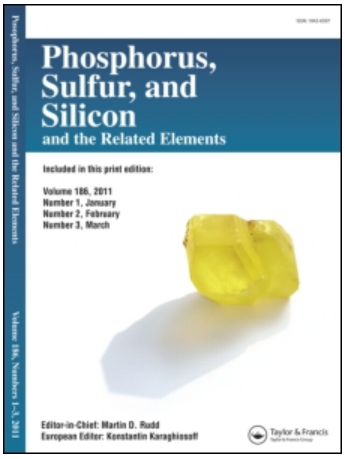


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# CHLOROSULFONATION OF SOME POLYNUCLEAR HETEROCYCLIC COMPOUNDS

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# CHLOROSULFONATION OF SOME POLYNUCLEAR HETEROCYCLIC COMPOUNDS

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Dibenzofuran (**1**), dibenzothiophen (**20**) and the 5,5-dioxide (**29**), carbazole (**43**) and fluorene (**50**) have been reacted with chlorosulfonic acid. The resultant sulfonyl chlorides (**2**, **12**, **18**, **21**, **23**, **27**, **30**, **37**, **44**, **46** and **51**) were condensed with amines and hydrazine to afford 32 derivatives for biological screening. The orientation of chlorosulfonation has been determined by NMR spectral analysis and is compared with the chlorosulfonation of the analogous acyclic compounds. Selected compounds were tested as potential pest control agents.

*Key words:* Dibenzofuran; dibenzothiophen; carbazole; fluorene; chlorosulfonation.



## INTRODUCTION

The work described in this paper, the chlorosulfonation of dibenzofuran, dibenzothiophen, carbazole and fluorene, forms part of our general programme concerned with the chemistry and biological activity of arylsulfonyl derivatives.[1–3] In particular, it extends the results previously obtained[4–6] for the chlorosulfonation of the analogous bridged acyclic compounds of general type (Ph X Ph, where X = O, S, NH and $CH_2$ respectively).

## DISCUSSION

With dibenzofuran (**1**) (Chart 1) sulfonation is known[7,8] to occur preferentially in the 2- and 2,8- positions (*para* to the strongly electron-donating oxygen atom).

The 2-sulfonyl chloride (**2**) was prepared by reaction of (**1**) with chlorosulfonic acid (1 mol equivalent) in carbon tetrachloride followed by heating the sodium sulfonate with phosphorus oxychloride as previously described.[9] We however found that the last step was achieved in higher yield (82%) by using thionyl chloride. The chloride (**2**) was also obtained by heating (**1**) with chlorosulfonic acid (1 mol equivalent) in thionyl chloride. The chloride (**2**) was condensed with amines to give a range of sulfonamides (**3–6**); treatment with hydrazine afforded the hydrazide (**7**) which reacted with carbonyl compounds to give the derivatives (**8–11**) (Chart 1 and Table I).

Dibenzofuran (**1**) by boiling with chlorosulfonic acid (2 mol equivalents) in thionyl chloride, gave an excellent yield (89%) of the 2,8-disulfonyl chloride (**12**).

Treatment of (**1**) with chlorosulfonic acid (6 mol equivalents) in carbon tetrachloride at room temperature and 50°C gave lower yields of (**12**) (50 and 45% respectively).

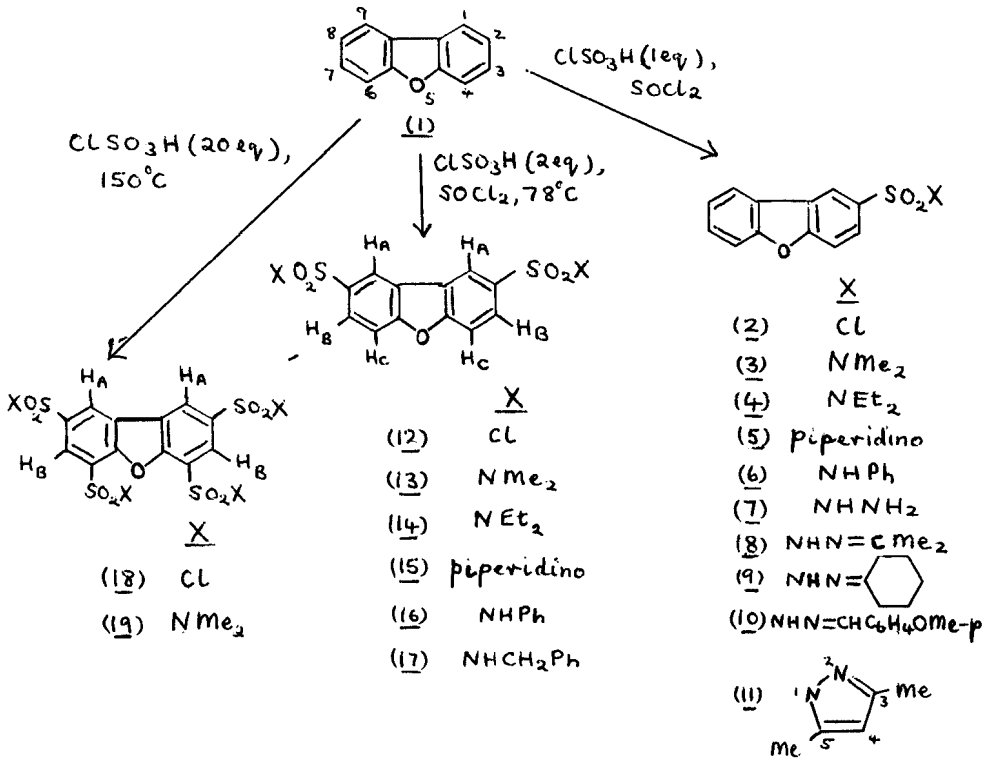


CHART 1 Sulfonyl derivatives of dibenzofuran (**1**)

The disulfonyl chloride (**12**) was condensed with amines to yield the sulfonamides (**13**–**17**) (Chart 1).

Dibenzofuran on reaction with a large excess (20 mol equivalents) of chlorosulfonic acid at room temperature afforded a mixture of the di- and trisulfonyl chlorides. Subsequent condensation with dimethylamine gave the corresponding dimethylsulfonamides: 2 spots on TLC and MS showed molecular ions at 382 and 488. On the other hand when the reaction mixture was heated at 150°C, dibenzofuran (**1**) was converted into the tetrasulfonyl chloride (**18**), which was characterized as the dimethylsulfonamide (**19**).

The product gave one spot (TLC), MS showed the molecular ion ($M^+$, 596) and the pmr spectrum exhibited an AB splitting pattern in the aromatic region. The aromatic protons HA and HB resonated as doublets ($\delta$ 8.3, 9.3 respectively) with a coupling constant $J$, 3.1 Hz indicative of *meta* coupling. The HB protons are shifted downfield due to the powerful deshielding effect of the two adjacent dimethylsulfamoyl groups. The methyl protons of the dimethylsulfamoyl groups resonated as two distinct singlets ($\delta$ 2.8, 3.0) and the spectrum showed the correct aliphatic/aromatic ratio of 6:1 in agreement with the proposed structure (**19**).

