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Novel symmetrical and asymmetrical disaryl hydrazono sulphur-containing direct dyes as possible alternatives for benzidine-based dyestuffs

Mokhtar A. Hanna [a,*], Ahmed A. Al-Sarawy [b], Ibrahim G. Rashed [b], Farouk K.M. Wali [a]

[a] *Damietta Faculty of Science, Mansoura University, P.O. Box 48, 35516 Mansoura, Egypt*
[b] *Mansoura Faculty of Engineering, Mansoura University, P.O. Box 48 , 35516 Mansoura, Egypt*

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Abstract

Two novel series of disaryl azo 2-(thiadiazin-2-yl)-1,2,4-benzothiadiazine-based direct dyes have been synthesized. The produced dyes, being accommodating solubilizing functions, are likely to undergo oxidation and/or hydrolysis to soluble metabolites thus ensure lack of carcinogenicity and in turn, might satisfy the basic requirements for a satisfactory replacement of the prohibited benzidine-based dyes.

The assigned structures for the hitherto prepared dyes were confirmed on the basis of elemental analysis and spectral data and, whenever possible, by alternative synthetic routes. Moreover, the predominant tautomeric forms for these highly colored dyes were tested and discussed on the basis of different spectral investigations.

Keywords: Benzidine dye alternatives; Sulphur-containing heterocyclic dyestuffs; 1,2,4-Benzothiadiazine-based dyes; Symmetrical and asymmetrical disaryl hydrazono direct dyestuffs; Predominant tautomeric structures

1. Introduction

The production and use of disaryl azo benzidine-based dyes have 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 dyes for dyeing purposes, and the second approach involves the use of other diamines, i.e., diaminostilbene disulphonic acid [1] and diaminodiphenylaminesulphonic acid [2] in the dye synthesis. The first solution does not usually ensure obtaining all the hues possible from disaryl azo benzidine-based dyestuffs; it is more expensive, and often requires 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 pollution of the environment.

In the latter diamine-based dyestuffs, the azo functions are directly linked to aromatic nuclei and 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 of these disaryl azo dyestuffs are non-biodegradable and their breakdown products are toxic and/or exhibit mutagenic effects [3–5].

In continuation of our interest [6–11] in synthesizing new mono and/or disaryl azo dyestuffs, we report herein on the synthesis of a novel group of mono and disaryl azo dyestuffs that are based on the 1,2,4-benzothiadiazine 1,1-dioxide moiety. The produced dyes, having their azo function attached to aliphatic side chain and accommodating solubilizing functions (sulphonic and sulphonamide moieties), are likely to undergo

* Corresponding author.
E-mail address: mokhtarah@myway.com (M.A. Hanna).

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simple oxidation and/or hydrolysis to soluble metabolites, thus ensure lack of carcinogenicity [2] and in turn satisfy the basic requirements for a satisfactory replacement of the prohibited benzidine-based dyes.

2. Results and discussion

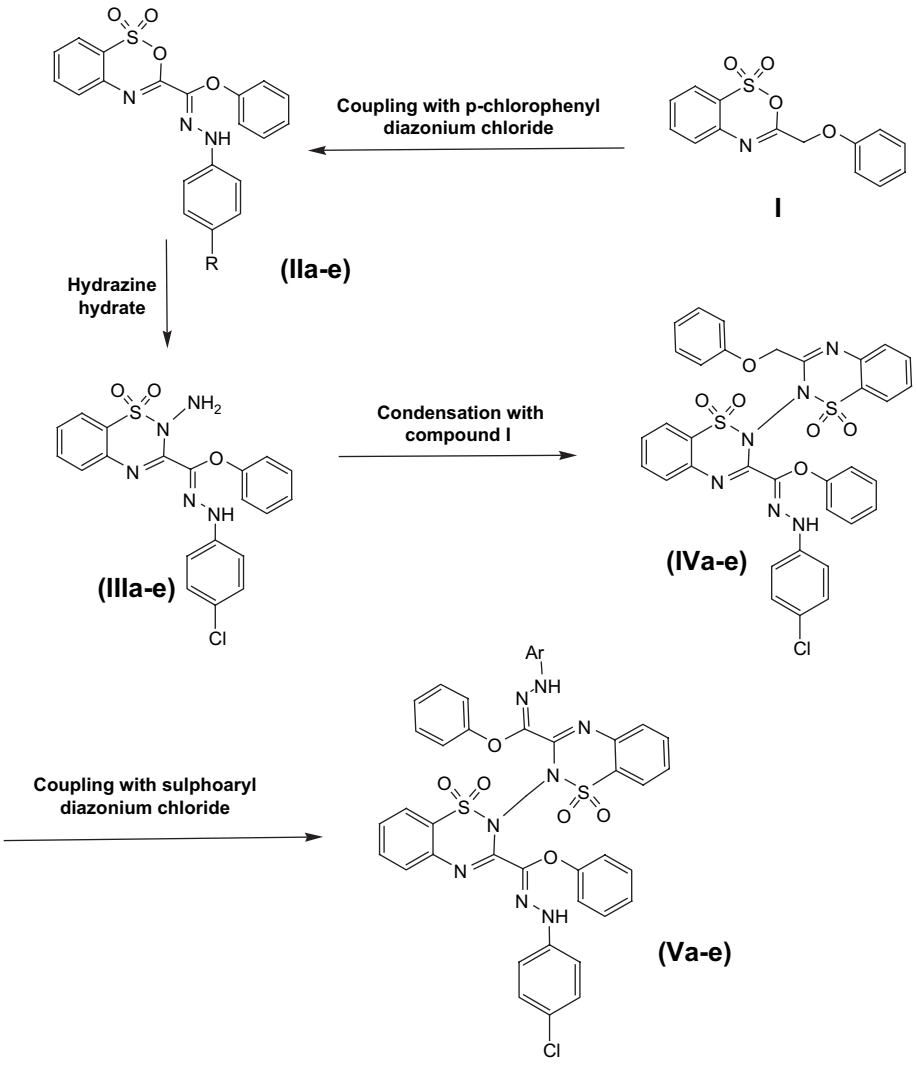
Perusal in literature revealed that doubling of chromophoric moieties in molecular structure of aryl azo dyestuffs highly enhances fastness properties of these dyes [2,10–13]. In view of these findings and in continuation of a research program directed for the synthesis of new categories of mono and disaryl azo heterocyclic dyestuffs, which might overcome the disadvantages of the benzidine-based disaryl azo dyes, it becomes worthy to evaluate the synthetic potentiality of the parent 3-phenoxymethyl-2,1,4-benzoxathiazine derivative (**I**) [14] for preparation of such dyes. Plan for synthesis of the first series of the target coupling products (**Va–o**) involved a prior preparation of the coupling products 3-[α-(aryl-hydrazono)-phenoxymethyl]-2,1,4-benzoxathiazine 1,1-dioxide (**IIa–c**) as illustrated in Scheme 1.

