Synthetic and Spectroscopic Studies on N-(i,j-Disubstituted Phenyl)-4-Substituted Benzenesulphonamides, 4-X'$C_6H_4SO_2NH$(i,j-$X_2C_6H_3$), where X' = H, CH_3, C_2H_5, F, Cl or Br; i, j = 2, 3; 2, 4; 2, 5; 2, 6 or 3, 4; and X = CH_3 or Cl

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Fifty four N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides of the general formula 4-X'$C_6H_4SO_2NH$(i,j-$X_2C_6H_3$), where X' = H, CH_3, C_2H_5, F, Cl or Br; i, j = 2, 3; 2, 4; 2, 5; 2, 6 or 3, 4; and X = CH_3 or Cl, are prepared and characterized and their infrared, ^{1}H and ^{13}C NMR spectra in solution are studied. The N-H stretching vibrations ν_{N-H} absorb in the range 3305 – 3205 cm^{-1}, while the asymmetric and symmetric SO_2 vibrations vary in the ranges 1377 – 1307 cm^{-1} and 1184 – 1128 cm^{-1}, respectively. The N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides show C-S, S-N and C-N stretching vibrations in the ranges 844 – 800 cm^{-1}, 945 – 891 cm^{-1} and 1309 – 1170 cm^{-1}, respectively. The compounds do not exhibit particular trends in the variation of these frequencies on substitution either at *ortho* or *meta* positions with either a methyl group or Cl. The observed ^{1}H and ^{13}C chemical shifts of
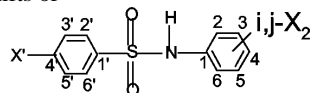
are assigned to protons and carbon atoms of the two benzene rings. Incremental shifts of the ring protons and carbon atoms due to –SO_2NH(i,j-$X_2C_6H_3$) groups in $C_6H_5SO_2NH$(i,j-$X_2C_6H_3$) and 4-X'$C_6H_4SO_2NH$– groups in 4-X'$C_6H_4SO_2NH(C_6H_5)$ are computed and employed to calculate the chemical shifts of the ring protons and carbon atoms in the substituted compounds 4-X'$C_6H_4SO_2NH$(i,j-$X_2C_6H_3$). The different methods of calculation lead to almost the same values in most cases and agree well with the observed chemical shifts, indicating the validity of the principle of additivity of the substituent effects with chemical shifts in these compounds.

Key words: IR; ^{1}H and ^{13}C NMR; N-(Disubstituted phenyl)-4-substituted Benzenesulphonamides.

1. Introduction

The chemistry of sulphonamides and their derivatives is of interest due to their distinct physical, chemical and biological properties. Hence we are interested in the synthetic, spectroscopic, structural and kinetic aspects of these compounds [1 – 18]. We have recently reported the synthesis, characterization, infrared and NMR spectral properties of N-(2-/3-/4-substituted phenyl)-4-substituted benzenesulphonamides of the general formula, 4-X'$C_6H_4SO_2NH$(2-/3-/4-XC_6H_4), where X' or X = H, CH_3, C_2H_5, F, Cl or Br [18]. This paper reports the synthesis, characterization, infrared, ^{1}H and ^{13}C NMR spectral proper-

ties of fifty four N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides of the general formula 4-X'$C_6H_4SO_2NH$(i,j-$X_2C_6H_3$), where X' = H, CH_3, C_2H_5, F, Cl or Br; i,j = 2,3; 2,4; 2,5; 2,6 or 3,4 and X = CH_3 or Cl.

2. Experimental

2.1. Materials and Methods

The preparations of all the fifty four N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides (Table 1) involved two steps: (i) chlorosulphonation of substituted benzenes and (ii) conversion of the re-

Table 1. Melting points of N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides, $4\text{-X'}C_6H_4SO_2NH(i,j\text{-}X_2C_6H_3)$.