The formation of the tetrasulfonyl chloride (**18**) is in contrast to the behaviour of the acyclic analogue, diphenyl ether, which only affords the 2,4,4′-trisulfonyl chloride under comparable conditions.[10] The difference is probably due to the

TABLE I

Analytical data of the prepared compounds

| Comp No | Yield (%) | m.p. (°C) | molecular formula | microanalysis found (calc.) % C | H | N | MS ($M^+$) |
|---|---|---|---|---|---|---|---|
| 2 | 82 | 133-135[a] | $C_{12}H_7ClO_3S$ | | | | 266* |
| 3 | 78 | 129-131 | $C_{14}H_{13}NO_3S$ | 61.4 (61.1) | 4.8 (4.7) | 5.9 (5.2) | 275 |
| 4 | 41 | 127-128 | $C_{16}H_{17}NO_3S$ | 63.2 (63.4) | 5.7 (5.6) | 4.6 (4.6) | 303 |
| 5 | 75 | 157-158 | $C_{17}H_{17}NO_3S$ | 64.5 (64.7) | 5.5 (5.4) | 4.5 (4.5) | 315 |
| 6 | 65 | 174-176 | $C_{18}H_{13}NO_3S$ | 66.7 (66.8) | 4.0 (4.0) | 4.4 (4.3) | 323 |
| 7 | 50 | 202 | $C_{12}H_{10}N_2O_3S$ | | | | 262 |
| 8 | 20 | 148 | $C_{15}H_{14}N_2O_3S$ | 59.7 (59.6) | 4.6 (4.6) | 8.3 (8.8) | 302 |
| 9 | 19 | 159 | $C_{18}H_{18}N_2O_3S$ | 62.8 (63.2) | 5.2 (5.3) | 8.8 (8.2) | 342 |
| 10 | 33 | 160-161 | $C_{20}H_{16}N_2O_4S$ | 63.0 (63.2) | 4.0 (4.2) | 7.6 (7.4) | |
| 11 | 34 | 180-181 | $C_{17}H_{14}N_2O_3S$ | 61.9 (62.5) | 4.1 (4.2) | 8.3 (8.5) | 326 |
| 12 | 89 | 215-217[b] | $C_{12}H_6Cl_2O_5S_2$ | | | | 364* |
| 13 | 93 | 125-127 | $C_{16}H_{18}N_2O_5S_2$ | 50.6 (50.3) | 4.6 (4.7) | 7.0 (7.3) | 382 |
| 14 | 62 | 192-194 | $C_{20}H_{26}N_2O_5S_2$ | 54.9 (54.8) | 6.0 (5.9) | 6.2 (6.4) | 438 |
| 15 | 40 | 195-196 | $C_{22}H_{26}N_2O_5S_2$ | 56.0 (56.1) | 5.4 (5.6) | 5.8 (6.1) | 462 |
| 16 | 60 | 276 | $C_{24}H_{18}N_2O_5S_2$ | 60.6 (60.3) | 3.6 (3.7) | 5.6 (5.8) | 478 |
| 17 | 68 | 210-211 | $C_{26}H_{22}N_2O_5S_2$ | 61.4 (61.7) | 4.2 (4.3) | 5.6 (5.5) | 506 |
| 18 | 52 | 165 | $C_{12}H_4Cl_4O_9S_4$ | | | | 530* |
| 19 | 57 | 335 | $C_{20}H_{28}N_4O_9S_4$ | 40.0 (40.3) | 4.7 (4.7) | 9.1 (9.4) | 596 |

a) lit [9] 140°C
b) lit [9] 219°C

* = lowest molecular ion of the ion cluster quoted.

capacity of *ortho*-substituted chlorosulfonyl diphenyl ether derivatives to cyclise to the corresponding sulfones.

Benzofuran-2-sulfonic acid has been prepared by treatment of benzofuran with sulphur trioxide-pyridine complex,[11] however attempted reaction with chlorosulfonic acid (1 mol equivalent) in thionyl chloride at 0°C appeared to cause acid-catalysed polymerization of the substrate. The product was a high molecular mass ($M^+$, 368) brown solid m.p. > 360°C; repetition of the reaction in dioxan was also unsuccessful.

Dibenzothiophen (**20**), like dibenzofuran (**1**), undergoes preferential sulfonation in the 2- and 2,8-positions[7,8]; these positions are relatively unhindered and are *para* to the electron-donating sulfur atom. (**20**) by reaction with chlorosulfonic acid (1.1

mol equivalent) in thionyl chloride afforded the 2-sulfonyl chloride (**21**, 62%), characterized as the dimethylsulfonamide (**22**) (Chart 2 and Table III). The pmr spectrum showed the aromatic protons as a complex multiplet ($\delta$ 7.3–8.5, 7H) and the methyl protons resonated as a singlet ($\delta$ 3.0, 6H); the mass spectrum showed the molecular ion ($M^+$, 291). When (**20**) was treated with more chlorosulfonic acid (6 mol equivalents or 2.1 equivalents in thionyl chloride), the 2,8-disulfonyl chloride (**23**) was isolated (87%); this was condensed with amines to give the sulfonamides (**24–26**). The pmr spectrum of the dimethylsulfonamide (**24**) showed the aromatic proton resonances as a well-defined ABC splitting pattern ($\delta$ 7.9–8.6, 6H) and the methyl protons as a singlet ($\delta$ 2.9, 12H). Comparison of the spectrum with that of the corresponding derivative from dibenzofuran (**13**) (Chart 1) indicated considerable difference in the shielding effects of the oxygen and sulfur atoms on the 4 and 6 positions. In **13**, the HA, HB and HC protons resonated at $\delta$ 8.75, 8.40 and 7.95. In accord with expectations; the HA, HB protons appeared downfield as a result of the deshielding effect of the adjacent dimethylsulfamoyl groups, while the HC proton is relatively shielded by the +M effect of the hetero oxygen atom. In contrast, the pmr spectrum of (**24**) showed that the analogous HC proton ($\delta$ 8.10) was less deshielded than the HB proton ($\delta$ 7.90). These results are in good agreement with data[12] on the shielding of *o*, *m* and *p*-protons of the phenyl ring by mesomeric effect of oxygen and sulfur atoms as illustrated in Table II.

The results (Table II) clearly demonstrate the deshielding effect of the sulfur atom on the *ortho* proton and the weak overlap of the sulfur lone pair of electrons with the Π-electron cloud of the phenyl ring.

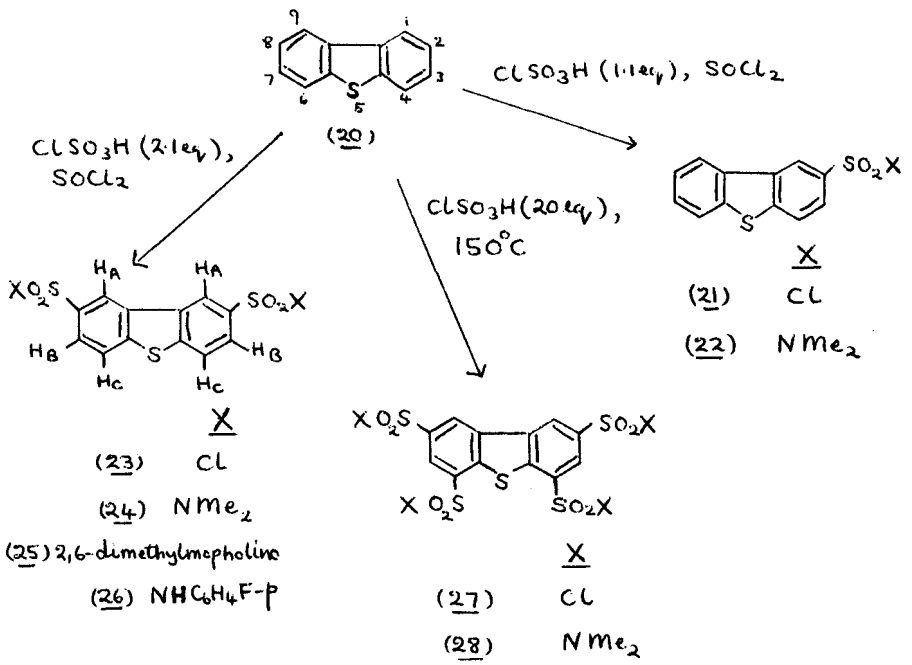


CHART 2 Sulfonyl derivatives of dibenzothiophen (**20**)

