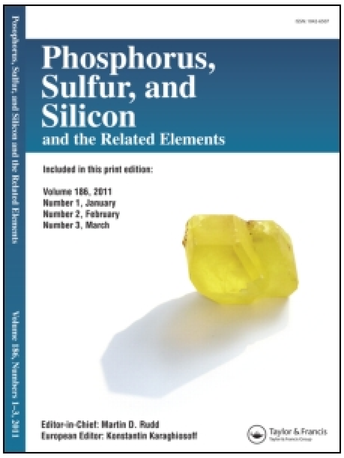

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CHLOROSULFONATION OF DIARYL AZINES

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CHLOROSULFONATION OF DIARYL AZINES

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Benzaldehyde- and *o*-, *m*-, *p*-anisaldehyde azines; thiophene-2-carboxaldehyde, and biphenyl-4-carboxaldehyde azines (**1–8**) reacted with excess chlorosulfonic acid to give the disulphonyl chlorides (**1a–8a**). These were condensed with amines and hydrazine to give 27 derivatives, (Table I) for biocidal evaluation. The orientation of sulfonation is discussed in relation to the stereoelectronic factors and the spectral data. Attempted chlorosulfonation of furan-2-carboxaldehyde azine (**9**) gave an impure product which could not be clearly characterized as the morpholidate derivative.

Key words: Diaryl Azines; chlorosulfonation.

INTRODUCTION

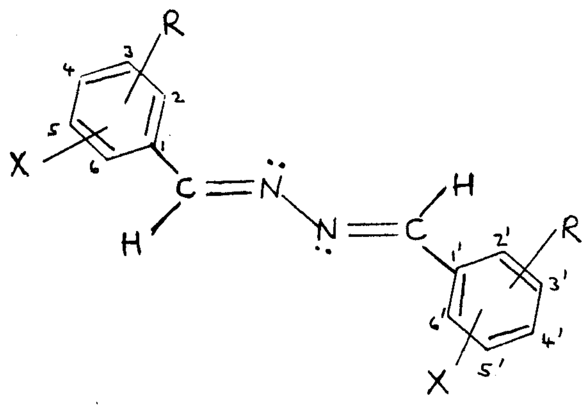
The work described forms part of our general programme on the chemistry and biological activity of arylsulfonyl derivatives.[1–3] Diarylazines are known[4] to be readily formed by condensation of the appropriate aryl aldehyde with hydrazine hydrate. However, the chlorosulfonation of these compounds has not been previously reported. In view of the known ability of diaryl azines to undergo 1,3-dipolar cycloaddition reactions with maleic acid derivatives,[5] it was of interest to examine the preparation of the sulfonated diaryl azines as potential substrates in cycloadditions.

DISCUSSION

In diaryl azines, the C=N group is a deactivating substituent with regard to electrophilic substitution. In agreement, at room temperature no reaction was observed between benzaldehyde azine (**1**; R=X=H) and a large excess (16 equivalents) of chlorosulfonic acid, as only the unreacted azine was recovered. With a slightly smaller excess of the reagent (12 equivalents) at 50–60°C, reaction was observed, but TLC indicated that it was incomplete. On increasing the temperature (120°C) for 4 hours the product, obtained by trituration of the yellow gum with chloroform, was a disulfonyl chloride in low yield (38%). The yield was increased (68%)

by the addition of thionyl chloride after heating. These results demonstrate that the N—N bond does not undergo fission under the reaction conditions adopted and that the imino group is deactivating to electrophilic attack. The ^1H NMR spectrum of the disulfonyl chloride contained an unsymmetrical aromatic region. On the basis of substituent orientation, the formation of the 3,3'-disulfonyl chloride (**1a**; R=H, X=SO_2Cl) (Chart 1) is most likely. The product was characterized by the formation of the bis-sulfonamides (**1b–1e**) (Table I and Chart 1) by reaction with dimethylamine, morpholine, 2,6-dimethylmorpholine and piperidine respectively. The hydrazide (**1f**) was prepared by reaction with hydrazine and the intermediate hydrazide was treated with an excess of acetone to give the bis-hydrazone (**1g**).