where X', i,j-X_2 =	Systematic names of the compounds	M. p. [°C]
H, 2,3-$(CH_3)_2$	N-(2,3-dimethylphenyl)-benzenesulphonamide	86
H, 2,4-$(CH_3)_2$	N-(2,4-dimethylphenyl)-benzenesulphonamide	110
H, 2,5-$(CH_3)_2$	N-(2,5-dimethylphenyl)-benzenesulphonamide	50
H, 2,6-$(CH_3)_2$	N-(2,6-dimethylphenyl)-benzenesulphonamide	80
H, 2,3-Cl_2	N-(2,3-dichlorophenyl)-benzenesulphonamide	99
H, 2,4-Cl_2	N-(2,4-dichlorophenyl)-benzenesulphonamide	103
H, 2,5-Cl_2	N-(2,5-dichlorophenyl)-benzenesulphonamide	116
H, 2,6-Cl_2	N-(2,6-dichlorophenyl)-benzenesulphonamide	92
H, 3,4-Cl_2	N-(3,4-dichlorophenyl)-benzenesulphonamide	67
CH_3, 2,3-$(CH_3)_2$	N-(2,3-dimethylphenyl)-4-methylbenzene-sulphonamide	136
CH_3, 2,4-$(CH_3)_2$	N-(2,4-dimethylphenyl)-4-methylbenzene-sulphonamide	58
CH_3, 2,5-$(CH_3)_2$	N-(2,5-dimethylphenyl)-4-methylbenzene-sulphonamide	40
CH_3, 2,6-$(CH_3)_2$	N-(2,6-dimethylphenyl)-4-methylbenzene-sulphonamide	82
CH_3, 2,3-Cl_2	N-(2,3-dichlorophenyl)-4-methylbenzene-sulphonamide	105
CH_3, 2,4-Cl_2	N-(2,4-dichlorophenyl)-4-methylbenzene-sulphonamide	98
CH_3, 2,5-Cl_2	N-(2,5-dichlorophenyl)-4-methylbenzene-sulphonamide	121
CH_3, 2,6-Cl_2	N-(2,6-dichlorophenyl)-4-methylbenzene-sulphonamide	68
CH_3, 3,4-Cl_2	N-(3,4-dichlorophenyl)-4-methylbenzene-sulphonamide	78
C_2H_5, 2,3-$(CH_3)_2$	N-(2,3-dimethylphenyl)-4-ethylbenzene-sulphonamide	92
C_2H_5, 2,4-$(CH_3)_2$	N-(2,4-dimethylphenyl)-4-ethylbenzene-sulphonamide	98
C_2H_5, 2,5-$(CH_3)_2$	N-(2,5-dimethylphenyl)-4-ethylbenzene-sulphonamide	52
C_2H_5, 2,6-$(CH_3)_2$	N-(2,6-dimethylphenyl)-4-ethylbenzene-sulphonamide	138
C_2H_5, 2,3-Cl_2	N-(2,3-dichlorophenyl)-4-ethylbenzene-sulphonamide	79
C_2H_5, 2,4-Cl_2	N-(2,4-dichlorophenyl)-4-ethylbenzene-sulphonamide	93
C_2H_5, 2,5-Cl_2	N-(2,5-dichlorophenyl)-4-ethylbenzene-sulphonamide	115
C_2H_5, 2,6-Cl_2	N-(2,6-dichlorophenyl)-4-ethylbenzene-sulphonamide	64
C_2H_5, 3,4-Cl_2	N-(3,4-dichlorophenyl)-4-ethylbenzene-sulphonamide	88
F, 2,3-$(CH_3)_2$	N-(2,3-dimethylphenyl)-4-fluorobenzene-sulphonamide	78
F, 2,4-$(CH_3)_2$	N-(2,4-dimethylphenyl)-4-fluorobenzene-sulphonamide	140
F, 2,5-$(CH_3)_2$	N-(2,5-dimethylphenyl)-4-fluorobenzene-sulphonamide	112
F, 2,6-$(CH_3)_2$	N-(2,6-dimethylphenyl)-4-fluorobenzene-sulphonamide	122
F, 2,3-Cl_2	N-(2,3-dichlorophenyl)-4-fluorobenzene-sulphonamide	119
F, 2,4-Cl_2	N-(2,4-dichlorophenyl)-4-fluorobenzene-sulphonamide	75
F, 2,5-Cl_2	N-(2,5-dichlorophenyl)-4-fluorobenzene-sulphonamide	117
F, 2,6-Cl_2	N-(2,6-dichlorophenyl)-4-fluorobenzene-sulphonamide	73
F, 3,4-Cl_2	N-(3,4-dichlorophenyl)-4-fluorobenzene-sulphonamide	76

Table 1 (continued).

