Synthetic, Infrared, ^{1}H and ^{13}C NMR Spectral Studies on *N*-(2/3/4-Substituted Phenyl)-2,4-Disubstituted Benzenesulphonamides, 2,4-$(CH_3)_2$/2-CH_3-4-Cl/2,4-$Cl_2C_6H_3SO_2NH$(*i*-XC_6H_4) (*i*-X = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-Br)

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Twenty six *N*-(2/3/4-substituted phenyl)-2,4-disubstituted benzenesulphonamides of the general formulae 2,4-$(CH_3)_2C_6H_3SO_2NH$(*i*-XC_6H_4), 2-CH_3-4-$ClC_6H_3SO_2NH$(*i*-XC_6H_4) and 2,4-$Cl_2C_6H_3SO_2NH$(*i*-XC_6H_4), where *i*-X = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-Cl, 3-Cl, 4-Cl, 4-F or 4-Br, have been prepared, characterized and their infrared spectra in the solid state and ^{1}H and ^{13}C NMR spectra in solution studied. The infrared N-H stretching vibrational frequencies vary in the range 3298 – 3233 cm^{-1}. Asymmetric and symmetric SO stretching vibrations appear in the ranges 1373 – 1311 cm^{-1} and 1177 – 1140 cm^{-1}, respectively, while C-S, S-N and C-N stretching absorptions vary in the ranges 840 – 812 cm^{-1}, 972 – 908 cm^{-1} and 1295 – 1209 cm^{-1}, respectively. The various ^{1}H and ^{13}C NMR chemical shifts are assigned to the protons and carbon atoms of the two benzene rings in line with those for similar compounds. The incremental shifts due to the groups in the parent compounds have been computed by comparing the chemical shifts of the protons or carbon atoms in these compounds with those of benzene or aniline, respectively. The computed incremental shifts and other data were used to calculate the ^{1}H and ^{13}C NMR chemical shifts of the substituted compounds in three different ways. The calculated chemical shifts by the three methods compared well with each other and with the observed chemical shifts. It is observed that there are no particular trends in the variation of either the infrared absorption frequencies or the chemical shifts with the nature or site of substitution.

Key words: IR; ^{1}H and ^{13}C NMR; *N*-(Monosubstituted Phenyl)-Disubstituted Benzenesulphonamides.

1. Introduction

The chemistry of sulphonamides and their derivatives is of interest due to their distinct physical, chemical and biological properties. Many arylsulphonamides and their *N*-halo compounds exhibit pharmacological, fungicidal and herbicidal activities due to their oxidizing action in aqueous, partial aqueous and non-aqueous media. Thus we are interested in the synthetic, spectroscopic, structural and kinetic aspects of these compounds [1 – 16]. We have recently reported the synthesis, characterization, infrared and NMR spectral studies on *N*-(mono/disubstituted)-4-substituted benzenesulphonamides [8, 10, 11]. We report here the synthesis, characterization, infrared, ^{1}H and ^{13}C NMR spectral studies on twenty six *N*-(2/3/4-substituted phenyl)-2,4-disubstituted benzenesulphonamides of the general formulae 2,4-$(CH_3)_2$-$C_6H_3SO_2NH$(*i*-XC_6H_4), 2-CH_3-4-$ClC_6H_3SO_2NH$-(*i*-XC_6H_4) and 2,4-$Cl_2C_6H_3SO_2NH$(*i*-XC_6H_4) (where *i*-X = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-Cl, 3-Cl, 4-Cl, 4-F or 4-Br).

2. Experimental

2.1. Preparations of N-(Aryl)-disubstituted Benzenesulphonamides

Preparations of *N*-(2/3/4-substituted phenyl)-disubstituted benzenesulphonamides (Table 1) involved two steps [1, 17 – 21]: (i) chlorosulphonation of substituted benzenes and (ii) conversion of substituted benzenesulphonylchlorides to substituted benzenesulphonamides.

(i) Chlorosulphonation of substituted benzenes with chlorosulphonic acid: The substituted benzenes (10 g)

Table 1. The melting points (M. p.) of *N*-(monosubstituted phenyl)-2,4-dimethyl/2-methyl-4-chloro/2,4-dichlorobenzenesulphonamides.