TABLE II

Positions of proton resonances in PhX as cf. X=H

| Z = 7.26 | | | |
|---|---|---|---|
| X | $Z^{X}_{o}$ | $Z^{X}_{m}$ | $Z^{X}_{p}$ |
| -OPh | -0.29 | -0.05 | -0.23 |
| -S Ph | +0.06 | -0.09 | -0.15 |

TABLE III

Physical data for dibenzothiophen sulfonyl derivatives

| Comp No | Yield (%) | m.p. (°C) | molecular formula | microanalysis found (calc.) % C | H | N | MS ($M^+$) |
|---|---|---|---|---|---|---|---|
| 21 | 62 | >300 | $C_{12}H_7ClO_2S_2$ | | | | 282* |
| 22 | 32 | 130-132 | $C_{14}H_{13}NO_2S_2$ | 57.5 (57.7) | 4.5 (4.5) | 4.6 (4.8) | 291 |
| 23 | 87 | 280-281 | $C_{12}H_6Cl_2O_4S_3$ | 38.0 (37.8) | 1.7 (1.6) | 18.7 (18.6) | 380* |
| 24 | 74 | 250-251 | $C_{16}H_{18}N_2O_4S_3$ | 48.5 (48.2) | 4.4 (4.5) | 6.5 (7.0) | 398 |
| 25 | 74 | 215-217 | $C_{24}H_{30}N_2O_6S_3$ | 53.4 (53.5) | 5.3 (5.6) | 5.0 (5.2) | 538 |
| 26 | 38 | 232 | $C_{24}H_{16}F_2N_2O_4S_3$ | 53.9 (54.3) | 2.7 (3.0) | 5.4 (5.3) | 530 |
| 27 | 45 | 195 | $C_{12}H_4Cl_4O_8S_5$ | | | | 576* |
| 28 | 65 | 245-247 | $C_{20}H_{28}N_4O_8S_5$ | 39.1 (39.2) | 4.5 (4.6) | 8.9 (9.2) | 612 |

* = lowest molecular ion of the ion cluster quoted



When dibenzofuran (**20**) was refluxed with a large excess of chlorosulfonic acid (20 mol equivalents) the tetra-sulfonyl chloride (**27**) was isolated (45%); this was characterized by formation of the dimethylsulfonamide (**28**). MS showed the molecular ion ($M^+$, 612) and the pmr spectrum displayed an AB splitting pattern in the aromatic resonances ($\delta$ 8.2–9.4, 4H) with a meta-coupling constant ($J$, 2.5 Hz). The methyl protons of the dimethylsulfamoyl groups appeared as two distinct signals ($\delta$ 2.8, 2.9, 24H). The spectral data are therefore consistent with 2,4,6,8-tetrasulfonation as shown for compound (**28**). Our results indicate that dibenzofuran (**1**) is more reactive towards chlorosulfonic acid than dibenzothiophen (**20**) which is to be expected because oxygen has a more powerful (+M) mesomeric effect as compared with sulfur. Studies by Taylor[13] showed that the *ortho*-positions in diphenyl ether were appreciably more reactive to electrophilic substitution than the analogous positions in diphenyl sulfide. However, in the heterocyclic systems there was little difference in reactivity of the *ortho*-positions, possibly because the thiophen ring in dibenzothiophen is less strained than the furan ring in dibenzofuran.[13]

Dibenzothiophene-5,5-dioxide (**29**) (Chart 3 and Table IV) by heating with a large excess of chlorosulfonic acid (10 mol equivalents) gave the 3,7-disulfonyl chloride (**30**) (70%) which was converted into the sulfonamides (**31–36**). The pmr spectrum of the dimethylsulfonamide (**32**) showed the aromatic resonances ($\delta$ 8.2–

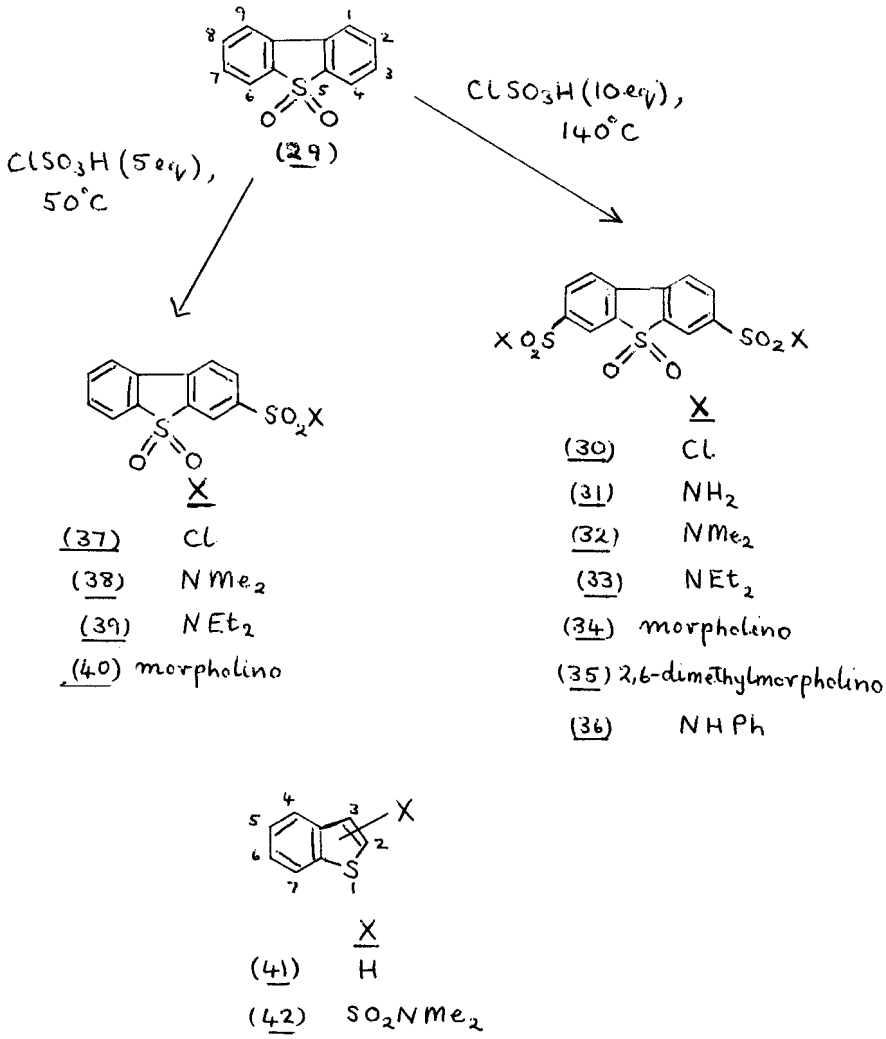


CHART 3 Sulfonyl derivatives of dibenzothiophen-5,5-dioxide (**29**)

8.7, 6H) as a clearly defined ABC splitting pattern indicative of symmetrical sulfonation and the methyl protons as a singlet ($\delta$ 2.8, 12H).