Structure of these products was established on the basis of elemental as well as spectral data (Section 4). Table 1 depicts the characteristic physical properties of these benzoxathiazine-based arylazo dyes.

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

These structures are referred to as the azo–CH form (**II-A**), the hydrazo form (**II-B**) and the azo–NH form (**II-C**). The available data indicated that the predominant tautomeric structure of **IIa–e** derivatives is the chelated hydrazono form (**II-B**).

On the basis of the information obtained from the study of IR spectrum of 3-phenoxymethyl-2,1,4-benzoxathiazine 1,1-dioxide (**I**), it is possible to assign the absorption bands of the diazonium coupling products **IIa–c** with some confidence. Each of the compounds examined, exhibits a strong band in the region of 1605 cm^{-1} which is assigned to the skeletal C=C in plane vibrations of phenyl rings [15]. The broad



Scheme 1.

Table 1
Physical data of compounds **II**, **III** and **IV**(**a**–**c**)

Compound no	R	Molecular formula (M.wt)	M.p./°C (yield/%)	Calcd/found (%)				
				C	H	N	S	Cl
IIa	*p*-Cl	$C_{20}H_{14}ClN_3O_4S$ (427.86)	212–214 (64)	56.14	3.30	9.82	7.49	8.29
				55.95	3.42	10.01	7.33	8.42
b	*m*-OMe	$C_{21}H_{17}N_3O_5S$ (423.44)	236–237 (59)	59.57	4.05	9.92	7.57	–
				59.64	4.12	9.83	7.76	
c	*m*-Me	$C_{21}H_{17}N_3O_4S$ (407.44)	251–253 (58)	61.90	4.21	10.31	7.87	–
				62.20	4.04	10.58	8.06	
IIIa	4-Cl	$C_{20}H_{16}ClN_5O_3S$ (441.89)	262–263 (52)	54.36	3.65	15.85	7.26	8.02
				54.43	3.70	15.96	7.43	8.19
b	*m*-OMe	$C_{21}H_{19}N_5O_4S$ (437.47)	278–279 (43)	57.66	4.38	16.01	7.33	–
				57.73	4.21	15.89	7.52	
c	*m*-Me	$C_{21}H_{19}N_5O_3S$ (421.47)	201–203 (56)	59.84	4.54	16.62	7.61	–
				60.01	4.23	16.94	7.33	
IVa	*p*-Cl	$C_{34}H_{25}ClN_6O_6S_2$ (713.18)	194–195 (66)	57.26	3.53	11.78	8.99	4.97
				57.40	3.61	11.85	9.07	5.14
b	*m*-OMe	$C_{35}H_{28}N_6O_7S_2$ (708.76)	243–245 (72)	59.31	3.98	11.86	9.05	–
				59.44	4.11	12.00	9.24	
c	*m*-Me	$C_{35}H_{28}BrN_6O_6S_2$ (692.76)	259–261 (70)	60.68	4.07	12.13	9.26	–
				60.74	4.37	12.32	9.40	

and strong absorptions near 1360 and 1145 cm^{-1} were ascribed to the asymmetric and symmetric stretching vibrations of the cyclic sulphonate ester function.

The parent benzoxathiazine derivative (**I**) was found to exhibit a moderate absorption near 1625 cm^{-1} corresponding to the endocyclic C=N stretching vibration. As to the coupling products **IIa**–**c**, each dye revealed two absorption bands of moderate intensity near 1625 and 1615 cm^{-1} that were assigned to its two C=N stretching vibrations.

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 Shawali et al. [16] for simple hydrazones, can result only from strong intramolecular hydrogen bonding as in structure **B**. The fact that compounds **IIa**–**c** show evidence for intramolecular hydrogen bonding, at all, is in favor of the hydrazone structure.

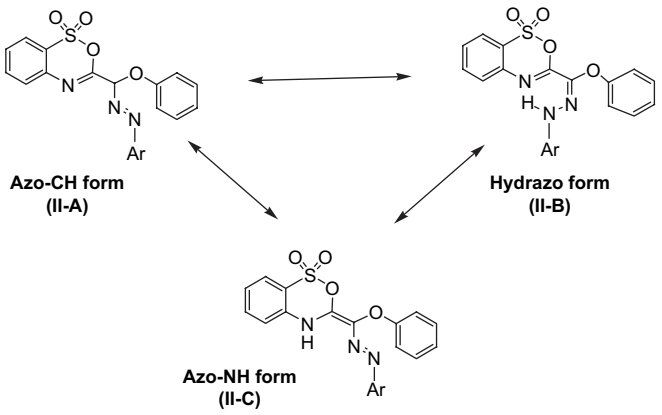


Chart 1. Tautotomeric structures of compounds **IIa**–**c**.