i-X	Compound	M. p. (°C)
2,4-$(CH_3)_2C_6H_3SO_2NH$(*i*-XC_6H_4):		
H	*N*-(Phenyl)-2,4-dimethylbenzenesulphonamide	94 – 96
2-CH_3	*N*-(2-Methylphenyl)-2,4-dimethylbenzenesulphonamide	132
3-CH_3	*N*-(3-Methylphenyl)-2,4-dimethylbenzenesulphonamide	82
4-CH_3	*N*-(4-Methylphenyl)-2,4-dimethylbenzenesulphonamide	116
2-Cl	*N*-(2-Chlorophenyl)-2,4-dimethylbenzenesulphonamide	106
3-Cl	*N*-(3-Chlorophenyl)-2,4-dimethylbenzenesulphonamide	124
4-Cl	*N*-(4-Chlorophenyl)-2,4-dimethylbenzenesulphonamide	91 – 93
4-F	*N*-(4-Fluorophenyl)-2,4-dimethylbenzenesulphonamide	68 – 70
2-CH_3-4-$ClC_6H_3SO_2NH$(*i*-XC_6H_4):		
H	*N*-(Phenyl)-2-Methyl-4-chlorobenzenesulphonamide	90
2-CH_3	*N*-(2-Methylphenyl)-2-methyl-4-chlorobenzenesulphonamide	142 – 144
3-CH_3	*N*-(3-Methylphenyl)-2-methyl-4-chlorobenzenesulphonamide	116
4-CH_3	*N*-(4-Methylphenyl)-2-methyl-4-chlorobenzenesulphonamide	90
2-Cl	*N*-(2-Chlorophenyl)-2-methyl-4-chlorobenzenesulphonamide	98
3-Cl	*N*-(3-Chlorophenyl)-2-methyl-4-chlorobenzenesulphonamide	108
4-Cl	*N*-(4-Chlorophenyl)-2-methyl-4-chlorobenzenesulphonamide	82 – 84
4-F	*N*-(4-Fluorophenyl)-2-methyl-4-chlorobenzenesulphonamide	59 – 61
4-Br	*N*-(4-Bromophenyl)-2-methyl-4-chlorobenzenesulphonamide	88 – 91
2,4-$Cl_2C_6H_3SO_2NH$(*i*-XC_6H_4):		
H	*N*-(Phenyl)-2,4-dichlorobenzenesulphonamide	122
2-CH_3	*N*-(2-Methylphenyl)-2,4-dichlorobenzenesulphonamide	128 – 130
3-CH_3	*N*-(3-Methylphenyl)-2,4-dichlorobenzenesulphonamide	134
4-CH_3	*N*-(4-Methylphenyl)-2,4-dichlorobenzenesulphonamide	102
2-Cl	*N*-(2-Chlorophenyl)-2,4-dichlorobenzenesulphonamide	92
3-Cl	*N*-(3-Chlorophenyl)-2,4-dichlorobenzenesulphonamide	140 – 142
4-Cl	*N*-(4-Chlorophenyl)-2,4-dichlorobenzenesulphonamide	84 – 86
4-F	*N*-(4-Fluorophenyl)-2,4-dichlorobenzenesulphonamide	74
4-Br	*N*-(4-Bromophenyl)-2,4-dichlorobenzenesulphonamide	84

(Spectrochem, India) were dissolved in chloroform (50 ml). The solutions were cooled to 0 °C and treated dropwise with chlorosulphonic acid (50 g). After the initial evolution of hydrogen chloride subsided, the reaction mixtures were brought to room temperature. The contents were poured into crushed ice in a beaker. The chloroform layers were separated, washed with cold water and allowed to evaporate slowly. The residual crude substituted benzenesulphonylchlorides were recrystallized from sulphonic solvent (choroform, ethanol or petroleum ether) and dried in vacuo over conc. H_2SO_4.

(ii) Conversion of sulphonylchlorides to sulphonamides with substituted anilines [21]: The substituted benzenesulphonylchlorides prepared as described above were boiled for 10 min with the corresponding substituted anilines (Sisco Research Laboratories, India) in the stoichiometric ratio. The reaction mixtures were cooled to room temperature and added to ice cold water (100 ml). The resultant solid *N*-(2/3/4-substituted phenyl)-disubstituted benzenesulphonamides were filtered under suction and thoroughly washed with cold water. They were then recrystallized to constant melting points from dilute ethanol. The purity of all the reagents was checked by determining their melting points (Table 1).

2.2. Spectral Measurements

Infrared spectral measurements were carried out on a SHIMADZU-8700 (Japan) FT-IR spectrometer. The scanning range was from 400 – 4000 cm^{-1}. The spectra were measured in the solid state as pressed KBr pellets (13 mm).

The ^1H and ^{13}C NMR spectra of all the *N*-(2/3/4-substituted phenyl)-*p*-substituted benzenesulphonamides were measured on a BRUKER Ac 300F, 300 MHz FT-NMR spectrometer. The spectra were recorded in $CDCl_3$ and DMSO with tetramethylsilane (Me_4Si) as internal standard.