A number of other azines were treated with chlorosulfonic acid in order to examine the influence of substitution. Thus, the reaction of *o*-, *m*- and *p*-anisal-



parent azines **1–8** (R=X=H)

Compd. No.	R	X	No.	X	No.	X
1a	H	3,3'—SO_2Cl	**2b**	SO_2NMe_2	**5b**	SO_2NMe_2
2a	2—OMe	5,5'—SO_2Cl	**2c**	sulfonyl-2,6-dimethylmorpholino	**5c**	sulfonyl-2,6-dimethylmorpholino
3a	3—OMe	6,6'—SO_2Cl	**2d**	SO_2NH_2	**6b**	SO_2NMe_2
4a	4—OMe	3,3'—SO_2Cl	**2e**	$SO_2NHN{=}C\ Me_2$	**7b**	SO_2NMe_2
5a	2—Me	5,5'—SO_2Cl	**2f**	$SO_2NHN{=}CH$-$C_6H_4NO_2$-*p*	**7c**	sulfonyl-2,6-dimethylmorpholino
6a	4—Cl	3,3'—SO_2Cl	**3b**	SO_2NMe_2		
7a	*p*-C_6H_5—C_6H_4	4,4'—SO_2Cl	**4b**	SO_2NMe_2		
1b	H	SO_2NMe_2	**4c**	sulfonylmorpholino		
1c	H	sulfonylmorpholino	**4d**	sulfonyl-2,6-dimethylmorpholino		
1d	H	sulfonyl-2,6-dimethylmorpholino	**4e**	SO_2NHCH_2Ph		
1e	H	sulfonylpiperidino	**4f**	SO_2NEt_2		
1f	H	SO_2NHNH_2	**4g**	SO_2NHPh		
1g	H	$SO_2NHN{=}CMe_2$	**4h**	$SO_2NHC_4H_4Me$-*p*		
			4i	$SO_2NHC_6H_4OMe$-*p*		