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 **IIa** as a typical example for this series of compounds, indicate its presence in the aryl hydrazono form rather than in the azo form. Thus, if the azo form (**II-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 benzoxathiazine **I**. Such a peak is actually absent. Moreover, the spectrum revealed a multiplet centered at 7.95–6.72 ppm and another small, broad and exchangeable hump near $\delta = 12.95$ ppm. These data are consistent with the hydrazone structure (**II-B**). The multiplet absorption in the region 7.95–6.72 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 [17], the peak can be reasonably assigned to the NH proton of the hydrazone moiety. On the basis of these visualizations, 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 **A** from the actual presentation of these coupling products. The presence of a characteristic signal for the *p*-chloro-anilinium cation in mass spectrum of this product (cf. Section 4) highly confirms the exclusion of the azo–NH form (**II-C**), and substantiates the presence of these products in the aryl hydrazono form (**II-B**). These visualizations are in accordance with the assigned structure for these products.

Subsequent reaction of the products (**IIa**–**c**) with hydrazine hydrate at the reflux temperature afforded the corresponding

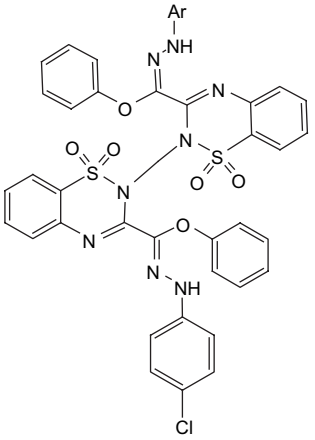
2-amino-3-[α-(arylhydrazono)-2-phenoxymethyl]-1,2,4-benzothiadiazine derivative (**IIIa–c**). Condensation of the latter products with **I** followed by coupling with sulphoaryl diazonium salt solutions furnished the target asymmetric disaryl azo dystuffs (**Va–o**) in an average good yield (Scheme 1).

Assignment of the disaryl hydrazono structure for the latter products based on IR spectrum of compound **Vk**, as a representative example for these products, revealed the absence of any absorption for the −N═N− azo linkage. The lack of any singlet signal corresponding to the two methylene protons, in ^{1}H NMR spectrum of **Vk**, and the presence of three broad exchangeable signals attributable to the three acidic protons of sulphonic and hydrazone moieties, add a strong support against the possible existence of these coupling products in the disaryl azo form and in turn confirm their presence in the corresponding hydrazo form. Further, confirmation for the predominant presence of these products in the disaryl hydrazono form was drawn from the straightforward off-resonance ^{13}C NMR spectral pattern of the same product that revealed the lack of any sp^3 doublet signals that might correspond to the −N═N−CH carbon atom of the possible azo form (cf. Section 4). Tables 2–4 depict the physical properties of these disaryl hydrazono dyestuffs.

Synthetic potentiality of the previously mentioned 3-phenoxymethyl-2,1,4-benzoxathiazine 1,1-dioxide derivative (**I**) was extended to include its use as a starting material in an alternative synthetic pathway for preparation of the latter products. Thus, prior preparation of compound **VI**, by coupling of ethanolic-buffered solution of 3-phenoxymethyl-2,1,4-benzoxathiazine 1,1-dioxide (**I**) with sulphophenyl diazonium chloride, and subsequent condensation of the product with the newly synthesized 2-amino-3-phenoxymethyl-1,2,4-benzothiadiazine 1,1-dioxide (**VII**) afforded the corresponding 2-[1′,1′-dioxo-3′-(phenoxymethyl)-benzothiadiazin-2′-yl]-3-[α-(4-sulphophenylhydrazono)phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide (**VIII**) in moderate yield. Coupling of the latter product with *p*-chlorobenzene diazonium chloride solution gave rise to the original disaryl azo dyestuff **Va** (Scheme 2) with no depression in m.p. or mixed m.p. when admixed with an authentic sample that was prepared according to Scheme 1.

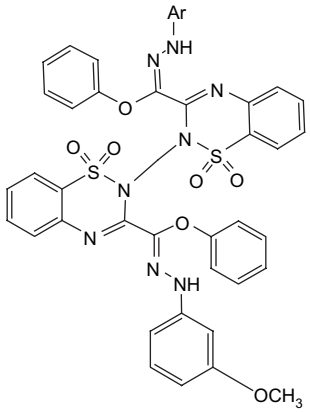
Further investigation for the synthetic potentiality of 3-phenoxymethyl-2,1,4-benzoxathiazine 1,1-dioxide derivative (**I**) in synthesis of a second group of symmetrical disaryl azo dyestuffs was achieved via prior preparation of the parent 2-[1′,1′-dioxo-3′-(phenoxymethyl)-benzothiadiazin-2′-yl]-3-phenoxymethyl-1,2,4-benzothiadiazine 1,1-dioxide (**IX**) and subsequent coupling of the latter product with different *p*-sulphoaryl diazonium salt solutions in slightly basic medium. Thus, mixing an ethanolic solution of **I** with 2-amino-3-phenoxymethyl-1,2,4-benzothiadiazine 1,1-dioxide (**VII**) in presence of a catalytic amount of piperidine, at the reflux temperature, yielded **IX**. Besides the correct elemental and spectral analysis (cf. Section 4), the assigned structure for the latter product was

Table 2
2-[1′,1′-Dioxo-3′-α′-(arylhydrazono)phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(*p*-chlorophenylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide derivatives (**Va–e**)



Compound no. (**V**)	Ar	Molecular formula (M.wt)	M.p./°C (yield/%)	Calcd/found (%)				
				C	H	N	S	Cl
a	4-Sulphophenyl	$C_{40}H_{29}ClN_8O_9S_3$ (897.36)	225–226 (65)	53.54	3.26	12.49	10.72	3.95
				53.32	3.73	12.72	10.69	3.61
b	2-Carboxy-4-sulphophenyl	$C_{41}H_{29}ClN_8O_{11}S_3$ (941.37)	234–235 (66)	52.31	3.11	11.90	10.22	3.77
				51.91	3.52	12.06	10.19	3.39
c	2,5-Dichloro-4-sulphophenyl	$C_{40}H_{27}Cl_3N_8O_9S_3$ (966.25)	286–288 (63)	49.72	2.82	11.60	9.96	11.01
				50.12	3.11	11.49	9.89	11.08
d	6-Sulphonaphthyl	$C_{44}H_{31}ClN_8O_9S_3$ (947.42)	266–267 (60)	55.78	3.30	11.83	10.15	3.74
				55.46	3.71	11.73	10.11	3.33
e	8-Sulphonaphthyl	$C_{44}H_{31}ClN_8O_9S_3$ (947.42)	>300 (61)	55.78	3.30	11.83	10.15	3.74
				56.10	3.50	11.96	10.46	3.32