Treatment of (**29**) with chlorosulfonic acid (5 mol equivalents) at 50°C gave the 3-sulfonyl chloride (**37**) (65%); condensation with amines afforded the derivatives (**38**–**40**).

The electron withdrawing character of the sulfonyl group in the 5,5-dioxide (**29**) is reflected in the more forcing conditions required for chlorosulfonation as compared with dibenzothiophen (**20**) (Charts 1 and 2). It also accounts for the preferred orientation of sulfonation at the 3- and 3,7-positions since these are *meta* to the sulfonyl group and *ortho*/*para* with respect to the bridge bond.[7]

The preferred orientation of sulfonation of the 5,5-dioxide (**29**) would be expected to be the 3- and 3,7-positions as a result of the electron-withdrawing nature

TABLE IV

Physical data for sulfonyl derivatives of dibenzothiophene-5,5-dioxide

| Comp No | Yield (%) | m.p. (°C) | molecular formula | microanalysis found (calc.) % C | H | N | MS ($M^+$) |
|---|---|---|---|---|---|---|---|
| 30 | 70 | 238-240[a] | $C_{12}H_6Cl_2S_3O_6$ | | | | 412* |
| 31 | 54 | 287-288 | $C_{12}H_{10}N_2O_6S_3$ | 38.2 (38.5) | 2.5 (2.7) | 7.5 (7.5) | 374 |
| 32 | 55 | 290-291 | $C_{16}H_{18}N_2O_6S_3$ | 44.6 (44.7) | 4.2 (4.2) | 6.1 (6.5 | 430 |
| 33 | 40 | 184-186 | $C_{20}H_{26}N_2O_6S_3$ | 49.3 (49.4) | 5.3 (5.3) | 5.9 (5.8) | 486 |
| 34 | 70 | 323 | $C_{20}H_{22}N_2O_8S_3$ | 46.2 (46.7) | 4.0 (4.3) | 5.1 (5.1) | 514 |
| 35 | 67 | 304 | $C_{24}H_{30}N_2O_8S_3$ | 50.4 (50.2) | 5.4 (5.3) | 5.2 (5.1) | 570 |
| 36 | 79 | 195-196 | $C_{24}H_{18}N_2O_6S_3$ | 54.5 (54.8) | 3.0 (3.4) | 5.0 (5.3) | 526 |
| 37 | 65 | 265-266 | $C_{12}H_7ClO_4S_2$ | | | | 314* |
| 38 | 90 | 228-229 | $C_{14}H_{13}NO_4S_2$ | 52.1 (52.0) | 4.0 (4.0 | 4.6 (4.3) | 323 |
| 39 | 42 | 163-164 | $C_{16}H_{17}NO_4S_2$ | 55.0 (54.7) | 4.9 (4.8) | 4.4 (4.0) | 351 |
| 40 | 81 | 208-209 | $C_{16}H_{15}NO_5S_2$ | 52.2 (52.6) | 3.9 (4.1) | 4.1 (3.8) | 365 |

a) lit.[26] 236°C

* = lowest molecular ion of the ion cluster quoted.



of the sulfonyl moiety, since these positions are *meta-* to the sulfonyl group and *para* to the bridged bond.[7]

The reaction of benzothiophene (**41**) with sulfonic acid has been reported[14] to yield the 3-sulfonic acid, while other workers[15,16] claimed mixtures of mono-, di- and tri-sulfonic acids. We reacted (**41**) with chlorosulfonic acid (1 mol equivalent) in excess thionyl chloride (2 days, RT) and obtained a high melting point (>300°C) solid which contained chlorine and sulfur (positive sodium fusion test). Condensation with dimethylamine afforded a product with molecular ion ($M^+$, 241) suggesting that it is the dimethylsulfonamide (**42**). The infrared spectrum also confirmed the presence of the $SO_2$ group (absorption bands at 1340, 1150 $cm^{-1}$). However, attempted purification of the product by recrystallization failed so a definite structure was not assigned.

The sulfonation of carbazole (**43**) has been extensively studied[7,8,17-19] and shown to occur preferentially in the 3- and 3,6-positions which are *para* to the strongly electron-donating NH group. Borodkin[17] examined the reaction of chlorosulfonic acid on solutions of carbazole (**43**) in organic solvents, e.g. nitrobenzene and obtained the 3- or 3,6-disulfonic acid depending on the conditions; the former product was also prepared by reaction in carbon tetrachloride.[20] Treatment of (**43**) with chlorosulfonic acid in the presence of varying proportions of phosphorus pentoxide is claimed[21-22] to yield the 3,6-di-, 1,3,6-tri- or 1,3,6,8-tetra-sulfonyl chlorides.

In our work, attempts to prepare carbazole mono- and di-sulfonyl chlorides by reacting (**43**) with chlorosulfonic acid (1 or 2 mol equivalents) in thionyl chloride

were unsuccessful. The product appeared to consist of a mixture of highly chlorinated compounds (4 spots on TLC and MS showed ions at 339, 337 and 335).

A similar result was observed[10] in the reaction of diphenylamine with a mixture of chlorosulfonic acid-thionyl chloride and may indicate that in substrates containing an amino group, chlorination occurs in preference to sulfonation. To substantiate this argument, carbazole (**43**) was treated with an excess of thionyl chloride at room temperature to give a mixture of polychloro derivatives.

Carbazole (**43**) was reacted with chlorosulfonic acid (7 mol equivalents) in chloroform to give the 1,3,6-tri-sulfonyl chloride (**44**, 72%); the product was characterized as the dimethylsulfonamide (**45**) (Chart 4 and Table IV). The pmr spectrum showed AB and ABC splitting patterns in the aromatic region ($\delta$ 7.8–8.8), three resonances ($\delta$ 2.78, 2.79, 2.85) for the methyl protons of the dimethylsulfamoyl groups and a broad singlet ($\delta$ 10.30) which was removed by $D_2O$ treatment, indicating the presence of the NH group. The mass spectrum showed the molecular ion ($M^+$, 488).