where X', i,j-X_2 =	Systematic names of the compounds	M. p. [°C]
Cl, 2,3-$(CH_3)_2$	N-(2,3-dimethylphenyl)-4-chlorobenzene-sulphonamide	76
Cl, 2,4-$(CH_3)_2$	N-(2,4-dimethylphenyl)-4-chlorobenzene-sulphonamide	36
Cl, 2,5-$(CH_3)_2$	N-(2,5-dimethylphenyl)-4-chlorobenzene-sulphonamide	52
Cl, 2,6-$(CH_3)_2$	N-(2,6-dimethylphenyl)-4-chlorobenzene-sulphonamide	86
Cl, 2,3-Cl_2	N-(2,3-dichlorophenyl)-4-chlorobenzene-sulphonamide	99
Cl, 2,4-Cl_2	N-(2,4-dichlorophenyl)-4-chlorobenzene-sulphonamide	107
Cl, 2,5-Cl_2	N-(2,5-dichlorophenyl)-4-chlorobenzene-sulphonamide	143
Cl, 2,6-Cl_2	N-(2,6-dichlorophenyl)-4-chlorobenzene-sulphonamide	86
Cl, 3,4-Cl_2	N-(3,4-dichlorophenyl)-4-chlorobenzene-sulphonamide	89
Br, 2,3-$(CH_3)_2$	N-(2,3-dimethylphenyl)-4-bromobenzene-sulphonamide	114
Br, 2,4-$(CH_3)_2$	N-(2,4-dimethylphenyl)-4-bromobenzene-sulphonamide	42
Br, 2,5-$(CH_3)_2$	N-(2,5-dimethylphenyl)-4-bromobenzene-sulphonamide	86
Br, 2,6-$(CH_3)_2$	N-(2,6-dimethylphenyl)-4-bromobenzene-sulphonamide	150
Br, 2,3-Cl_2	N-(2,3-dichlorophenyl)-4-bromobenzene-sulphonamide	122
Br, 2,4-Cl_2	N-(2,4-dichlorophenyl)-4-bromobenzene-sulphonamide	133
Br, 2,5-Cl_2	N-(2,5-dichlorophenyl)-4-bromobenzene-sulphonamide	132
Br, 2,6-Cl_2	N-(2,6-dichlorophenyl)-4-bromobenzene-sulphonamide	103
Br, 3,4-Cl_2	N-(3,4-dichlorophenyl)-4-bromobenzene-sulphonamide	102

sulting 4-substituted benzenesulphonylchlorides into N-(i,j-disubstituted phenyl)-4-substituted benzenesul-phonamides by treating the former with the i,j-disubstituted anilines, by methods similar to the ones described in our earlier papers [14, 18]. The solid N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides so prepared were recrystallized to constant melting points from dilute ethanol. The purity of all compounds was checked by determining their melting points (Table 1).

2.2. Spectral Measurements

Infrared spectral measurements were carried out on a JASCO-430 (Japan) FT-IR spectrometer. The resolution was set to 4 cm^{-1}, and 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 NMR spectra of all N-(i,j-disubstituted phenyl)-4-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. The experimental conditions employed were as follows: spectral frequency

(SF) 300.134 MHz, sweep width (SW) 6024.096, pulse width (PW) 8.0, relaxation delay (RD) 1.0 s, acquisition time (AQ) 1.360 s, receiver gain (RG) 10, decoupling power (DP) 63L CPD, filter to suppress noise (LB) 0.0, reference value (SR) 4125.36 ppm for H_2O internally.

The ^{13}C NMR spectra of all compounds were measured in $CDCl_3$ and DMSO with tetramethylsilane as the external reference standard. The following experimental conditions were employed in the ^{13}C spectral measurement: SF 75.469 MHz, SW 22727.273, PW 5.0, RD 1.0 s, AQ 0.360 s, RG 400, DP 14H CPD, LB 6.0, SR 701.89 ppm for DMSO at 39.5 ppm externally.

3. Results and Discussion

3.1. Infrared Spectra

The selected absorption frequencies of all the 54 N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides have been assigned in conformity with the literature values for similar compounds [5, 6, 8, 9, 13–15, 18–21], considering the fact that the precise frequency at which a specific group absorbs is dependent on its environment within the molecule and on its physical state.

The maximum and minimum frequencies at which the N-H stretching vibrations, ν_{N-H}, of N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides absorb are 3305 cm^{-1} and 3205 cm^{-1}, respectively, with most of the absorptions being in the range 3272–3248 cm^{-1}. These conform with the N-H symmetric stretching vibrations in the range 3305–3199 cm^{-1} observed for N-(2-/3-/4-substituted phenyl)-4-substituted benzenesulphonamides [14, 18]. The maximal and minimal asymmetric SO_2 stretching absorptions in N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides occur at 1377 cm^{-1} and 1307 cm^{-1}, respectively, with most of the values in the range, 1341–1325 cm^{-1} compared to the range of 1377–1309 cm^{-1} observed for the N-(2-/3-/4-substituted phenyl)-4-substituted benzenesulphonamides, whereas the symmetric SO_2 stretching vibrations of N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides appear in the general range 1184–1128 cm^{-1}, with most of them absorbing in the range of 1174–1151 cm^{-1}, compared to the range 1177–1148 cm^{-1} observed for the N-(2-/3-/4-substituted phenyl)-4-substituted benzenesulphonamides [14, 18]. These ranges