3. Results and Discussion

3.1. Infrared Spectra

The selected infrared absorption frequencies of all the 26 *N*-(2/3/4-substituted phenyl)-disubstituted

Table 2. The comparison of N-H, S=O (asym), S=O (sym), C-S, S-N, and C-N stretching infrared absorption frequencies (cm^{-1}) of *N*-(mono)-*para* and 2,4-disubstituted benzenesulphonamides.

	4-XC_6H_4/2,4-$XYC_6H_3SO_2NH$(*i*-XC_6H_4/*i,j*-$X_2C_6H_3$) where X and XY =								
i-X	H	CH_3	C_2H_5	F	Cl	Br	2,4-$(CH_3)_2$	2-CH_3-4-Cl	2,4-Cl_2
					N-H stretching				
H	3284.2w	3254.3w	3278.4w	3218.6s	3259.1m	3257.2m	3288.4s	3263.3s	3267.0s
2-CH_3	3216.7m	3268.8s	3266.8m	3275.5s	3284.2w	3266.8s	3263.0m	3263.3m	3278.8s
3-CH_3	3234.0s	3230.2w	–	3258.1s	3266.8m	3264.9s	3255.6m	3261.4m	3278.8s
4-CH_3	3270.7s	3234.0w	3263.9s	3270.7s	3233.1m	3234.0s	3274.9w	3271.0s	3278.8s
2-Cl	3253.3s	3263.9w	3268.8s	3255.3s	3272.6m	3246.6s	3286.0s	3246.0s	3294.2m
3-Cl	3199.3s	3246.6m	3248.5s	3285.1s	3258.1s	3236.0s	3298.0m	3298.0s	3263.3s
4-Cl	3284.2w	3305.4s	3262.0m	3284.2m	3259.1s	3258.1w	3263.3s	3273.0s	3263.3m
4-F	3250.4m	3258.1s	3269.7s	3250.4s	3245.6s	3251.7s	3271.3s	3269.1m	3267.2s
4-Br	3262.0m	3334.3s	3254.3m	3264.9m	3260.1s	3259.1s	–	3232.5s	3274.9s
					S=O (asym) stretching				
H	1376.9s	1373.1s	1373.0s	1337.4s	1343.2m	1374.0s	1325.0m	1336.6m	1326.9s
2-CH_3	1326.8s	1318.1s	1330.6m	1331.6s	1376.0m	1332.6s	1328.9s	1330.8s	1330.8s
3-CH_3	1308.5s	1330.6s	–	1327.8m	1328.7m	1331.6s	1321.1s	1325.0s	1334.6s
4-CH_3	1318.1m	1334.5m	1328.7s	1339.3m	1339.3s	1340.3s	1373.1s	1328.9s	1346.2s
2-Cl	1334.5m	1373.1s	1318.1s	1326.8s	1342.2s	1374.0s	1323.1s	1340.4s	1336.6m
3-Cl	1314.3m	1331.6m	1328.7m	1340.3s	1336.4m	1332.6s	1311.1s	1315.4s	1350.1m
4-Cl	1376.0m	1327.8s	1326.8m	1332.6m	1332.6m	1374.0s	1326.9s	1326.9s	1330.8m
4-F	1325.8m	1332.6s	1330.6s	1326.8s	1332.6s	1333.5m	1323.1s	1326.9m	1330.8s
4-Br	1311.4m	1341.3s	1329.7w	1316.2m	1330.6m	1329.7s	–	1326.9s	1326.9s
					S=O (sym) stretching				
H	1162.9s	1173.5s	1174.4s	1152.3s	1161.9s	1160.9s	1150.0s	1161.1s	1161.1s
2-CH_3	1154.2s	1148.4s	1163.8s	1156.1s	1163.8m	1164.8s	1161.1s	1163.0s	1164.9s
3-CH_3	1154.2s	1172.5s	–	1154.2s	1156.1s	1154.2s	1139.9s	1157.2s	1168.8s
4-CH_3	1155.2s	1174.4s	1159.0s	1152.3s	1164.8s	1165.8s	1176.5s	1157.2s	1164.9s
2-Cl	1168.7s	1173.5s	1148.4s	1155.2s	1167.7s	1166.7s	1149.5s	1170.7s	1166.9s