Carbazole, by reaction with more chlorosulfonic acid (12 mol equivalents) for 3 days followed by addition of thionyl chloride gave a product that was treated with

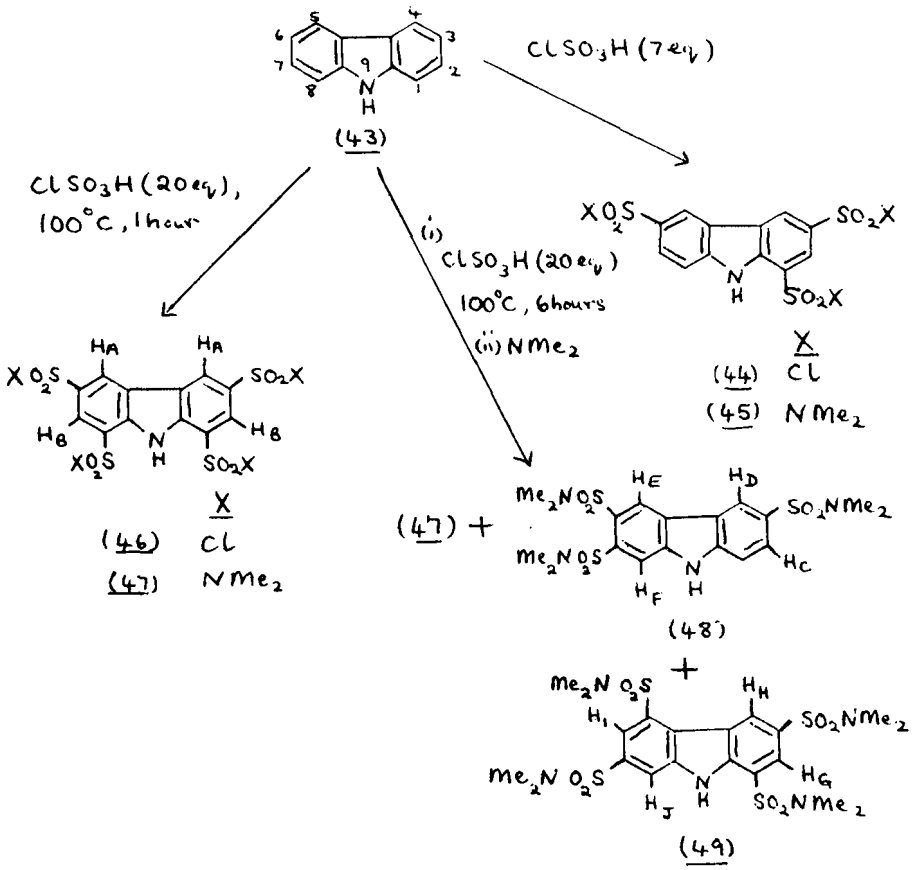


CHART 4 Sulfonyl derivatives of carbazole (**43**)

dimethylamine. The derivative showed 2 spots on TLC and the mass spectrum showed the highest mass ion ($M^+$, 595) corresponding to the tetra-dimethylsulfonamide (**46**).

Repeated recrystallization (ethanol) gave the 1,3,6-trisulfonamide (**45**), which was identical to the previously prepared product. There was no chlorination observed in this reaction; the initial sulfonation probably deactivates the carbazole ring towards chlorination.

When carbazole was reacted with a large excess of chlorosulfonic acid (20 mol equivalents) at room temperature a mixture of tri- and tetra-sulfonyl chlorides (**44**, **46**) was obtained (Chart 4, Table V).

On the other hand, when the mixture was heated at 100°C for 1 hour, the 1,3,6,8-tetra-sulfonyl chloride (**46**) was obtained in low yield (27%). The product was characterized as the dimethylsulfonamide (**47**); the pmr spectrum showed a well-defined AB splitting pattern in the aromatic region ($\delta$ 8.3–8.9) with the methyl resonances as a doublet ($\delta$ 2.80, 2.85) and the NH proton as a broad singlet ($\delta$ 11.10) which was reduced by treatment with $D_2O$.

In contrast, Karpukhin *et al.*[18] reported the formation of the 2,3,6,8-tetrasulfonic acid and this reaction is believed to involve the sulfonation of the N-protonated trisulfonic acid (**44**, X = H). The protonated NH group would be *meta*-directing and should therefore direct the last sulfonic acid group into the 3-position.

The relative case of formation of carbazole tetrasulfonyl chloride (**46**) as compared with the tetrasulfonation of dibenzofuran (**1**) and dibenzothiophen (**20**) is rather surprising since any protonation of the NH group would deactivate the phenyl rings. However, Borodkin[17] showed that carbazole (**43**) reacted with chlorosulfonic acid in dimethylaminobenzene to yield the N-sulfonic acid and this is unstable in acidic media. The facile migration of the $SO_3H$ group into the adjacent 1- and 8-positions may explain why sulfonation into these positions is more favorable than for the analogous positions in (**1**) and (**20**).

In an attempt to improve the yield of the tetra-sulfonyl chloride (**46**) the reaction of carbazole with chlorosulfonic acid (20 mol equivalents) was heated for a longer period (6 hours). This afforded an improved yield (55%) of a product, but after treatment with dimethylamine the derivative showed 2 spots on TLC ($R_F$ 0.40, 0.24). The mass spectrum showed the highest molecular ion ($M^+$, 595) in agreement with the tetradimethylsulfonamide derivative, while the pmr spectrum indicated

TABLE V

Physical data for sulfonyl derivatives of carbazole

| Comp No | Yield (%) | m.p. (°C) | molecular formula | microanalysis found (calc.) % C | H | N | MS ($M^+$) |
|---|---|---|---|---|---|---|---|
| 44 | 72 | 208-210 | $C_{12}H_6Cl_3NO_6S_3$ | | | | 461* |
| 45 | 84 | 290-291 | $C_{18}H_{24}N_4O_6S_3$ | 44.7 (44.3) | 5.2 (5.0) | 10.8 (10.7) | 488 |
| 46 | 27 | 275-277 | $C12H_5Cl_4NO_8S_4$ | | | | 559* |
| 47 | 68 | 307-308 | $C_{20}H_{29}N_5O_8S_4$ | 40.2 (40.3) | 5.1 (4.9) | 11.9 (11.8) | 595 |

* = lowest molecular ion of the ion cluster.

three NH proton resonances ($\delta$ 11.18, 12.18 and 12.50) this suggested the presence of three isomeric sulfonamides (**47**, **48** and **49**) (Chart 4). The presence of a mixture of these three compounds was indicated by analysis of the aromatic proton resonances as follows: $\delta$ $H_D$, $H_J$ (8.26), $H_A$ (8.29), $H_I$ (8.31), $H_G$ (8.41), $H_F$ (8.50), $H_B$, $H_C$ (8.82), $H_E$ (9.04), $H_H$ (9.46) and by the microanalytical results on the mixture (Found: C, 40.5; H, 5.0; N, 11.5. $C_{20}H_{29}N_5O_8S_4$ requires: C, 40.3; H, 4.9; N, 11.8%). Carbazole-2,3,6,8 tetrasulfonyl chloride (**48**) is probably derived from the protonated 1,3,6-trisulfonyl chloride (**44**), although the presence of the 1,3,5,7-tetrasulfonyl chloride (**49**) is surprising because it involves sulfonation *o*/*p*- to the bridged bond in one ring (protonated NH form) but in the other ring the orientation is apparently controlled by the +M effect of the amino group.

The results demonstrated that greater selectivity of chlorosulfonation was possible in carbazole as compared with the acyclic analogue, diphenylamine, in which all attempts to reproduce the reported preparation [23] of the 4,4′-disulfonyl chloride were unsuccessful. The only isolated product from the reaction of diphenylamine with chlorosulfonic acid was the 2,2′,4,4′-tetrasulfonyl chloride.[5]

In fluorene (**50**), the favored positions for electrophilic substitution are the 2,7 and 4,5-positions which are *o*/*p* with respect to the bridge bond due to the effect of through conjugation between the rings.[24] Thus, reaction of (**50**) with sulfuric acid has been reported[25] to give the 2,7-disulfonic acid; on the other hand, (**50**) with chlorosulfonic acid (6 or 12 mol equivalents or 3 equivalents in thionyl chloride) afforded a mixture of the 2- and 2,7-disulfonyl chloride.[6] In the current work, fluorene (**50**) was treated with a large excess (20 mol equivalents) of chlorosulfonic acid at room temperature to give the 2,4,7-trisulfonyl chloride (**51**, 45%) (Chart 5). The same product (**51**) was also isolated when the reaction mixture was heated at 100°C (5 hours) or at 150°C (4 hours). Attempts to characterize the trisulfonyl chloride (**51**) by condensation with dimethylamine failed to give a pure derivative, but with morpholine, the pure morpholidate (**52**) was obtained. The mass spectrum of (**52**) showed the molecular ion ($M^+$, 613) and there was no evidence of the tetra substituted derivative ($M^+$, 762). The pmr spectrum showed well-defined AB and ABC splitting patterns in the aromatic region ($\delta$ 7.8–8.9); the 5-H proton resonated at relatively low field ($\delta$ 8.9) probably as a consequence of the deshielding influence of the 4-sulfonyl group.