Table 3
2-[1′,1′-Dioxo-3′-α′-(arylhydrazono)phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(*m*-methoxyphenylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide derivatives (**Vf–j**)



Compound no. (**V**)	Ar	Molecular formula (M.wt)	M.p./°C (yield/%)	Calcd/found (%)				
				C	H	N	S	Cl
f	4-Sulphophenyl	$C_{41}H_{32}N_8O_{10}S_3$ (892.94)	198–199 (55)	55.15	3.61	12.55	10.77	–
				55.34	3.52	12.74	11.01	
g	2-Carboxy-4-sulphophenyl	$C_{42}H_{32}N_8O_{12}S_3$ (936.94)	211–212 (61)	53.84	3.44	11.96	10.27	–
				54.06	3.29	12.33	10.56	
h	2,5-Dichloro-4-sulphophenyl	$C_{41}H_{30}Cl_2N_8O_{10}S_3$ (961.83)	264–265 (49)	51.20	3.14	11.65	10.00	7.37
				51.50	3.37	11.84	10.28	7.01
i	6-Sulphonaphthyl	$C_{45}H_{34}N_8O_{10}S_3$ (942.99)	258–260 (66)	57.32	3.63	11.88	10.20	–
				57.59	3.72	12.03	10.48	
j	8-Sulphonaphthyl	$C_{45}H_{34}N_8O_{10}S_3$ (942.99)	271–273 (51)	57.32	3.63	11.88	10.20	–
				57.56	3.79	12.12	10.03	

confirmed by an alternative synthetic route that involved the condensation of a basic ethanolic solution of the 2-phenoxmethyl-2,1,4-benzoxathiazine 1,1-dioxide (**I**) with hydrazine hydrate in 2:1 molar ratio at the reflux temperature. The product showed no depression in m.p. or mixed m.p. when admixed with an authentic sample that was prepared by the previous procedure, as described in Scheme 3.

Subsequent coupling of compound **IX** with ice-cold solutions of sulphoaryl diazonium chloride solutions afforded highly colored disaryl hydrazono dyestuffs (**Xa–e**) as illustrated in the same scheme.

The predominant presence of the produced dyestuffs **Xa–e** in the disaryl hydrazono form was confirmed from IR and ^{1}H NMR spectral data that revealed the presence of the hydrazono NH proton signals (^{1}H NMR spectra) and lack of any characteristic absorption ascribable to the –N=N– azo linkage (in their IR spectra), (cf. Section 4). Table 2 lists the physical data of the hitherto prepared dyestuffs.

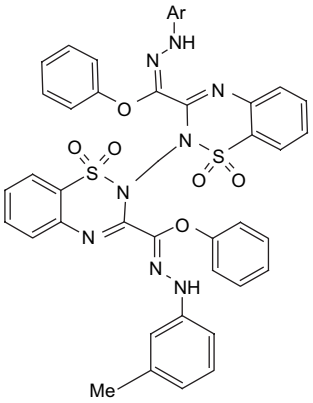
3. Conclusions

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 [2], 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 replacement of the harmful benzidine-based dyes. Detailed study for the dyeing performance, all-round fastness properties and evaluation of applying Fenton oxidation process [18] (as simple 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.

4. 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 FT-IR. ^{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 Micro-analytical Data Units at Cairo University and National Research Center (NRC), Cairo, Egypt. Nomenclature of the hitherto prepared dyestuffs is in line with IUPAC rules for nomenclature of organic compounds.

Table 4
2-[1′,1′-Dioxo-3′-α′-(arylhydrazono)phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(*m*-tolylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide derivatives (**Vk–o**)



Compound no. (**V**)	Ar	Molecular formula (M.wt)	M.p./°C (yield/%)	Calcd/found (%)				
				C	H	N	S	Cl
k	4-Sulphophenyl	$C_{41}H_{32}N_8O_9S_3$ (876.94)	269–270 (64)	56.15	3.68	12.78	10.97	–
				56.26	3.79	12.44	11.02	
l	2-Carboxy-4-sulphophenyl	$C_{42}H_{32}N_8O_{11}S_3$ (920.95)	167–169 (57)	54.78	3.50	12.17	10.45	–
				55.18	3.70	12.36	10.78	
m	2,5-Dichloro-4-sulphophenyl	$C_{41}H_{30}Cl_2N_8O_9S_3$ (945.83)	236–238 (61)	52.06	3.20	11.85	10.17	7.50
				52.32	3.47	11.53	9.96	7.88
n	6-Sulphonaphthyl	$C_{45}H_{34}N_8O_9S_3$ (926.99)	192–193 (58)	58.30	3.70	12.09	10.38	–
				58.44	3.54	11.89	10.00	
o	8-Sulphonaphthyl	$C_{45}H_{34}N_8O_9S_3$ (926.99)	177–178 (65)	58.30	3.70	12.09	10.38	–
				58.60	3.49	11.86	10.55	

*4.1. Synthesis of 3-[(α-arylhydrazono)phenoxymethyl]-2,1,4-benzoxathiazine 1,1-dioxide (**IIa–c**)*