CHART 1

TABLE I
Physical data for the diarylazine sulfonyl derivatives

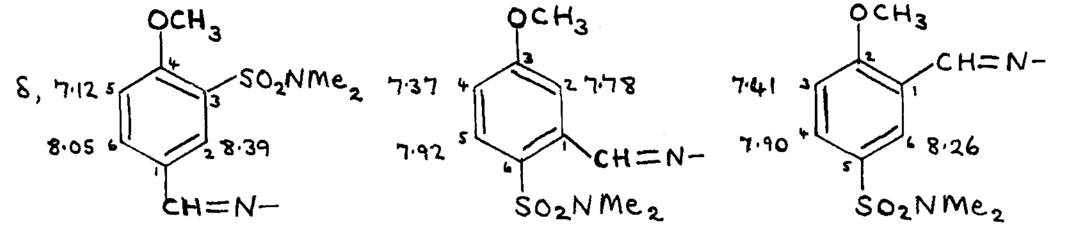
Compd No.	Yield (%)	M.p. (°C)	Molecular formula	Microanalysis found (calc.) % C	H	N	MS (M^+)
1b	65	197-199	$C_{18}H_{22}N_4O_4S_2$	50.7(51.1)	5.3(5.2)	13.3(13.3)	422
1c	64	271-273	$C_{22}H_{26}N_4O_6S_2$	52.6(52.2)	5.3(5.1)	11.5(11.1)	463†
1d	60	195-197	$C_{28}H_{38}N_4O_4S_2$	55.6(55.5)	6.1(6.1)	10.1(10.0)	562
1e	60	206-209	$C_{24}H_{30}N_4O_4S_2$	57.4(57.1)	6.0(6.0)	11.1(10.9)	502
1f	21	159-161	$C_{14}H_{14}N_6O_4S_2$	43.0(42.6)	3.3(3.5)	21.0(21.3)	-
1g	78	189-191	$C_{20}H_{24}N_6O_4S_2$	50.5(50.4)	5.1(5.0)	17.3(17.6)	244†
2b	84	268-270	$C_{20}H_{26}N_4O_6S_2$	50.3(49.9)	5.1(5.4)	11.8(11.6)	482
2c	80	277-279	$C_{28}H_{38}N_4O_8S_2$	53.8(54.0)	6.2(6.1)	9.2(9.0)	622
2d	30	317-320	$C_{16}H_{18}N_4O_6S_2$	48.2(48.5)	4.5(4.5)	13.8(14.1)	396
2e	70	210-212	$C_{22}H_{22}N_6O_6S_2 . 1H_2O$	47.0(47.1)	5.2(5.1)	15.4(15.1)	-
2f	75	260	$C_{30}H_{26}N_8O_6S_2 . 1H_2O$	51.0(49.7)	4.1(3.8)	15.9(15.8)	-
3b	62	159-161	$C_{20}H_{26}N_4O_6S_2$	50.0(49.8)	5.6(5.4)	12.0(11.6)	483*
4b	70	295-261	$C_{20}H_{26}N_4O_6S_2$	49.6(49.8)	5.6(5.4)	11.8(11.6)	241†
4c	70	270-275	$C_{24}H_{30}N_4O_8S_2$	50.5(50.8)	5.2(5.3)	9.90(9.90)	566
4d	68	240-241	$C_{28}H_{38}N_4O_8S_2$	53.9(54.0)	6.2(6.1)	9.2(9.0)	311†
4e	75	198-201	$C_{30}H_{30}N_4O_6S_2$	59.4(59.4)	5.1(5.1)	9.4(9.3)	303†
4f	70	202-204	$C_{24}H_{34}N_4O_6S_2$	53.3(53.5)	6.5(6.3)	10.2(10.4)	538
4g	80	205-207	$C_{28}H_{26}N_4O_4S_2$	61.4(61.5)	5.0(4.8)	10.0(10.2)	546
4h	70	194-196	$C_{30}H_{30}N_4O_4S_2$	62.8(62.7)	5.1(5.2)	9.8(9.7)	574
4i	70	198-199	$C_{30}H_{30}N_4O_6S_2$	59.6(59.4)	5.2(4.9)	9.0(9.2)	606
5b	80	245-251	$C_{20}H_{26}N_4O_4S_2$	53.0(53.3)	5.6(5.8)	12.1(12.4)	450
5c	63	237-239	$C_{28}H_{38}N_4O_6S_2$	57.0(56.9)	6.5(6.4)	9.6(9.9)	590
6b	65	267-268	$C_{18}H_{20}Cl_2N_4O_4S_2$	44.2(44.0)	4.2(4.1)	11.3(11.4)	490
7b	71	303-305	$C_{30}H_{30}N_4O_4S_2$	61.9(62.7)	5.2(5.2)	9.8(9.8)	574
7c	73	298	$C_{36}H_{42}N_4O_6S_2$	63.9(63.9)	5.9(5.8)	8.1(7.8)	714
8b	72	212-215	$C_{14}H_{18}N_4O_4S_4$	38.9(38.7)	4.2(4.2)	12.8(12.9)	435
8c	78	238-241	$C_{18}H_{22}N_4O_6S_4$	41.4(41.7)	4.1(4.2)	11.0(10.8)	518

† = largest molecular fragment ion in MS.

* = CI MS shows M^+ + 1 ion.

dehyde azines (**2–4**; R=*o*-, *m*-, *p*-OMe, X=H) with chlorosulfonic acid occurred under milder conditions than for benzaldehyde azine (**1**, R=X=H), consistent with electron donation by the substituent methoxyl group. Thus, reaction was achieved with a much smaller excess (6 equivalents) of the reagent, using thionyl chloride as chlorinating solvent, under reflux (4 hours). With more vigorous conditions (12 equivalents, 120°), the *o*-isomer (**2**; R=X=H) in particular gave a reduced yield (20%) of disulfonyl chloride, possibly due to partial demethylation in the strongly acidic medium, which made product isolation more difficult.