3-Cl	1155.6s	1161.9s	1158.0s	1177.3s	1160.9s	1150.3s	1149.5s	1159.1s	1161.1s
4-Cl	1163.8s	1160.9s	1157.1s	1161.9s	1159.0s	1160.9s	1166.9s	1161.1s	1163.0s
4-F	1154.2s	1160.9s	1160.0s	1151.3s	1159.0s	1158.0s	1163.0s	1161.1s	1163.0s
4-Br	1156.1s	1158.0s	1182.2s	1152.3s	1160.0s	1159.0s	–	1164.9s	1161.1s
					C-S stretching				
H	836.0m	810.9m	810.9m	818.6w	826.4w	820.6m	819.7m	823.5w	821.6s
2-CH_3	–	830.2w	832.1w	815.7m	822.1m	831.2w	819.7m	823.5m	825.5s
3-CH_3	794.5m	810.0m	–	836.0m	755.0m	819.6m	817.8w	825.5m	823.5m
4-CH_3	810.0m	810.0m	810.9s	834.1w	810.0s	811.9s	823.5w	815.8m	817.8s
2-Cl	–	810.9m	830.2w	834.1m	827.3m	819.6m	817.8m	820.0w	823.5m
3-Cl	884.2m	810.9w	835.0w	842.7s	826.4w	818.6w	840.0w	835.0w	821.6s
4-Cl	832.1m	826.4w	833.1w	824.4m	825.4m	819.6m	837.0s	823.5s	817.8s
4-F	828.3m	813.8m	829.2m	828.3s	825.4s	827.3m	829.3s	831.3m	819.7s
4-Br	837.0w	–	832.1m	837.9s	824.4m	820.6m	–	812.0m	813.9s
					S-N stretching				
H	–	921.8w	–	937.2w	924.7m	925.7w	912.3m	927.7s	925.8m
2-CH_3	916.0m	899.6w	911.2w	907.3m	905.4m	910.2w	912.3w	912.3m	925.8m
3-CH_3	907.3m	945.0w	–	892.9w	901.6w	898.7m	956.6m	956.6s	950.8m
4-CH_3	921.8m	912.2w	904.5s	925.7w	915.1s	917.0s	972.1m	925.8m	929.6s
2-Cl	906.4m	902.5w	899.6w	–	903.5m	–	918.1s	910.3m	923.8m
3-Cl	904.5w	928.6m	934.3m	904.5s	924.7w	941.1w	935.4s	933.5s	918.1s
4-Cl	905.4w	899.6m	930.5w	898.7w	904.4w	–	908.4s	921.9m	925.8w
4-F	924.7m	905.4m	902.5m	924.7m	906.4m	907.3w	910.3s	923.8m	933.5w
4-Br	920.8w	909.3m	–	907.3m	905.4w	904.5w	–	904.6m	941.2w
					C-N stretching				
H	1281.5m	1294.0m	1294.0m	1310.4w	1283.4m	1278.6m	1286.4m	1292.2m	1250.0w
2-CH_3	1225.5w	–	1235.2w	1296.9m	1281.5m	1276.7w	1284.5w	1276.8w	1244.0w
			1192.8w		1180.2m	1186.0m			
3-CH_3	–	1203.6m	–	1291.1m	1280.5m	1278.6m	1244.1m	1288.4w	1250.0w
4-CH_3	1296.9m	1186.1s	1298.8m	1293.0m	1299.8m	1299.8m	1286.4w	1290.3m	1222.8m
			1286.3m		1276.7m	1275.7m			
2-Cl	–	1294.0m	–	1291.1m	1280.5w	1278.6m	1280.6m	1272.9w	1234.4w
		1187.0s		1167.7s	1219.8w	1187.9s			
3-Cl	1270.9w	1293.0w	–	1295.0s	1279.5w	–	1222.8m	1276.8w	1230.5w
	1259.3w		1269.9w						
4-Cl	1281.5m	1248.7w	–	1280.5m	1280.5w	1278.6m	1284.5m	1282.6w	1244.0m
	1180.2s	1193.7m			1227.5m	1187.9s			
4-F	1309.4m	1304.6w	–	1294.0m	1280.5m	1277.6w	1295.0m	1209.3m	1250.0m
	1294.0m	1290.1w			1205.3m	1204.3w			
4-Br	1290.1m	–	–	1291.1m	1246.8m	1277.6w	–	1222.8m	1261.4m
	1186.0m			1271.8w		1216.9w			