The 4-position in fluorene shows a greater reactivity than the corresponding *ortho*-position in biphenyl, probably due to reduced steric hindrance an additional factor may be the coplanarity of the aromatic rings in (**50**) permitting increased resonance interaction.

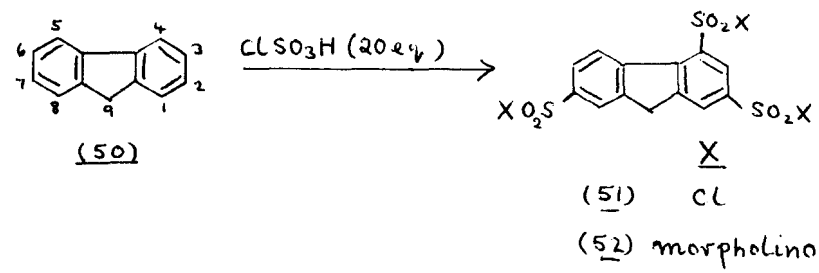


CHART 5 Sulfonyl derivatives of fluorene (**50**)

The polynuclear heterocyclic compounds (**1**, **20**, **43**) all gave the tetrasulfonyl chlorides by reaction with a large excess of chlorosulfonic acid, the exception was fluorene (**50**) which only afforded the trisulfonyl derivative. With the acyclic analogues, PhXPh (X = Bond, O, S, NH and $CH_2$ respectively), only diphenylamine afforded the tetrasulfonyl chloride. In these compounds, the situation is complicated by possible cyclisation of the polysulfonyl chlorides to cyclic sulfone derivatives.[10]

Selected compounds have been screened for biocidal properties against a range of target insects, fungi and weeds but none showed appreciable activity.

## EXPERIMENTAL

Melting points were determined using a Gallenkamp electric apparatus and are uncorrected. The pmr spectra were recorded with a Bruker AC250 spectrometer using tetramethylsilane as internal standard and deuterochloroform as solvent unless otherwise stated. Resonances indicated by an asterisk were removed by $D_2O$ treatment. I.R. spectra were recorded as KBr discs using a Perkin-Elmer 237 spectrophotometer. Mass spectra were determined with a VG micromass V15 spectrometer operating at 70 eV. TLC was carried out using Camlab silica gel plates sensitized the UV 256 nm and ethyl acetate-cyclohexane (1:2) for the sulfonyl chlorides or petroleum ether-ethylacetate (2:3) as eluants for the derivatives unless otherwise stated.



*Dibenzofuran-2-sulfonyl chloride* (**2**)

*Method 1:* Chlorosulfonic acid (24.5 g, 0.21 mol) was added dropwise over 15 minutes to a stirred solution of dibenzofuran (**1**) (33.6 g, 0.2 mol) in dry carbon tetrachloride (100 ml) at room temperature. After 45 minutes, the aqueous layer was extracted with ether and neutralized with 10% aqueous sodium carbonate to give the sodium sulfonate (16.6 g, 42%), m.p. > 300°C. The dry product (5 g, 0.02 mol) was refluxed with thionyl chloride (20 ml) for 5½ hours and the solution poured onto crushed ice to give the sulfonyl chloride (4.1 g, 82%).

*Method 2:* Chlorosulfonic acid (4.9 g, 0.042 mol) was added to a solution of dibenzofuran (6.7 g, 0.04 mol) in thionyl chloride (20 ml) at 0°C. The mixture was refluxed for 3 hours and allowed to cool to room temperature. The solution was poured onto crushed ice and the resultant gum immediately treated with dimethylamine.

The crude product was recrystallized from ethanol to give the dimethylsulfonamide (6.8 g). TLC showed 1 spot $R_F$ 0.37. IR $\upsilon_{max}$ 1600 (ArC=C), 1350, 1140 ($SO_2$) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.4–7.3 (m, 7H, ArH), 2.7 (s, 6H, $CH_3$). MS: 275 ($M^+$), 260 ($M^+$-Me), 231 ($M^+$-$NMe_2$), 167 ($M^+$-$SO_2NMe_2$).

*Dibenzofuran-2,8-disulfonyl chloride* (**12**). Chlorosulfonic acid (9.8 g, 0.084 mol) was added dropwise to a solution of dibenzofuran (**1**) (6.7 g, 0.04 mol) in thionyl chloride (20 ml). The solution was refluxed for 3 hours and poured onto crushed ice. The precipitate was filtered off, washed with water and dried to give the disulfonyl chloride (12.92 g, 89%).

*Dibenzofuran-2,4,6,8-tetrasulfonyl chloride* (**18**). Dibenzofuran (**1**) (10 g, 0.06 mol) was gradually added to chlorosulfonic acid (138 g, 1.2 mol) at room temperature. The solution was refluxed for 4 hours, allowed to cool to room temperature and slowly poured onto crushed ice to give (**18**) (17.3 g, 52%) TLC showed 1 spot $R_F$ 0.66.

*Dibenzothiophen-2-sulfonyl chloride* (**21**). Chlorosulfonic acid (7.1 g, 0.061 mol) was gradually added to dibenzothiophen (**20**) (10 g, 0.054 mol) in thionyl chloride (20 ml). The mixture was left at room temperature for 10 days and poured onto ice, the resultant precipitate was filtered off, washed with water and dried to give (**21**) (9.45 g, 62%). TLC showed 1 spot $R_F$ 0.79. IR $\upsilon_{max}$ 1600 (ArC=C), 1340, 1150 ($SO_2$) $cm^{-1}$. MS: 286, 284, 282 ($M^+$), 247 ($M^+$-Cl), 183 ($M^+$-$SO_2Cl$).

*Dibenzothiophen-2,8-disulfonyl chloride* (**23**). Chlorosulfonic acid (13.4 g, 0.11 mol) was added dropwise to a solution of dibenzothiophen (**20**) (10 g, 0.054 mol) in thionyl chloride at 0°C. The mixture was left at room temperature for 10 days and poured onto crushed ice. The light yellow precipitate was filtered off and the solid recrystallized from petroleum ether (bp 60–80°C) to give (**23**) (17.97 g, 87%). TLC showed 1 spot $R_F$ 0.70. IR $\upsilon_{max}$ 1610 (ArC=C), 1350, 1170 ($SO_2$) $cm^{-1}$. MS: 384, 382, 380 ($M^+$), 347, 345 ($M^+$-Cl), 283, 281 ($M^+$-$SO_2Cl$), 182 ($M^+$-$(SO_2Cl)_2$).