The orientation of substitution can be deduced by the ^{1}H NMR spectra of the bis-N,N-dimethylsulfonamides of compounds (**2–4**). The aromatic regions all contain readily-analysed ABC patterns, which demonstrate the presence of 1,2,4-trisubstitution in each case. The proposed orientations and the assigned shifts are shown below:



On the basis of the combined electronic effects of the imino and methoxyl groups, the preferred position of electrophilic attack in **4b** and **2b** are respectively 3 and 5. The proton *ortho* to the methoxyl group in each of these derivatives is, as expected more shielded than the remaining protons, the latter being deshielded by the combined anisotropic and electronic effects of the imino and sulfamoyl groups. In the case of **3b**, the aromatic region contained no resonance signal greater than δ 8.0. Hence, the imino and sulfamoyl groups are almost certainly *ortho* to one another. Consequently, the preferred orientation of substitution must be *para* to the methoxyl group, which results in the 6,6′-disulfonyl chloride (**3a**).

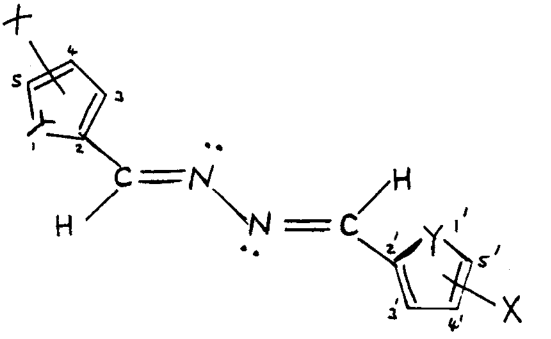
When the chlorosulphonation of the azine (**3**) was prolonged using a large excess of the reagent (12 equivalents) in excess thionyl chloride (80°C) for 10 hours the 4,4′,6,6′-tetrasulfonyl chloride was obtained clearly indicating the importance of the activating influence of the methoxyl group. In this compound, the H^1 NMR spectrum showed very simple aromatic resonances containing two slightly-broadened singlets (AB system with very little *para* coupling).

o-Tolualdehyde azine (**5**) reacted with chlorosulfonic acid under identical conditions to those used for *o*-anisaldehyde azine (**2**), (6 equivalents of chlorosulfonic acid in excess boiling thionyl chloride, 5 hours). It was not possible to differentiate between the activating influence of the methyl and methoxyl groups.

4-Chlorobenzaldehyde azine (**6**) did not react with chlorosulfonic acid under similar conditions to those used for the anisaldehyde azines (**2–4**). The lack of reactivity in (**6**) can be attributed to the combined deactivating and steric effects of the chlorine atom. However with a much larger excess of the reagent (12 equivalents) at 120°C for 6 hours, a reasonable yield (65%) of a disulfonyl chloride (**6a**) was obtained. On the basis of the combined stereoelectronic effects of the chlorine and imino groups it is concluded that the orientation of sulfonation is probably 3,3′-.

p-Biphenylcarboxaldehyde azine (**7**) reacted with chlorosulfonic acid (6 equivalents) in excess thionyl chloride at 60°C (3 hours) to give an unstable sulfonyl chloride which was characterized as the dimethylamide and morpholidate derivatives (**7b, 7c**) (Table I).

Sulfonation occurs preferentially in the *para*-position of the biphenyl ring[6] and sulfonation in the *ortho*-position only occurs under very vigorous conditions.[7]



	X	Y
8	H	S
8a	SO_2Cl	S
8b	SO_2NMe_2	S
8c	$SO_2C_4H_8N$	S
9	H	O

CHART 2

In contrast, the much more electron-rich thiopene-2-carboxaldehyde azine (**8**) (Chart 2), reacted easily with chlorosulfonic acid (8 equivalents) in excess thionyl chloride under milder conditions (60°C, 3 hours). The greater reactivity of thiophene ring results from electron donation from the hetero sulfur atom which is known[8] to favour 4- or 5-sulfonation depending on the nature of the substituents.

Generally electron-donor substituents direct further electrophilic substitution mainly into the 5-position of the thiophene ring, while electron-withdrawing groups favour further attack in the 4-position. The latter would therefore be anticipated to be the major product from sulphonation of (**8**), however TLC and ^1H NMR spectroscopy of the dimethylsulfonamide and morpholidate derivatives (**8b, 8c**) indicated a mixture of the 4- and 5-isomers. Purification of the morpholidate by fractional recrystallization gave a single product (1 spot on TLC). The ^1H NMR spectrum of the pure morpholidate (**8c**) showed an AB pattern in the aromatic resonances at δ 7.8, 7.7 with a coupling constant ($J \simeq 3$ Hz), consistent with coupling between the thiophen 3- and 4-protons and hence indicative of 5-sulfonation.