s, strong; m, medium; w, weak.

Table 3. Observed ^{1}H NMR chemical shifts (δ, ppm) of various aromatic and other protons in *N*-(2/3/4-substituted phenyl)-2,4-disubstituted benzenesulphonamides.

i-X	H-2	H-3	H-4	H-5	H-6	H-3′	H-5′	H-6′	N-H	Alkyl H
					2,4-$(CH_3)_2C_6H_3SO_2NH$(*i*-XC_6H_4)					
H	7.17d	7.06m	7.0	7.06m	7.17m	7.19m	7.22m	7.87d	–	2.6, 2.33
2-CH_3	–	6.97m	6.97m	6.97m	7.0m	7.03m	7.04m	7.63d	8.86	2.52, 2.29, 2.1
3-CH_3	6.97m	–	6.72d	6.95d	7.08m	7.08d	7.21d	7.82d	9.68	2.55, 2.23, 2.16
4-CH_3	7.10s	6.93s	–	6.93s	7.10s	7.40s	7.60s	8.65s	9.55	2.87, 2.83, 2.23
2-Cl	–	7.05m	6.93m	7.05m	7.14m	7.20d	7.24d	7.83d	–	2.61, 2.28
3-Cl	7.10s	–	6.94m	7.05m	7.09s	7.12d	7.25s	7.88m	7.76	2.61, 2.33
4-Cl	7.12d	6.97m	–	6.97m	7.12d	7.15d	7.15d	7.83d	7.57	2.6, 2.32
4-F	7.0m	7.04m	–	7.04m	7.0m	7.02d	7.02d	7.79d	7.62	2.59, 2.29
					2-CH_3-4-$ClC_6H_3SO_2NH$(*i*-XC_6H_4)					
H	7.17m	7.14m	7.03m	7.14m	7.17m	7.17d	7.20d	7.89d	–	2.60
2-CH_3	–	7.04d	6.82s	7.09m	7.10m	7.19d	7.22d	7.81d	–	2.55, 2.15
3-CH_3	7.03m	–	6.85m	7.04m	7.08m	7.18d	7.22d	7.90d	7.57	2.61, 2.21
4-CH_3	7.0m	6.93m	–	6.93m	7.0m	7.18s	7.23m	7.85d	–	2.60, 2.23
2-Cl	–	7.13m	7.01m	7.13m	7.15m	7.18d	7.22d	7.86d	7.27	2.63
3-Cl	7.17m	–	7.04m	7.13s	7.17m	7.22d	7.29m	7.91t	9.30	2.62
4-Cl	7.17m	7.15m	–	7.15m	7.17m	7.21d	7.72d	7.86d	–	2.60
4-F	7.15m	7.50m	–	7.50m	7.15m	7.19m	7.21m	7.85m	10.0	2.61
4-Br	7.23m	6.92d	–	6.92d	7.23m	7.27m	7.32m	7.87d	–	2.61
					2,4-$Cl_2C_6H_3SO_2NH$(*i*-XC_6H_4)					
H	7.30d	7.16m	7.0m	7.16m	7.30d	7.43d	7.43d	8.0d	10.1	–
2-CH_3	–	7.02m	6.98m	7.07m	7.24d	7.49d	7.49d	7.83d	8.76	2.24
3-CH_3	7.23s	–	6.78d	7.06m	7.26d	7.38d	7.38d	7.97d	9.70	2.20
4-CH_3	7.25m	7.01m	–	7.01m	7.25m	7.40d	7.40d	7.95d	9.91	2.16
2-Cl	–	7.17m	7.0m	7.17m	7.29m	7.53d	7.53d	8.0d	–	–
3-Cl	7.37m	–	7.0m	7.16m	7.35m	7.45m	7.45m	8.03d	10.5	–
4-Cl	7.37m	7.16s	–	7.16s	7.37m	7.50d	7.49d	8.02t	10.6	–
4-F	7.28m	7.31m	–	7.31m	7.28m	7.51d	7.50d	7.87d	–	–
4-Br	7.32m	7.03m	–	7.03m	7.32m	7.49d	7.49d	7.92d	–	–

benzenesulphonamides have been assigned to various modes of vibrations in conformity with the literature values for similar compounds [1, 2, 4, 5, 7, 8, 10, 11, 20 – 24]. Considering the fact that although the ranges of frequencies for various groups are quite well defined, the precise frequency at which a specific group absorbs is dependent on its environment within the molecule and on its physical state (Table 2). In particular, the assignments are in agreement with the assignments of bands in *p*-substituted benzenesulphonamides [1] and *N*-(mono/disubstituted phenyl)-4-substituted benzenesulphonamides [8, 10, 11].

