.052 mol, 3.6 g) in water (10 mL) was added. The resulting solution was slowly added with 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 stirred for 15 min, where the fine crystals of a diazo component were soon separated. The suspension was kept in an ice bath for a further 10 min and poured with stirring to a solution of VI (0.005 mol, 3.2 g) in a cold 10% sodium hydroxide solution (50 mL), and the whole mixture was cooled to 0–3°C. Coupling readily took place, and the dyestuff separated as a paste. The whole mixture was stirred well for 10 min and warmed until the paste dissolved completely; 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 (VII)$_{a-e}$ in an average yield of 68–73%. The prepared dyestuffs together with their physical data are depicted in Table II.

IR (ν/cm^{-1}) for VII$_d$: 3420 (OH), 3320(NH), 1730 (ester function), 1675(tert. amidic CO), 1630–1625 (C=N functions), 1370, 1360, 1160 and 1140 (sulphonic acid and cyclic sulphonamide moieties), and 1065 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 13.55 and 12.90 (br., 2H, hydrazone moieties), 10.45 (br., 1H, OH), 8.00–6.80 (m, 24H, Ar-H), 5.66 (s, 1H, C-2 proton of thiazolone moiety), 3.96 (q, 2H, O-C$\underline{H}_2$-CH$_3$), and 1.70 (t, 3H, O-CH$_2$-C$\underline{H}_3$).

Synthesis of N-Phenyl-[1′, 1′-dioxo-3′-[α-(p-tolylhydrazono)phenoxy-methyl]-1′,2′,4′-benzothiadiazin-2′-yl] Thiourea (VIII)

A mixture of IV$_c$ (0.01 mol, 4.2 g), phenylisothiocyanate (0.01 mol, 1.4 mL), and piperidine (0.3 mL) in absolute ethanol (10 mL) was refluxed under anhydrous conditions for 4 h and left to cool to r.t. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure product of m. p. 196°C in a 48% yield.

For $C_{28}H_{24}N_6O_3S_2$ (556.66) calcd.: C, 60.41; H, 4.35; N, 15.10; S, 11.52%. Found: C, 60.43; H, 4.70; N, 14.95; S, 11.38%. IR (ν/cm^{-1}) for (VIII): 3315–3305 (NH), 1630–1620 (C=N functions), 1360 and 1160 (cyclic sulphonamide function), and 1060 (ether linkage). M/e (%): 556 (M$^+$, 63), 151 (66), 106 (89), 93 (59), and 77 (94).

Synthesis of 2-(4′-Oxo-3′-phenyl-1′,3′ -thiazol-2′-ylimino)-3-[α-(p-tolyl-hydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-Dioxide (IX)

A mixture of VIII (0.01 mol), 5.6 g chloroacetic acid (0.01 mol, 0.95 g), and piperidine (0.3 mL) in absolute ethanol (10 mL) was refluxed under anhydrous conditions for 4 h and left to cool to r.t. The resulting solid that formed after cooling was filtered off and recrystallized from ethanol to give the pure product of m. p. 213°C in a 53% yield.

For $C_{30}H_{24}N_6O_4S_2$ (596.68) calcd.: C, 60.39; H, 4.05; N, 14.08; S, 10.75. Found: C, 60.13; H, 4.12; N, 13.89; S, 10.41%. IR (ν/cm^{-1}) for (IX): 3315 (NH), 1680 (amidic CO), 1630 and 1615 (C=N functions), 1360 and 1165 (cyclic sulphonamide function), and 1060 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 1295 (br., 1H, NH), 8.05–6.70 (m, 18H, Ar-H), 3.16 (s, 2H, methylene protons of thiazolone moiety), and 2.38 (s, 3H, methyl protons).

Synthesis of 2-(4′-Oxo-3′-phenyl-5′-arylhydrazono-1′,3′-thiazol-2′-yl-imino)-3-[α-(p-tolyl-hydrazono)-phenoxymethyl]-1,2,4-benzothia-diazine 1,1-Dioxide Derivatives $(X)_{a-e}$

These coupling products were prepared by following the general procedure that was described for preparation of sulphoaryl hydrazone derivatives $(VII)_{a-e}$.

The crude products were recrystallized from acetic acid to give highly colored crystals of the pure dyestuffs $(X)_{a-e}$ in an average yield of 61–79%. The prepared dyestuffs together with their physical data are given in Table III.

IR (ν/cm^{-1}) for (Xa): 3425(OH), 3315(NH), 1670 (amidic CO), 1630 and 1620 (C=N functions), 1360, 1345, 1165 and 1150 (sulphonic acid and cyclic sulphonamide functions), and 1065 (ether linkage). ^{1}H-NMR spectrum (δ in ppm): 13.50 and 12.90 (br., 2H, NH of hydrazone moiety), 10.35 (br., 1H, OH), 8.05–6.85 (m, 22H, Ar-H), and 2.41 (s, 3H, methyl protons).

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