In the case of furan-2-carboxaldehyde azine (**9**) (Chart 2), there will be even more powerful electron donation from the hetero oxygen atom. This was the most reactive system studied and chlorosulfonation was examined under milder conditions: chlorosulfonic acid (2.2 equivalents) in excess thionyl chloride at room temperature.

Addition of the substrate to the sulfonating mixture caused intense darkening, even when performed at 0°C. The product (48%), mp 110–115°C was a complex mixture (8 spots on TLC); reaction with morpholine gave a solid mp 208–212°C (39%) again a mixture. The ^1H NMR showed a complex series of aromatic resonances (δ 7.3–6.8) with a high aromatic:aliphatic ratio. MS showed a weak molecular ion for the morpholidate derivative (M^+, 486) and a fragment ion indicating loss of the sulfonylmorpholidate moiety. Peaks at 260, 258, 256 in the MS could arise from the presence of the dichloro derivative of furan-2-carboxaldehyde azine ($C_{10}H_6Cl_2N_2O_2$) possibly formed by some chlorination of the highly reactive substrate by the reagents.

Furan is well known[9] to decompose with highly acidic sulfonating reagents, e.g., chlorosulfonic and sulfuric acids. It was hoped the electron-withdrawing C=N group might sufficiently stabilize the furan ring to allow sulphonation, as was observed with furan-2-carboxamide[10] and 2-carboxanilide[11] but clearly this is not the case.

The derivatives (**7b, 7c**) were not sufficiently soluble in DMSO to permit determination of the NMR spectra in this solvent, however spectra were obtained using trifluoroacetic acid as solvent. The aromatic resonances were complex and a clearly defined AA'BB' pattern was not observed; however the extra electron donation from the *para* phenyl ring are likely to outweigh the electron-withdrawing influence of CH=N group and favour *p*-sulfonation in this compound.

EXPERIMENTAL

Melting points were determined with a Gallenkamp electric apparatus and are uncorrected. NMR spectra were recorded on a Bruker WP 80 spectrometer using tetramethylsilane as internal standard and DMSO-d^6 as solvent unless otherwise stated. The resonances indicated by an asterisk were removed by D_2O treatment.

MS were recorded with a VG Micromass V15 instrument and IR spectra were measured as nujol mulls on a Perkin Elmer 781 or a Unicam SP1800 spectrophotometer. TLC was carried out on Camlab Polygram silica gel plates sensitized to UV 254 nm using cyclohexane-ethyl acetate (1:1) as eluent, unless otherwise stated.

Microanalyses were carried by the courtesy of Shell Research Ltd, Sittingbourne, Kent, England.

General procedure for preparation of the diaryl azines (**1–8**). The aromatic aldehyde (0.1 mole) was gradually added to a stirred solution of hydrazine hydrate (98%) (0.05 mole) in ethanol (100 ml). The mixture was warmed on the steam bath for ½ hour and left at room temperature (3 hours). The solid product was filtered off and recrystallised from ethanol to give the diaryl azine. By this procedure the following azines were prepared:

benzaldehyde (**1**) (90%), mp 92–94°C (lit.[12] 93°C)
o-anisaldehyde (**2**) (85%), mp 145–146°C (lit.[13] 138°C)
m-anisaldehyde (**3**) (78%), mp 77–78°C (lit.[13] 76°C)
p-anisaldehyde (**4**) (80%), mp 169–170°C (lit.[4] 170°C)
o-tolualdehyde (**5**) (74%), mp 101–102°C (lit.[14] 101°C)
p-chlorobenzaldehyde (**6**) (76%), mp 213°C (lit.[13] 205–206.5°C)
biphenyl-4-carboxaldehyde (**7**) (70%), mp 248–250°C (lit.[15] 230°C)
thiophen-2-carboxaldehyde (**8**) (72%), mp 153–156°C (lit.[16] 157.5–158.5°C)
furan-2-carboxaldehyde (**9**) (80%), mp 111–113°C (lit.[4] 111–112.3°C)

Benzaldehyde azine-3,3'-disulfonyl chloride (**1a**).