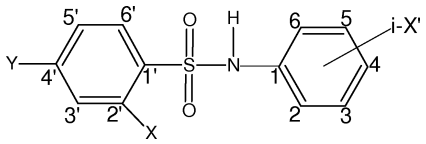
The N-H stretching vibrational frequencies, ν_{N-H}, of *N*-(2/3/4-substituted phenyl)-2,4-disubstituted benzenesulphonamides vary in the range 3298 – 3233 cm^{-1}. They are in conformity with the values of N-H symmetric stretching vibrations reported in the ranges of 3305 – 3199 cm^{-1} and 3266 – 3240 cm^{-1}, respectively, for the *N*-(2/3/4-substituted phenyl)-*p*-substituted benzenesulphonamides [8, 10, 11] and *p*-substituted benzenesulphonamides [1], respectively. Asymmetric and symmetric SO stretching vibrations appear in the ranges 1373 – 1311 cm^{-1} and 1177 – 1140 cm^{-1}, respectively, compared to the ranges of 1377 – 1307 cm^{-1} and 1184 – 1128 cm^{-1}, respectively, observed for the *N*-(2/3/4-substituted phenyl)-*p*-substituted benzenesulphonamides [8, 10, 11] and the ranges of 1344 – 1327 cm^{-1} and 1187 – 1147 cm^{-1}, respectively, for the *p*-substituted benzenesulphonamides [1]. *N*-(2/3/4-Substituted phenyl)-2,4-disubstituted benzenesulphonamides exhibit C-S, S-N and C-N stretching vibrational absorptions in the ranges, 840 – 812 cm^{-1}, 972 – 908 cm^{-1} and 1295 – 1209 cm^{-1}, respectively, compared to the ranges of 844 – 800 cm^{-1}, 945 – 891 cm^{-1} and 1310 – 1168 cm^{-1} observed for *N*-(2/3/4-substituted phenyl)-*p*-substituted benzenesulphonamides.

The comparison of ν_{N-H}, $\nu_{S=O(asym)}$, $\nu_{S=O(sym)}$, ν_{C-S}, ν_{S-N} and ν_{N-C} vibrational frequencies of *N*-(2/3/4-substituted phenyl)-2,4-disubstituted benzenesulphonamides and those of *N*-(2/3/4-substituted phenyl)-*p*-substituted benzenesulphonamides [8, 10, 11], with variations in either the substituent or the site of substitution in the two benzene rings, shows that there

are no particular trends in the variation of the frequencies depending on substitution with either the electron withdrawing or electron donating groups or with the change in the site of substitution.

3.2. ^{1}H NMR Spectra

The ^{1}H NMR chemical shifts of aromatic and alkyl protons of all the *N*-(2/3/4-substituted phenyl)-2,4-dimethylbenzenesulphonamides, *N*-(2/3/4-substituted phenyl)-2-methyl-4-chlorobenzenesulphonamides and *N*-(2/3/4-substituted phenyl)-2,4-dichlorobenzenesulphonamides are shown in Table 3. The aromatic protons and carbon atoms are numbered as shown in the following general structure:



The various chemical shifts are assigned to the protons of two benzene rings in line with those for similar compounds [1, 24 – 28]. Further, the incremental shifts due to 2,4-$(CH_3)_2C_6H_3SO_2NH$-, 2-CH_3-4-$ClC_6H_3SO_2NH$- and 2,4-$Cl_2C_6H_3SO_2NH$-, and 2,4-$(CH_3)_2C_6H_3SO_2$-, 2-CH_3-4-$ClC_6H_3SO_2$- and 2,4-$Cl_2C_6H_3SO_2$-groups in the compounds, 2,4-$(CH_3)_2C_6H_3SO_2NH(C_6H_5)$, 2-$CH_3$-4-$ClC_6H_3SO_2$-$NH(C_6H_5)$ and 2,4-$Cl_2C_6H_3SO_2NH(C_6H_5)$ were computed by comparing the chemical shifts of the protons in these compounds with those of benzene and aniline, respectively. The computed incremental shifts are shown in Table 4.

The chemical shifts of the aromatic protons in the aniline phenyl ring of the compounds, 2,4-$(CH_3)_2$-$C_6H_3SO_2NH(i\text{-}XC_6H_4)$, 2-$CH_3$-4-$ClC_6H_3SO_2NH$-$(i\text{-}XC_6H_4)$ and 2,4-$Cl_2C_6H_3SO_2NH(i\text{-}XC_6H_4)$, where *i*-X = H, 2-$CH_3$, 3-$CH_3$, 4-$CH_3$, 2-Cl, 3-Cl, 4-Cl, 4-F or 4-Br, were then calculated either by adding the incremental shifts due to the substituents *i*-X [23] to the chemical shifts of the corresponding protons in the compounds 2,4-$(CH_3)_2C_6H_3SO_2NH(C_6H_5)$, 2-$CH_3$-4-$ClC_6H_3SO_2NH(C_6H_5)$ and 2,4-$Cl_2C_6H_3$-$SO_2NH(C_6H_5)$ or adding the incremental shifts due to 2,4-$XYC_6H_3SO_2NH$-groups to the chemical shifts of the corresponding protons in substituted benzenes or adding the incremental shifts due to 2,4-XYC_6H_3-SO_2-groups to the chemical shifts of the protons in substituted anilines. The calculated chemical shifts by these methods (values not shown) compared reasonably well with each other and were in good agreement with the experimental chemical shifts, indicating that the different methods of calculations lead to almost the same values.