*Dibenzothiophen-2,4,6,8-tetrasulfonyl chloride* (**27**). Dibenzothiophen (**20**) (10 g, 0.054 mol) was refluxed with chlorosulfonic acid (134 g, 1.1 mol) for 4 hours, the mixture was allowed to cool to room temperature and was poured onto crushed ice to give (**27**) (11.7 g, 45%). TLC showed 1 spot $R_f$ 0.79.

*Dibenzothiophen-5,5-dioxide-3,7-disulfonyl chloride* (**30**). Dibenzothiophen-5,5-dioxide (**29**) (10.9 g, 0.05 mol) was heated with chlorosulfonic acid (58 g, 0.5 mol) at 140°C for 4 hours. Addition of the reaction mixture to crushed ice afforded (**30**) (12.3 g, 70%). IR $\upsilon_{max}$ 1600 (ArC=C), 1370, 1160 ($SO_2$) $cm^{-1}$. MS: 416, 414, 412 ($M^+$), 379, 377 ($M^+$-Cl), 315, 313 ($M^+$-$SO_2Cl$), 214 ($M^+$-$(SO_2Cl)_2$).

*Dibenzothiophen-5,5-dioxide-3-sulfonyl chloride* (**37**). Dibenzothiophen-5,5-dioxide (5 g, 0.023 mol) was heated with chlorosulfonic acid (13.3 g, 0.12 mol) at 50°C for 2 hours. The mixture was added to crushed ice to give (**37**) (4.75 g, 65%). IR: $\upsilon_{max}$ 1590 (ArC=C), 1370, 1160 ($SO_2$) $cm^{-1}$. MS: 316, 314 ($M^+$), 279 ($M^+$-Cl), 215 ($M^+$-$SO_2Cl$).

*Carbazole-1,3,6-trisulfonyl chloride* (**44**). Chlorosulfonic acid (24.3 g, 0.21 mol) was added dropwise to a suspension of carbazole (**43**) (5 g, 0.03 mol) in chloroform (10 ml). The solution was left for 1 week at room temperature and poured onto crushed ice to give (**44**) (9.9 g, 72%).

*Carbazole-1,3,6,8-tetrasulfonyl chloride* (**46**). Carbazole (**43**) (5 g, 0.03 mol) was heated with chorosulfonic acid (69.5 g, 0.60 mol) at 100°C for 1 hour. The mixture was allowed to cool to room temperature and was gradually added to crushed ice to give (**46**) (4.5 g, 27%).

*General procedure for the preparation of sulfonamides.* The sulfonyl chloride (0.01 mol) was added to a stirred solution of the appropriate amine (0.03 mol)* in ethanol (30 ml). The mixture was stirred for 6 hours at room temperature and added to crushed ice-water mixture. The precipitate was filtered off, washed with water and dried. The crude product was recrystallized from ethanol unless otherwise stated. *With di-, tri- and tetra-sulfonyl chlorides (0.1 mol) larger quantities of the amine (0.6, 0.9 or 1.2 mol) respectively are required.

*Compound* (**4**). TLC showed 1 spot $R_F$ 0.52. IR $\upsilon_{max}$ 1600 (ArC=C), 1330, 1150 ($SO_2$) $cm^{-1}$. $^1H$ NMR; $\delta$ 8.0–7.4 (m, 7H, ArH), 3.6–3.2 (q, 4H, $\underline{CH_2}CH_3$), 1.3–1.0 (t, 6H, $CH_2\underline{CH_3}$). MS: 303 ($M^+$), 288 ($M^+$-$CH_3$), 231 ($M^+$-$NEt_2$), 167 ($M^+$-$SO_2NEt_2$).

*Compound* (**5**). Purified by recrystallization from toluene TLC showed 1 spot $R_F$ 0.53. IR $\upsilon_{max}$ 1610 (ArC=C), 1350, 1160 ($SO_2$) $cm^{-1}$. $^1H$ NMR (DMSO $d_6$): $\delta$ 8.1–7.2 (m, 7H, ArH), 3.1–1.1 (m, 10H, alkyl-H). MS: 315 ($M^+$), 231 ($M^+$-$NC_5H_{10}$), 167 ($M^+$-$SO_2NC_5H_{10}$).

*Compound* (**13**). TLC showed 1 spot $R_F$ 0.40. IR $\upsilon_{max}$ 1600 (ArC=C), 1350, 1150 ($SO_2$) $cm^{-1}$. 1H NMR: $\delta$ 8.8–7.9 (m, 6H, ArH, ABC pattern), 2.9 (s, 12H, $CH_3$). MS: 382 ($M^+$), 338 (M-$NMe_2$), 274 ($M^+$-$SO_2NMe_2$), 166 (M-$(SO_2NMe_2)_2$).

*Compound* (**15**). TLC showed 1 spot $R_F$ 0.34. IR $\upsilon_{max}$ 1600 (ArC=C), 1350, 1160 ($SO_2$) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.6–7.7 (m, 6H, ArH, ABC pattern), 3.2–1.2 (m, 20H, alkyl H). MS: 462 ($M^+$), 378 ($M^+$-$NC_5H_{10}$). 167 ($M^+$-$SO_2NC_5H_{10}$).

*Compound* (**19**). TLC showed 1 spot $R_F$ 0.23. IR $\upsilon_{max}$ 1610 (ArC=C), 1350, 1160 ($SO_2$) $cm^{-1}$. $^1H$ NMR [$(CD_3)_2CO$]: $\delta$ 9.3–8.3 (dd, 4H, ArH), 3.0 (s, 12H, $CH_3$), 2.8 (s, 12H, $CH_3$).

*Compound* (**22**). TLC showed 1 spot $R_F$ 0.85. IR $\upsilon_{max}$ 1610 (ArC=C), 1350, 1160 ($SO_2$) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.6–7.4 (m, 7H, ArH), 2.8 (s, 6H, $CH_3$). MS: 291 ($M^+$), 247 (M-$NMe_2$), 183 ($M^+$-$SO_2NMe_2$).

*Compound* (**24**). TLC showed 1 spot $R_F$ 0.63. IR $\upsilon_{max}$ 1600 (ArC=C), 1340, 1160 ($SO_2$) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.6–7.9 (m, 6H, Ar-H, ABC pattern), 2.9 (s, 12H, $CH_3$). MS: 398 ($M^+$-$NMe_2$), 354 ($M^+$-$NMe_2$), 290 ($M^+$-$SO_2NMe_2$), 246 ($M^+$-$SO_2NMe_2$, -$NMe_2$), 182 [$M^+$-$(SO_2NMe_2)_2$].

*Compound* (**28**). TLC showed 1 spot $R_F$ 0.28. IR $\upsilon_{max}$ 1590 (ArC=C), 1360, 1150 ($SO_2$) $cm^{-1}$. $^1H$ NMR [$(CD_3)_2CO$]: $\delta$ 9.4–8.2 (2d, 4H, ArH), 2.9 (s, 12H, $CH_3$), 2.8 (s, 12H, $CH_3$). MS: 612 ($M^+$), 504 ($M^+$-$SO_2NMe_2$), 396 ($M^+$-$(SO_2NMe_2)_2$).

*Compound* (**31**). TLC showed 1 spot $R_F$ 0.11. IR $\upsilon_{max}$ 3330 ($NH_2$). 1600 (ArC=C), 1350, 1160 ($SO_2$) $cm^{-1}$. $^1H$ NMR (DMSO $d_6$): $\delta$ 8.6–8.1 (m, 6H, ArH, ABC pattern), 7.5* (s, 4H, $NH_2$) MS: 374 ($M^+$), 214 ($M^+$-$(SO_2NH_2x2)$).