Method 1

Benzaldehyde azine (2 g, 0.0096 mole) was gradually added to chlorosulfonic acid (13.0 g, 0.115 mole) with swirling. The exothermic reaction (60°C) was allowed to proceed without cooling. The solution was heated at 120°C for 4 hours, cooled and very slowly added to crushed ice with vigorous stirring. The resultant yellow gum was extracted with chloroform (100 ml); filtration removed the insoluble sulfonic acid and the filtrate, by evaporation *in vacuo*, afforded the disulfonyl chloride (**1a**) as a yellow solid (1.4 g, 39%), mp 139–142°C. TLC showed one spot, R_F 0.64. Sodium fusion test indicated presence of N, Cl and S. IR ν_{max} 1600 (ArC=C), 1380, 1170 (SO_2) cm^{-1}. MS (408, 406, 404) (M^+), 369 (M—Cl), 305 (M—SO_2Cl), 299, 205.

Method 2

The above reaction was repeated, except that after heating for 4 hours, the solution was allowed to cool to room temperature and thionyl chloride (20 ml) added. The mixture was left at room temperature for 2 hours and poured onto crushed ice to give (**1a**) as a yellow powder (2.8 g, 70%).

o-Anisaldehyde azine-5,5'-disulfonyl chloride (**2a**). *o*-Anisaldehyde azine (2 g, 0.0075 mole) was added portionwise to a mixture of chlorosulfonic acid (4.0 ml, 0.056 mole) in excess thionyl chloride (15 ml); the exothermic reaction was allowed to proceed without cooling. The yellow solution was refluxed for 5 hours, cooled and slowly poured onto crushed ice. The solid precipitate was filtered off with suction, washed with cold water and dried in a vacuum desiccator to give (**2a**) (2.83 g, 82%), mp 229–231°C. Sodium fusion test was positive for N, S, Cl. TLC showed one spot, R_F 0.43 IR ν_{max} 1600 (ArC═C), 1380, 1180 (SO_2), 1270, 1030 (Ar—O—CH_3) cm^{-1}.

m-Anisaldehyde azine-6,6'-disulfonyl chloride (**3a**). *m*-Anisaldehyde azine (2 g) was refluxed with a mixture of chlorosulfonic acid (6.92 g) in excess thionyl chloride (15 ml) at 80°C for 5 hours to give (**3a**) (2.2 g, 54%), mp 98–100°C. IR ν_{max} 1620 (ArC═C), 1390, 1180 (SO_2) cm^{-1}.

p-Anisaldehyde azine-3,3'-disulfonyl chloride (**4a**). *p*-Anisaldehyde azine was similarly refluxed with chlorosulfonic acid-thionyl chloride to give (**4a**) (64%), mp 178–182°C. TLC showed one spot, R_F 0.74, IR ν_{max} 1605 (ArC═C), 1380, 1180 (SO_2) cm^{-1}.

o-Tolualdehyde azine-5,5'-disulfonyl chloride (**5a**). *o*-Tolualdehyde azine was similarly converted into (**5a**) (84%), mp 213–216°C. TLC showed one spot, R_F 0.71, IR ν_{max} 1620 (ArC═C), 1380, 1180 (SO_2) cm^{-1}.

p-Chlorobenzaldehyde azine-3,3'-disulfonyl chloride (**6a**). *p*-Chlorobenzaldehyde azine (2.0 g, 0.0096 mole) was added portionwise to chlorosulfonic acid (5.2 ml, 0.1152 mol). The mixture was heated at 120°C for 6 hours, after cooling thionyl chloride (15 ml) was added and the mixture refluxed for 2 hours. The cold mixture was carefully added to crushed ice (100 ml). The pale yellow precipitate was filtered off with suction, washed with cold water and dried (IR lamp) to give **6a** (2.3 g, 65%), mp 267–268°C.
TLC showed one major spot, R_F 0.50, IR ν_{max} 1600 (ArC═C), 1380, 1180 (SO_2) cm^{-1}.