Table 4. The incremental shifts (δ, ppm) of aromatic protons due to the groups 2,4-$XYC_6H_3SO_2NH$- and 2,4-$XYC_6H_3SO_2$- in 2,4-$XYC_6H_3SO_2NH(i\text{-}XC_6H_4)$.

Group	H-2,6	H-3,5	H-4
2,4-$(CH_3)_2C_6H_3SO_2NH$-	−0.10	0.21	−0.27
2-CH_3-4-$ClC_6H_3SO_2NH$-	−0.10	−0.13	−0.24
2,4-$Cl_2C_6H_3SO_2NH$-	0.03	−0.11	−0.27
2,4-$(CH_3)_2C_6H_3SO_2$-	0.69	0.01	0.33
2-CH_3-4-$ClC_6H_3SO_2$-	0.69	0.09	0.36
2,4-$Cl_2C_6H_3SO_2$-	0.82	0.11	0.33

3.3. ^{13}C NMR Spectra

The ^{13}C NMR chemical shifts of the aromatic and alkyl carbon atoms of all the 26 *N*-(2/3/4-substituted phenyl)-2,4-dimethylbenzenesulphonamides, *N*-(2/3/4-substituted phenyl)-2-methyl-4-chlorobenzenesulphonamides and *N*-(2/3/4-substituted phenyl)-2,4-dichlorobenzenesulphonamides are shown in Table 5. The various chemical shifts are assigned to the different carbon atoms of the two benzene rings in conformity with the literature for similar compounds [1, 8 – 11, 24 – 29]. Further, the incremental shifts due to 2,4-$(CH_3)_2C_6H_3SO_2NH$-, 2-CH_3-4-$ClC_6H_3SO_2NH$- and 2,4-$Cl_2C_6H_3SO_2NH$-, and 2,4-$(CH_3)_2C_6H_3SO_2$-, 2-CH_3-4-$ClC_6H_3SO_2$- and 2,4-Cl_2-$C_6H_3SO_2$-groups in the compounds 2,4-$(CH_3)_2C_6H_3$-$SO_2NH(C_6H_5)$, 2-CH_3-4-$ClC_6H_3SO_2NH(C_6H_5)$ and 2,4-$Cl_2C_6H_3SO_2NH(C_6H_5)$ were computed by comparing the chemical shifts of the aromatic carbon atoms in these compounds with those of benzene and aniline, respectively. The computed incremental shifts are shown in Table 6. These shifts and the incremental shifts due to the substituents *i*-X [23] were used to calculate the ^{13}C NMR chemical shifts of the substituted compounds of the general formulae 2,4-$(CH_3)_2C_6H_3SO_2NH(i\text{-}XC_6H_4)$, 2-$CH_3$-4-$ClC_6H_3SO_2NH(i\text{-}XC_6H_4)$ and 2,4-$Cl_2C_6H_3$-$SO_2NH(i\text{-}XC_6H_4)$ in three different ways as described earlier. The calculated chemical shifts (values not shown) agreed well with each other and with the experimental chemical shifts. Further, it has been observed that there are no particular trends in the variation of the chemical shifts depending on the nature or site of substitution.

Table 5. Observed ^{13}C NMR chemical shifts (δ, ppm) of various aromatic carbon atoms in *N*-(2/3/4-substituted phenyl)-2,4-disubstituted benzenesulphonamides, 2,4-$(CH_3)_2C_6H_3SO_2NH$(*i*-XC_6H_4), 2-CH_3-4-$ClC_6H_3SO_2NH$(*i*-XC_6H_4), and 2,4-$Cl_2C_6H_3SO_2NH$(*i*-XC_6H_4.