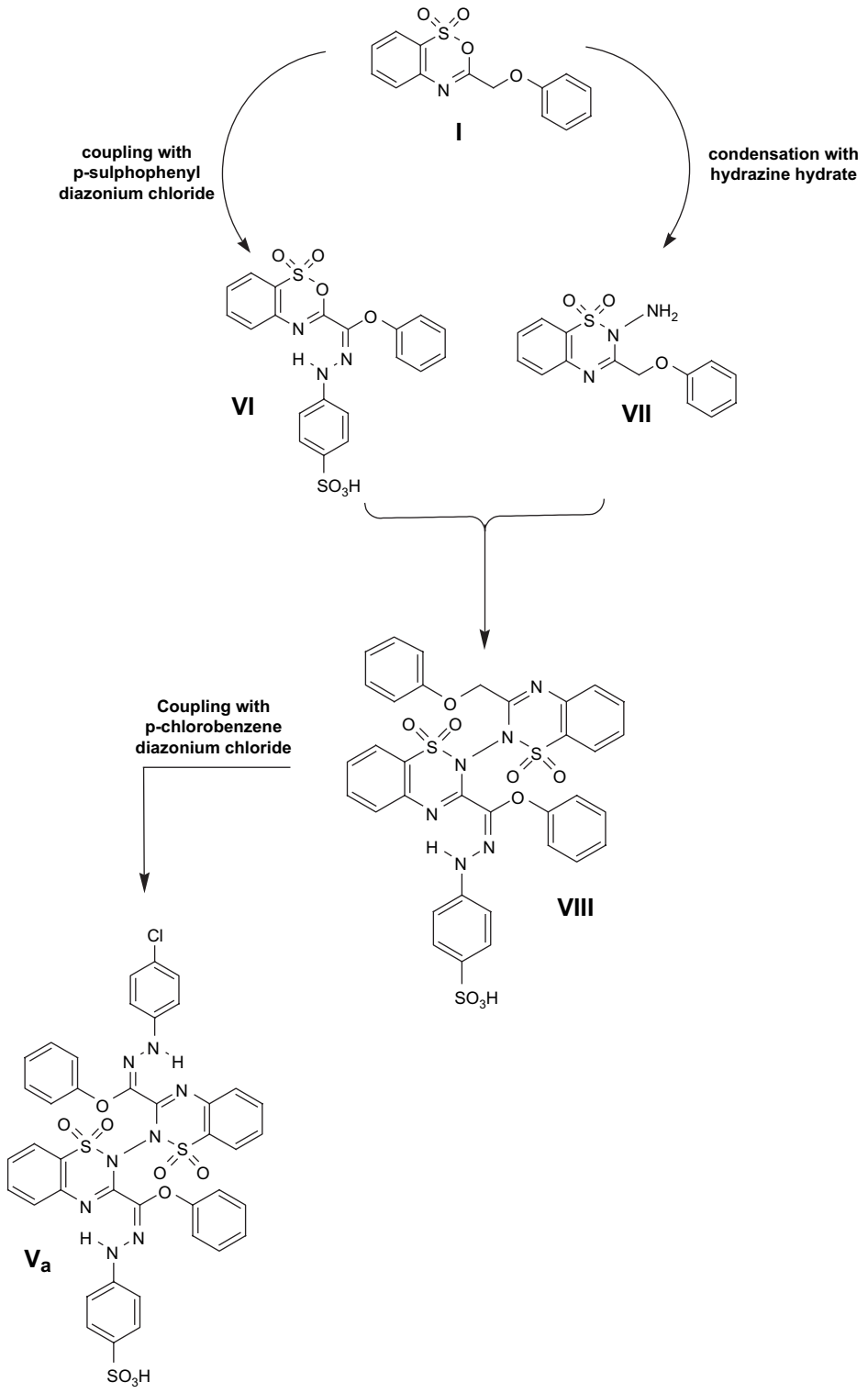
The aromatic amine (0.005 mol) was dissolved in 3 ml of 6 M hydrochloric acid, and the solution was cooled below 5 °C. To the resulting cold solution, 10 ml of 0.6 M sodium nitrite solution was added and the temperature of the mixture was kept below 5 °C during the addition. After complete addition, the solution was stirred for additional 10 min. In a 250 ml beaker, 0.005 mol (1.5 g), of **I** was stirred in 50 ml of 0.3 N aqueous sodium hydroxide solution, to which 2 g of sodium acetate trihydrate was added. Few drops of ethanol were added to ensure the complete dissolution of the entire solid materials. The resulting solution was cooled in an ice–salt bath and mechanically stirred. To the cold solution of **I**, the diazonium salt solution was added dropwise while stirring. The temperature was kept below 5 °C during the addition which took about 15 min and the whole reaction mixture was left overnight in a refrigerator. The precipitated colored products were filtered off, washed three times with water and recrystallized from glacial acetic acid to give the pure products in 58–64% yield. Physical data of these arylazo dyestuffs are listed in Table 1.

For **IIa**: IR ($\overline{\nu}$/cm^{-1}): 3310 (NH of hydrazone moiety), 1360 and 1145 (cyclic sulphonate function), 1625, 1615 (C=N), 1605 (C=C) and 1065 (ether linkage). ^{1}H NMR spectrum (δ in ppm): 12.90 (br, exchangeable, 1H, hydrazone moiety), 7.95–6.72 (m, 13H, Ar–H); ^{13}C NMR spectrum (δ in ppm): 161.3 (C-3 of benzothiadiazine moiety), 155.2 (α-carbon of phenoxy function), 153.7 (oxy methyl-carbon), 145.8 (β-carbon of *m*-methoxy phenyl function), 138.4 (C-8_a of benzothiadiazine moiety), 125.8 (α-carbon of *p*-chlorophenylhydrazone function), 122.6 (C-4_a of benzothiadiazine moiety); *m/e* (%): 423 (M^+, 73), 182 (62), 122 (91), 93 (47) and 77 (82).

*4.2. Synthesis of 2-amino-3-[(α-arylhydrazono)-phenoxymethyl]-2,1,4-benzoxathiadiazine 1,1-dioxide (**IIIa–c**)*

A mixture of **II** (0.01 mol in each case), 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 room temperature. The resulting solid material was filtered off and recrystallized from ethanol to give the pure products (**IIIa–c**) in 43–56% yield. Physical data of the prepared compounds are given in Table 1.