p-Biphenylcarboxaldehyde azine-4,4'-disulfonyl chloride (**7a**). *p*-Biphenylcarboxaldehyde azine (2 g, 0.0056 mole) was gradually added to a mixture of chlorosulfonic acid (3.84 g, 0.033 mole) and thionyl chloride (20 ml). The exothermic reaction was allowed to proceed with a darkening of colour. The mixture was refluxed (80°C) for 4 hours during this period evolution of hydrogen chloride gas was observed. The cooled mixture was carefully added to crushed ice (150 ml) with formation of a fawn precipitate; this was collected, washed with water and dried *in vacuo* to give **7a** (2.2 g, 71%). TLC showed one spot R_F 0.69, IR ν_{max} 1610 (ArC═C), 1360, 1180 (SO_2) cm^{-1}. The product was unstable but was characterized as the sulfonamides (**7b, 7c**) (Table I).

Thiophen-2-carboxaldehyde azine-4(5)-disulfonyl chloride (**8a**). Thiophen-2-carboxaldehyde azine (2 g, 0.0091 mole) was added to chlorosulfonic acid (4.9 ml, 0.073 mole) at room temperature. The brown solution was heated at 60°C for 3 hours. After cooling for 30 minutes, the reaction mixture was poured onto crushed ice (150 ml). The yellow precipitate was filtered off under suction, well washed with cold water and dried under the IR lamp to give **8a** (3.5 g, 87%), mp 180–182°C.
TLC showed one major spot R_F 0.71. IR ν_{max} 1630 (ArC═C), 1380, 1180 (SO_2) cm^{-1}.

General procedure for the reaction of the sulfonyl chlorides (**1a–8a**) *with amines*. The sulfonyl chloride (0.01 mole) in acetone or methanol (15 ml) was treated with the appropriate amine (0.045 moles) in acetone or methanol (15 ml) with stirring. After 3 hours at room temperature, the reaction mixture was poured onto crushed ice. The precipitate was collected by filtration on the Buchner funnel and washed with cold water. The crude product was recrystallised from acetone or methanol to give the sulfonamides (Table 1).
The aromatic sulfonamides (**4g, 4h, 4i**) were obtained by reaction of *p*-anisaldehyde azine-3,3'-disulfonyl chloride (**4a**) (0.01 mole) with a mixture of the arylamine (0.02 mole) and triethylamine (0.02 mole) in methanol at room temperature (12 hours).

Compound (**1b**). TLC showed one spot R_F 0.35. IR ν_{max} 1640 (ArC═C), 1350, 1160 (SO_2) cm^{-1}. MS: 422 (M^+), 379 (M—NMe_2), 314 (M—SO_2NMe_2), 238. NMR: δ 8.8 (s, 2H, $C\underline{H}$═N), 8.4–7.6 (m, 8H, ArH), 2.8 (s, 12H, NMe_2).

Compound (**2c**). TLC showed one spot, R_F 0.71. IR ν_{max} 1600 (ArC=C), 1360, 1160 (SO_2) cm^{-1}. MS: 622 (M^+), 508 (M—$C_6H_{12}NO$), 444 (M—$SO_2C_6H_{12}NO$). NMR: δ 8.9 (s, 2H, C$\underline{H}$=N), 8.4–7.4 (m, 6H, ArH), 4.1 (s, 6H, OMe), 3.9–3.7 (m, 8H, CH_2—N—CH_2), 2.1–1.9 (t, 4H, C$\underline{H}$—O), 1.1 (d, 12H, morpholino-CH_3).

Compound (**3b**). TLC showed one spot, R_F 0.21. IR ν_{max} 1600 (ArC=C), 1360, 1160 (SO_2) cm^{-1}. NMR: δ 9.2 (s, 2H, CH=N), 8.0–7.2 (m, 6H, ArH), 4.0 (s, 6H, OMe), 2.8 (s, 12H, NMe_2).

Compound (**4b**). NMR δ: 8.63 (s, 2H, N=CH), 8.34–7.17 (m, 6H, ArH), 4.0 (s, 6H, MeO), 2.87 (s, 6H, SO_2NMe_2).