*Compound* (**32**). TLC showed 1 spot $R_F$ 0.72. IR $\upsilon_{max}$ 1610 (ArC=C), 1350, 1170 ($SO_2$) $cm^{-1}$. $^1H$ NMR (DMSO $d_6$): $\delta$ 8.7–8.2 (m, 6H, ArH, ABC pattern), 2.8 (s, 12H, $CH_3$). MS: 430 ($M^+$), 386 ($M^+$-$NMe_2$), 322 ($M^+$-$SO_2NMe_2$), 214 ($M^+$-$SO_2NMe_2x2$).

*Compound* (**38**). TLC showed 1 spot $R_F$ 0.37. IR $\upsilon_{max}$ 1600 (ArC=C), 1350, 1150 ($SO_2$) $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 8.6–7.6 (m, 7H, ArH), 2.8 (s, 6H, $CH_3$). MS: 323 ($M^+$), 308 ($M^+$-$CH_3$), 279 ($M^+$-$NMe_2$), 215 ($M^+$-$SO_2NMe_2$).

*Compound* (**40**). TLC showed 1 spot $R_F$ 0.21. $^1$H NMR (DMSO-$d_6$): $\delta$ 8.6–7.5 (m, 7H, ArH), 3.8–2.9 (m, 8H, alkyl H). MS: 365 ($M^+$), 279 ($M^+$-$NC_4H_8O$), 215 ($M^+$-$SO_2NC_4H_8O$).

*Compound* (**45**). TLC showed 1 spot $R_F$ 0.53. IR $\upsilon_{max}$ 3300 (NH), 1610 (ArC=C), 1370, 1160 ($SO_2$) cm$^{-1}$. $^1$H NMR: $\delta$ 10.3* (s, 1H, NH), 8.8–7.8 (m, 5H, ArH), 2.85 (s, 6H, $CH_3$), 2.79 (s, 6H, $CH_3$), 2.78 (s, 6H, $CH_3$). MS: 488 ($M^+$), 380 ($M^+$-$SO_2NMe_2$), 272 ($M^+$-$SO_2NMe_2)_2$), 164 ($M^+$-$SO_2NMe_2)_3$).

*Compound* (**47**). TLC showed 1 spot $R_F$ 0.40. IR $\upsilon_{max}$ 3250 (NH), 1600 (ArC=C), 1350, 1140 ($SO_2$) cm$^{-1}$. $^1$H NMR: $\delta$ 11.1* (s, 1H, NH), 8.9–8.3 (2d, 4H, ArH), 285 (s, 12H, $CH_3$), 2.80 (s, 12H, $CH_3$), MS: 595 ($M^+$), 551 ($M^+$-$NMe_2$), 487 ($M^+$-$SO_2NMe_2$), 379 ($M^+$-$SO_2NMe_2x_2$).

*Fluorene-2,4,7-trisulfonyl chloride* (**51**). Fluorene (**50**) (5 g, 0.03 mol) was gradually added to chlorosulfonic acid (69 g, 0.6 mol) at 0°C. The solution was left at room temperature (1 week) and poured onto crushed ice to give (**51**) (6.1 g, 45%) m.p. 185°C. TLC showed 1 spot $R_F$ 0.46. The sulfonyl chloride (**51**) reacted with morpholine to give the tri-morpholidate (**52**) (42%), m.p. 230–232°C, TLC showed 1 spot $R_F$ 0.23. (Found: C, 48.6; H, 4.8; N, 6.8. $C_{25}H_{31}N_3O_9S_3$ requires C, 48.9; H, 5.1; N, 6.9%). IR $\upsilon_{max}$ 1600 (ArC=C), 1350, 1170 ($SO_2$) cm$^{-1}$. $^1$H NMR: $\delta$ 8.9–7.8 (m, 5H, ArH), 4.2 (s, 2H, 9-$CH_2$), 3.8–3.0 (m, 24H, alkyl H). MS: 613 ($M^+$), 464 ($M^+$-$SO_2NC_4H_8O$), 313 ($M^+$-$SO_2NC_4H_8O)_2$).

*Dibenzofuran-2-sulfonylhydrazide* (**7**). Dibenzofuran-2-sulfonyl chloride (**2**) (8 g, 0.03 mol) was refluxed with hydrazine hydrate (3.1 g, 0.06 mol) in methanol (40 ml) for 30 minutes. After standing at room temperature (24 hours), the solution was poured onto crushed ice, the precipitate was filtered off, washed with water and dried to give the hydrazide (4.1 g, 50%), m.p. 202°C, TLC showed 1 spot $R_F$ 0.72. IR $\upsilon_{max}$ 3250, 3200 ($NH_2$), 1600 (ArC=C), 1350, 1150 ($SO_2$) cm$^{-1}$. MS: 262 ($M^+$), 246 ($M^+$-$NH_2$), 231 ($M^+$-$NHNH_2$), 167 ($M^+$-$SO_2NHNH_2$).

*Acetone hydrazone* (**8**). TLC showed 1 spot $R_F$ 0.39. IR $\upsilon_{max}$ 3250 (NH), 1600 (ArC=C), 1320, 1160 ($SO_2$) cm$^{-1}$. $^1$H NMR (DMSO-$d_6$): $\delta$ 10.1* (s, 1, NH), 8.3–7.3 (m, 7H, ArH), 1.8 (s, 6H, $CH_3$) MS: 302 ($M^+$), 231 ($M^+$-NHN=$CMe_2$), 167 ($M^+$-$SO_2NHN$=$CMe_2$).

The other hydrazones were prepared as follows: The sulfonyl hydrazide (**7**, 2 g) was dissolved in dry acetonitrile and the carbonyl compound (1 mol equivalent) was added to the solution and the mixture was left 24 hours at room temperature. The resultant precipitate was collected and recrystallized from methanol.

*Cyclohexanone derivative* (**9**). TLC showed 1 spot $R_F$ 0.12. IR $\upsilon_{max}$ 3300 (NH), 1600 (ArC=C), 1350, 1150 ($SO_2$) cm$^{-1}$. $^1$H NMR (DMSO $d_6$): $\delta$ 10.2* (s, 1H, NH), 8.3–7.3 (m, 7H, ArH) 3.3–1.5 (m, 10H, alkyl H). MS: 342 ($M^+$), 331 ($M^+$-$NHNC_6H_{10}$), 167 ($M^+$-$SO_2NHNC_6H_{10}$).

*Compound* (**10**). TLC showed 1 spot $R_F$ 0.54. IR $\upsilon_{max}$ 3250 (NH, 1600 (ArC=C, 1350, 1160 ($SO_2$) cm$^{-1}$. $^1$H NMR: $\delta$ 8.2* (s, 1H, NH), 8.8–6.8 (m, 12H, ArH, CH), 3.8 (s, 3H, $OCH_3$).

*Compound* (**11**). TLC showed 1 spot $R_F$ 0.46. $^1$H NMR (DMSO-$d_6$)): $\delta$ 8.7–7.4 (m, 7H, ArH), 5.8 (s, 1H, pyrazole-4H), 2.6 (s, 3H, $CH_3$), 2.3 (s, 3H, $CH_3$).

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