For **IIIa**: IR ($\overline{\nu}$/cm^{-1}): 3340, 3330 (NH_2), 1625, 1615 (C=N), 1605 (C=C), 1350, 1145 (cyclic sulphonamide function) and 1065 (ether linkage). ^{1}H NMR spectrum (δ in ppm): 13.00 (br, exchangeable, 1H, hydrazone moiety), 8.10–6.80 (m, 13H, Ar–H) and 4.90 (br, exchangeable, 2H, amino function).

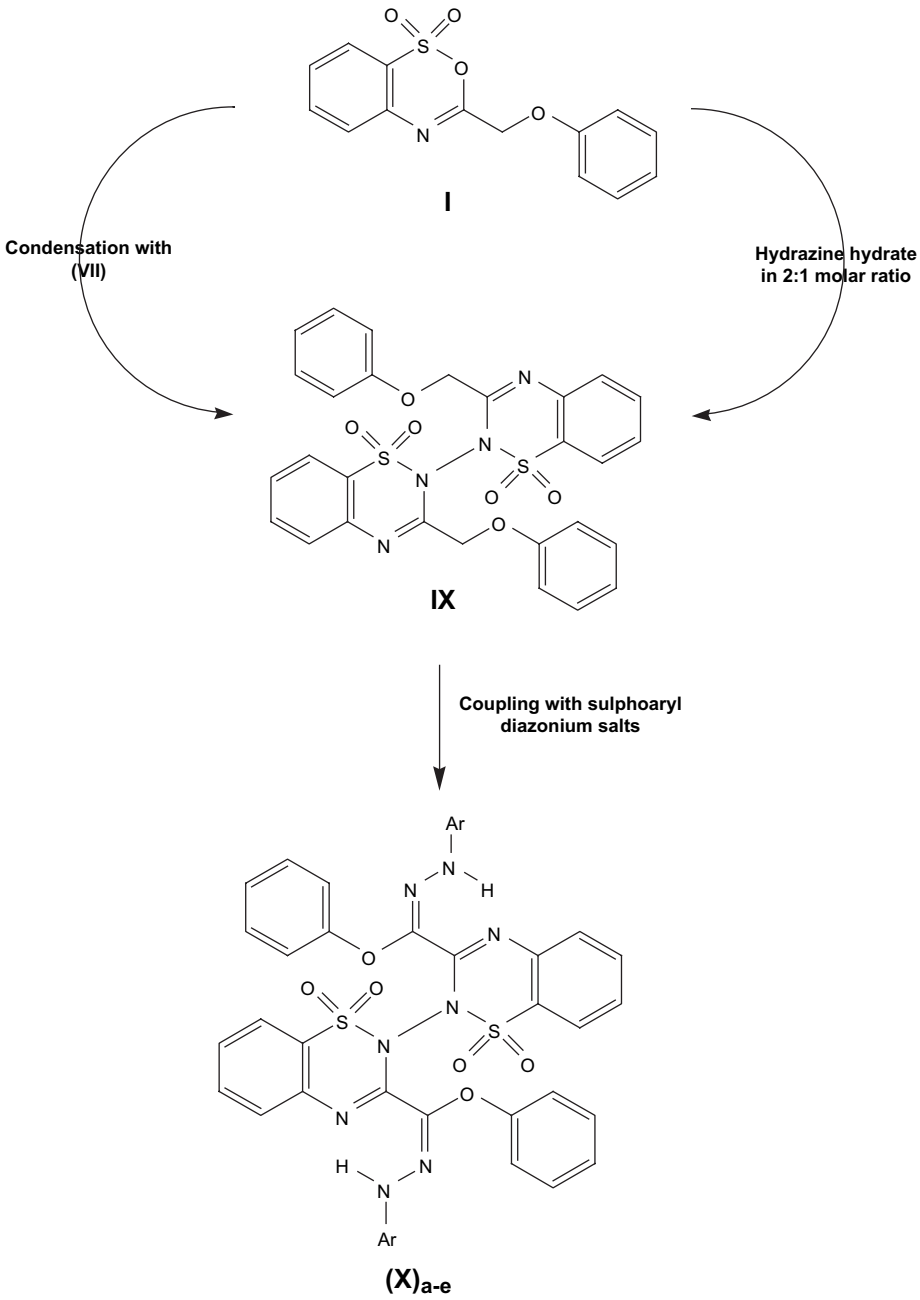


Scheme 2. A representative scheme for the alternative synthetic route of compound **Va**.

*4.3. Synthesis of 2-[1′,1′-dioxo-3′-phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(aryl-hydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide (**IVa–c**)*

A mixture of **III** (0.01 mol in each case), **I** (0.01 mol, 2.9 g) 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 precipitated solid was filtered off and recrystallized from ethanol or acetic acid to give the pure products in an average moderate yield. Physical properties are listed in Table 1.

For (**IVc**): IR ($\bar{\nu}$/cm^{-1}): 3315 (NH), 1630 and 1625 (C=N functions), 1605 (C=C), 1350 and 1145 (cyclic sulphonamide



Scheme 3.

function) and 1060 (ether linkage). ^{1}H NMR spectrum (δ in ppm): 12.95 (br, exchangeable, 2H, hydrazone moieties), 8.00–6.80 (m, 22H, Ar–H) and 4.05 (s, 2H, methylene protons), 2.2 (s, 3H, CH_3).