Compound (**4c**). TLC showed one spot, R_F 0.32 (1:1 CH_2Cl_2-isopropyl ether as eluant). IR ν_{max} 1620 (ArC=C), 1360, 1160 (SO_2) cm^{-1}. NMR: δ 8.6 (s, 2H, C$\underline{H}$=N), 8.2–7.1 (m, 6H, ArH), 4.0 (s, 6H, OMe), 2.9–3.2 (m, 16H, morpholino H).

Compound (**4g**). NMR δ: 10.1* (s, 2H, NH), 8.69 (s, 2H, N=CH), 8.30–7.0 (m, 16H, ArH), 3.94 (s, 6H, OMe).

Compound (**4h**). NMR δ: 10.28* (s, 2H, NH), 9.03 (s, 2H, N=CH), 8.64–7.35 (m, 14H, ArH), 4.33 (s, 6H, OMe), 2.49 (s, 6H, Me).

Compound (**4i**). NMR δ: 9.7* (s, 2H, NH), 8.64 (s, 2H, N=CH), 8.34–6.8 (m, 14H, ArH) (6.8–6.7, AA'BB' pattern for the *p*-tolyl H), 3.99, 3.62 (2s, 12H, OMe).

Compound (**5b**). TLC showed one spot R_F 0.21, IR ν_{max} 1620 (ArC=C), 1350, 1160 (SO_2) cm^{-1}.

Compound (**6b**). TLC showed one spot, R_F 0.61 (1:1 CH_2Cl_2-isopropyl ether). IR ν_{max} 1600 (ArC=C), 1380, 1190 (SO_2) cm^{-1}. MS: 490 (M^+), 447 (M—NMe_2), 411 (M—Cl, —NMe_2), 382 (M—SO_2NMe_2), 340, 276, 165.

Compound (**7b**). TLC showed one spot, R_F 0.25. IR ν_{max} 1610 (ArC=C), 1360, 1170 (SO_2) cm^{-1}. NMR: δ 9.3 (s, 2H, CH=N), 8.5–8.0 (m, 16H, ArH), 3.1 (s, 12H, NMe_2).

Compound (**8c**). TLC showed one spot, R_F 0.32. IR ν_{max} 1610 (ArC=C), 1380, 1180 (SO_2) cm^{-1}. NMR: δ 8.9 (s, 2H, C$\underline{H}$=N), 7.8–7.7 (m, 4H, thiophen-3, 4H; $J_{3,4}$ 2.8 Hz), 3.75–2.95 (m, 16H, morpholino H).

Hydrazides and hydrazones (**1f, 1g, 2e, 2f**). These were obtained by stirring the sulfonyl chloride (0.01 mole) with hydrazine hydrate (0.06 mole of 98%) in methanol (30 ml) at 0°C. The mixture was left at room temperature for 3 hours and poured onto ice-water (60 ml); the precipitate was filtered off, washed with water and dried *in vacuo* to give **1f** (Table I). Beilstein test for Cl was negative; IR spectrum showed NH stretch (3300 cm^{-1}).

The product (**1f**) was refluxed with acetone (8 ml) in the presence of concentrated sulfuric acid (1 drop) for 5 minutes to give the acetone hydrazone (**1g**).

Reaction of *o*-anisaldehyde-5,5'-disulfonyl chloride (**2a**) with hydrazine gave the hydrazide (93%) which decomposed, but was characterised by formation of the acetone hydrazone (**2e**). Warming the hydrazide (0.005 mole) with *p*-nitrobenzaldehyde (0.01 mole) in dry THF (10 minutes) gave the hydrazone (**2f**) (Table I).

Compound (**1f**). IR ν_{max} 3300, 3180 (NH), 1620 (ArC=C), 1350, 1160 (SO_2) cm^{-1}.

Compound (**1g**). TLC showed one spot, R_F 0.24 (1:1 CH_2Cl_2-isopropyl ether). IR ν_{max} 3210 (NH), 1630 (ArC=C), 1330, 1160 (SO_2) cm^{-1}. NMR δ 10.2* (s, 2H, NH), 8.9 (s, 2H, C$\underline{H}$=N), 8.2–7.6 (m, 6H, ArH), 1.9 (s, 12H, N=CMe_2).

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