i-X	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	Alkyl C
						2,4-$(CH_3)_2C_6H_3SO_2NH$(*i*-XC_6H_4)							
H	134.5	120.4	130.3	124.8	130.3	120.4	136.7	137.1	133.4	143.9	126.9	129.4	21.3, 20.3
2-CH_3	134.6	129.1	132.8	125.9	126.3	–	135.9	136.6	133.7	142.7	126.3	130.4	20.8, 20.0, 17.6
3-CH_3	135.0	120.4	139.6	125.5	131.2	116.5	136.9	137.6	133.0	143.0	126.3	129.7	21.2, 20.2, 19.9
4-CH_3	136.5	119.9	130.9	138.2	130.9	119.9	138.2	140.5	130.9	145.2	128.7	129.2	20.3, 19.9, 19.7
2-Cl	133.9	124.9	130.2	123.5	127.7	120.2	133.9	137.1	133.4	144.2	126.7	129.3	21.2, 20.1
3-Cl	134.0	119.7	134.9	124.5	130.3	117.6	137.1	138.0	133.5	144.3	127.0	130.2	21.3, 20.3
4-Cl	133.3	121.4	129.9	130.1	129.9	121.4	135.2	137.0	133.8	144.1	129.2	126.9	21.2, 20.2
4-F	130.1	123.1	116.1	161.7	116.1	123.1	134.0	137.1	133.3	144.0	126.8	130.1	21.1, 20.2
						2-CH_3-4-$ClC_6H_3SO_2NH$(*i*-XC_6H_4)							
H	135.8	120.4	131.4	125.0	131.4	120.4	136.2	139.1	132.4	139.2	126.3	129.3	20.1
2-CH_3	134.1	126.9	131.6	123.0	126.3	–	136.7	139.1	132.4	139.2	126.5	131.0	20.4, 17.7
3-CH_3	136.0	121.1	139.2	125.8	131.4	117.3	136.1	138.1	132.4	139.4	126.3	129.1	21.1, 20.2
4-CH_3	132.3	121.5	131.5	135.2	131.5	121.5	135.9	139.1	133.3	139.2	126.3	129.9	20.7, 20.3
2-Cl	133.1	126.2	131.5	125.5	129.5	121.1	135.5	139.3	132.5	139.4	126.2	127.8	20.5
3-Cl	134.6	119.5	138.2	124.2	131.8	117.5	135.9	139.0	132.4	139.2	126.2	130.2	20.1
4-Cl	134.7	121.9	131.4	130.7	131.4	121.9	135.4	139.2	132.6	139.5	126.5	129.5	20.2
4-F	131.3	122.0	116.3	116.8	116.3	122.0	136.1	138.0	133.3	139.0	125.1	130.5	19.8
4-Br	133.2	122.3	132.6	118.5	132.6	122.3	135.5	139.2	132.5	139.7	126.6	131.5	19.9
						2,4-$Cl_2C_6H_3SO_2NH$(*i*-XC_6H_4)							
H	135.4	119.0	128.7	124.0	128.7	119.0	136.3	132.4	130.9	138.8	126.8	130.9	–
2-CH_3	133.8	127.0	131.1	125.3	126.4	–	136.4	133.5	132.4	138.9	130.7	132.2	17.8
3-CH_3	135.4	120.7	138.8	125.2	128.7	117.0	136.2	132.6	131.1	139.0	127.0	131.1	21.1
4-CH_3	132.6	120.4	129.4	133.9	129.4	120.4	135.5	133.7	132.4	138.8	126.9	130.9	20.3
2-Cl	132.7	125.7	129.7	124.2	127.3	120.8	134.9	132.9	131.7	140.2	127.9	131.7	–
3-Cl	135.0	119.0	134.0	123.7	129.9	117.1	137.9	132.4	131.0	139.1	126.9	131.0	–
4-Cl	132.6	120.9	128.8	130.3	128.8	120.9	135.4	132.3	131.3	138.9	127.2	131.0	–
4-F	131.3	116.5	116.1	159.3	116.1	116.5	134.5	133.0	132.3	140.1	127.6	131.4	–
4-Br	134.6	123.1	132.3	119.2	132.3	123.1	135.6	133.8	133.4	140.3	127.5	133.0	–

Table 6. The incremental shifts (δ, ppm) of aromatic carbon atoms due to the groups 2,4-$XYC_6H_3SO_2NH$- and 2,4-$XYC_6H_3SO_2$- in 2,4-$XYC_6H_3SO_2NH$(*i*-XC_6H_4).

Group	C-1	C-2,6	C-3,5	C-4
2,4-$(CH_3)_2C_6H_3SO_2NH$-	6.0	−8.1	1.8	−3.7
2-CH_3-4-$ClC_6H_3SO_2NH$-	7.3	−8.1	2.9	−3.5
2,4-$Cl_2C_6H_3SO_2NH$-	6.9	−9.5	0.2	−4.5
2,4-$(CH_3)_2C_6H_3SO_2$-	−11.7	5.8	1.5	7.0
2-CH_3-4-$ClC_6H_3SO_2$-	−10.4	5.8	2.6	7.2
2,4-$Cl_2C_6H_3SO_2$-	−10.8	4.4	−0.1	6.2

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