*4.4. Synthesis of 2-[1′,1′-dioxo-3′-(α′-arylhydrazono)-phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(arylhydrazono)phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide derivatives (**Va–e**)*

4.4.1. 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 which was then cooled to about 15 °C and a solution of sodium nitrite (0.052 mol, 3.6 g) in water (10 ml) was added. The solution was slowly added with stirring to a 600 ml beaker containing hydrochloric acid (12 ml, 30%) and crushed ice (100 g) and tested for the presence of slight excess nitrous acid. The whole mixture was kept stirred for a further 15 min where the fine crystals of diazo component were soon separated. The cold suspension was poured with stirring into a solution of **IV** (0.005 mol) in cold 10% sodium hydroxide solution (50 ml) and the mixture was chilled to 0–3 °C. Coupling takes place readily and the dyestuff separates as a paste. The mixture was stirred well for 10 min and warmed until the paste has dissolved completely and concentrated sodium chloride solution (20 ml) was added

to the mixture. The solution was left for 1 h to cool to room temperature then chilled to in an ice bath till 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 aqueous solution of the produced salts with dilute acetic acid afforded the crude products which were recrystallized from acetic acid to give highly colored crystals of the pure derivatives (**Va–e**) in an average yield of 49–66%. The prepared dyestuffs together with their physical data are depicted in Tables 2–4.

For **Vk**: IR ($\bar{\nu}$/cm^{-1}): 3420 (OH), 3310 (NH), 1630 and 1625 (C=N functions), 1605 (C=C), 1360 and 1160 (asym. and sym. stretching vibrations of sulphonic acid group), 1350 and 1145 (cyclic sulphonamide function) and 1060 (ether linkage). ^{1}H NMR spectrum (δ in ppm): 13.55 (br, 1H, NH of 4-sulphophenyl hydrazone moiety), 12.90 (br, 1H, NH of *m*-tolylhydrazone moiety), 10.30 (br, 1H, OH) and 8.00–6.90 (m, 26H, Ar–H); ^{13}C NMR spectrum (δ in ppm): 168.3 (C-3 of benzothiadiazine moiety), 157.8 (C-1 of phenoxy function), 155.7, 152.9 (*p*-sulpho and *m*-tolylhydrazono-carbons), 145.4 (C-δ of *p*-sulphophenyl moiety), 141.8 (C-γ of *m*-tolyl moiety), 139.4 (C-α of *p*-sulphophenyl moiety), 132.2 (C-8_a of benzothiadiazine moiety), 125.6 and 123.5 (C-α and α′ of *m*-tolyl moiety), 121.8 (C-4_a of benzothiadiazine moiety) and 25.6 (sp^3 carbon of methyl function).

*4.4.2. Alternative synthetic route for synthesis of 2-[1′,1′dioxo-3′-[α-(p-chlorophenylhydrazono)-phenoxymethyl]-1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(p-sulphophenylhydrazono)phenoxymethyl]-1,2,4-benzothiadiazine 1,1 dioxide (**Va**)*

*4.4.2.1. Synthesis of 3-[α-(p-sulphophenylhydrazono)phenoxymethyl]-2,1,4-benzoxathiazine 1,1-dioxide (**VI**).* *p*-Amino benzenesulphonic acid (0.005 mol, 0.9 g) was mixed with anhydrous sodium carbonate (2.6 g) and water (100 ml) and the whole mixture was refluxed until a clear solution was obtained which was then cooled to about 15 °C and 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) and crushed ice (100 g) and the whole reaction mixture was tested for the presence of slight excess nitrous acid and kept stirred for 15 min into a mixture of hydrochloric acid (12 ml, 30%) and ice (100 g) where fine crystals of diazo component were soon separated. The suspension was chilled in an ice bath for a further 10 min and poured with stirring into a solution of **II** (0.005 mol, 1.4 g) in cold 10% sodium hydroxide solution (50 ml) and the whole mixture was cooled to 0–3 °C. Coupling takes place readily and the dyestuff separates as a paste. The whole mixture was stirred well for 10 min and warmed until the paste has dissolved completely and then concentrated sodium chloride solution (20 ml) was added to the mixture. The solution was left for 1 h to cool to room temperature then chilled to in an ice bath till 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 aqueous solution of the produced salt with dilute acetic acid afforded the crude product which was recrystallized from acetic acid to give the pure product **VI** of m.p. 233 °C in 73% yield.

For $C_{20}H_{15}N_3O_7S_2$ (473.48) Calcd: C, 50.73%, H, 3.19%, N, 8.87%, S, 13.54%; found: C, 50.28%, H, 3.39%, N, 9.06%, S, 13.78%. IR ($\bar{\nu}$/cm^{-1}): 3420 (OH), 3310 (NH), 1630 and 1625 (C–N functions), 1605 (C=C), 1365 and 1160 (asym. and sym. stretching vibration of sulphonic group), 1360 and 1145 (cyclic sulphonate function) and 1055 (ether linkage).

*4.4.2.2. Synthesis of 2-[1′,1′-dioxo-3′-phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(p-sulphophenylhydrazono)phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide (**VIII**).* A mixture of **VI** (0.01 mol, 4.7 g), **VII** [14] (0.01 mol, 3.0 g), 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 ethanol to give the pure product of m.p. 246 °C in 49% yield.

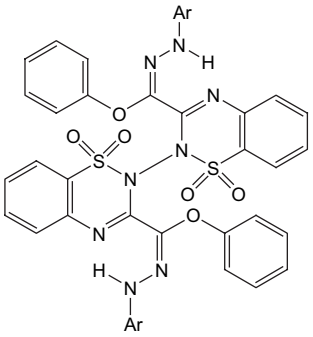
For $C_{34}H_{26}N_6O_9S_3$ (758.80) Calcd: C, 53.82%, H, 3.45%, N, 11.08%, S, 12.68%; found: C, 53.98%, H, 3.68%, N, 11.26%, S, 12.29%. IR ($\bar{\nu}$/cm^{-1}): 3420 (OH), 3315 (NH), 1630 and 1625 (C–N functions), 1605 (C=C), 1365 and 1160 (asym. and sym. stretching vibration of sulphonic group), 1355 and 1145 (cyclic sulphonamide function) and 1060 (ether linkage).

*4.4.2.3. Synthesis of 2-[1′,1′-dioxo-3′-(α′-p-chlorophenylhydrazono)phenoxymethyl 1′,2′,4′-benzothiadiazine-2′-yl]-3-[α-(p-sulphophenylhydrazono)phenoxymethyl)]-1,2,4-benzothiadiazine 1,1 dioxide (**Va**).* *p*-Chloroaniline (0.005 mol, 0.6 g) was dissolved in 3 ml of 6 M hydrochloric acid, the solution was cooled below 5 °C. To the resulting cooled solution, 10 ml of 0.6 M sodium nitrite solution was slowly added while stirring and keeping the temperature of the mixture below 5 °C. After the addition was complete, the solution was stirred for additional 10 min. In a 250 ml beaker, 0.005 mol (3.8 g) of **VIII** was stirred in 50 ml of 0.3 N aqueous sodium hydroxide solution, and to which 2 g of sodium acetate trihydrate was added. Few drops of ethanol were added to ensure the complete dissolution of the entire coupling component. The resulting solution was chilled in an ice–salt bath and mechanically stirred. To the cold solution of **VIII**, the diazonium salt solution was added dropwise while stirring and keeping the temperature between 0 and 5 °C. 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 to give the pure product of m.p. 226 °C in 44% yield.

*4.5. Synthesis of 2-[1′,1′-dioxo-3′-phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-phenoxymethyl-1,2,4-benzothiadiazine 1,1-dioxide (**IX**)*

A mixture of 0.01 mol, (3 g) of 2-amino-3-phenoxmethyl-1,2,4-benzthiadiazine (**VII**), 0.01 mol, (2.9 g) of 3-phenoxymethyl-2,1,4-benzoxathiazine 1,1-dioxide (**I**) and piperidine (0.3 ml) in absolute ethanol (10 ml) was refluxed under

Table 5
2-[1′,1′-Dioxo-3′-[(α′-sulphoarylhydrazono)phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-(α-sulphoarylhydrazono)phenoxymethyl-1,2,4-benzothiadiazine] 1,1-dioxide derivatives (**Xa–e**)



Compound no.	Ar	Molecular formula (M.wt)	M.p./°C (yield/%)	Calcd/found (%)				
				C	H	N	S	Cl
a	4-Sulphophenyl	$C_{40}H_{30}N_8O_{12}S_4$ (942.98)	206–208 (67)	50.95	3.21	11.88	13.60	–
				51.18	3.52	12.08	13.91	
b	2-Carboxy-4-sulphophenyl	$C_{42}H_{30}N_8O_{16}S_4$ (1031.00)	235–237 (65)	48.93	2.93	10.87	12.44	–
				49.11	3.06	10.98	12.02	
c	2,5-Dichloro-4-sulphophenyl	$C_{40}H_{26}Cl_4N_8O_{10}S_3$ (1080.76)	218–220 (61)	44.45	2.42	10.37	11.87	13.12
				44.66	2.58	10.60	11.69	12.99
d	6-Sulphonaphthyl	$C_{48}H_{34}N_8O_{12}S_4$ (1043.09)	271–273 (58)	55.27	3.29	10.74	12.30	–
				54.91	3.18	10.90	12.43	
e	8-Sulphonaphthyl	$C_{48}H_{34}N_8O_{12}S_4$ (1043.09)	289–291 (63)	55.27	3.29	10.74	12.30	–
				55.48	3.39	10.58	12.49	

anhydrous conditions for 4 h and left to cool to room temperature. The precipitated solid material was filtered off and recrystallized from ethanol to give the pure product of m.p. 251 °C in 63% yield.

For $C_{28}H_{22}N_4O_6S_2$ (574.63) Calcd: C, 58.52%, H, 3.86% N, 9.75%, S, 11.16%; found: C, 58.91%, H, 3.48% N, 9.94%, S, 11.42%. For **XV**: IR ($\overline{\nu}$/cm^{-1}): 1350 and 1145 (cyclic sulphonamide function), 1630 (C=N functions), 1605 (C=C) and 1060 (ether linkage). ^{1}H NMR spectrum (δ in ppm): 7.95–6.90 (m, 18H, Ar–H) and 4.10 (s, 4H, two methylene moieties).

*4.6. Alternative synthetic route for synthesis of 2-[1′, 1′-dioxo-3′-phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-phenoxymethyl-1,2,4-benzothiadiazine 1,1-dioxide (**IX**)*

A mixture of 0.01 mol, (2.9 g) of 3-phenoxymethyl-2,1,4-benzoxathiazine 1,1-dioxide (**I**), 0.005 mol of hydrazine hydrate and piperidine (0.3 ml) in absolute ethanol (10 ml) was refluxed for 4 h and left to cool to room temperature. The precipitated solid was filtered off and recrystallized from ethanol to give the pure product of m.p. 251 °C in 75% yield.

*4.7. Synthesis of 2-[1′,1′-dioxo-3′-[(α′-sulphoarylhydrazono)phenoxymethyl-1′,2′,4′-benzothiadiazine-2′-yl]-3-(α-sulphoarylhydrazono)-phenoxymethyl-1,2,4-benzothiadiazine]-1,1-dioxide derivatives (**Xa–e**)*

These coupling products were prepared by following the general procedure that was described for preparation sulphoaryl hydrazone derivatives (**Va–o**).

The crude products were recrystallized from acetic acid to give highly colored crystals of the pure dyestuffs (**Xa–e**) in an average yield of 58–67%. The prepared dyestuffs together with their physical data are given in Table 5.

For **Xa**: IR ($\overline{\nu}$/cm^{-1}): 3420 (OH), 3310 (NH), 1630 and 1625 (C–N functions), 1605 (C=C), 1365 and 1155 (asym. and sym. stretching vibrations of sulphonic acid group), 1350 and 1145 (cyclic sulphonamide function) and 1060 (ether linkage). ^{1}H NMR spectrum (δ in ppm): 12.95 (br, exchangeable, 2H, NH of hydrazone moieties), 10.35 (br, exchangeable, 2H, OH proton of sulphonic group) and 8.05–6.80 m, 26H, Ar–H).

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