Table 2. Comparison of N-H stretching infrared absorption frequencies (cm^{-1}) of N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides with N-(i-substituted phenyl)-4-substituted benzenesulphonamides.

| | 4-X'C$_6$H$_4$SO$_2$NH(i-XC$_6$H$_4$ / i,j-X$_2$C$_6$H$_3$) where X' = | | | | |
	H	CH$_3$	C$_2$H$_5$	F	Cl	Br
i-X						
H	3284.2w	3254.3w	3278.4w	3218.6s	3259.1m	3257.2m
2-CH$_3$	3216.7m	3268.8s	3266.8m	3275.5s	3284.2w	3266.8s
3-CH$_3$	3234.0s	3230.2w	–	3258.1s	3266.8m	3264.9s
4-CH$_3$	3270.7s	3234.0w	3263.9s	3270.7s	3233.1m	3234.0s
2-Cl	3253.3s	3263.9w	3268.8s	3255.3s	3272.6m	3246.6s
3-Cl	3199.3s	3246.6m	3248.5s	3285.1s	3258.1s	3236.0s
4-Cl	3284.2w	3305.4s	3262.0m	3284.2m	3259.1s	3258.1w
i,j-X$_2$						
2,3-(CH$_3$)$_2$	3209.0m	3249.5s	3263.0m	3247.5s	3247.5w	3205.1w
2,4-(CH$_3$)$_2$	3255.3m	3263.0w	3263.0m	3268.0m	3284.2w	3263.0m
2,5-(CH$_3$)$_2$	3264.9w	3263.9s	3263.0m	3267.8s	3267.8m	3259.1s
2,6-(CH$_3$)$_2$	3305.4s	3265.9m	3271.6s	3267.8s	3288.0s	3290.0s
2,3-Cl$_2$	3263.0m	3209.9s	3267.8m	3263.0m	3259.1m	3256.2s
2,4-Cl$_2$	3290.9s	3260.1w	3284.2w	3249.5s	3269.7w	3242.7w
2,5-Cl$_2$	3284.2m	3264.9m	3261.0m	3263.0m	3263.9s	3261.0w
2,6-Cl$_2$	3271.6m	3258.1w	3263.0m	3255.3s	3263.0m	3263.0s
3,4-Cl$_2$	3263.0m	3255.3w	3259.1s	3239.8m	3260.1s	3236.0w

s = strong, m = medium, and w = weak.

Table 3. Comparison of S=O (asym) and S=O (sym) infrared absorption frequencies (cm^{-1}) of N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides with N-(i-substituted phenyl)-4-substituted benzenesulphonamides.

| | 4-X'C$_6$H$_4$SO$_2$NH(i-XC$_6$H$_4$ / i,j-X$_2$C$_6$H$_3$) where X' = | | | | |
	H	CH$_3$	C$_2$H$_5$	F	Cl	Br
i-X	S=O (asym)				
H	1376.9s	1373.1s	1373.0s	1337.4s	1343.2m	1374.0s
2-CH$_3$	1326.8s	1318.1s	1330.6m	1331.6s	1376.0m	1332.6s
3-CH$_3$	1308.5s	1330.6s	–	1327.8m	1328.7m	1331.6s
4-CH$_3$	1318.1m	1334.5m	1328.7s	1339.3m	1339.3s	1340.3s
2-Cl	1334.5m	1373.1s	1318.1s	1326.8s	1342.2s	1374.0s
3-Cl	1314.3m	1331.6m	1328.7m	1340.3s	1336.4m	1332.6s
4-Cl	1376.0m	1327.8s	1326.8m	1332.6m	1332.6m	1374.0s
i,j-X$_2$						
2,3-(CH$_3$)$_2$	1324.9w	1328.7s	1326.8m	1329.7m	1328.7m	1326.8m
2,4-(CH$_3$)$_2$	1330.6m	1330.6m	1334.5m	1332.6s	1332.6m	1336.4m
2,5-(CH$_3$)$_2$	1328.7w	1330.6s	1332.6m	1336.4s	1331.6m	1331.6s
2,6-(CH$_3$)$_2$	1327.8s	1324.9m	1323.9s	1329.7s	1322.9s	1324.9s
2,3-Cl$_2$	1329.7w	1306.5m	1334.5s	1329.7m	1338.4w	1336.4m
2,4-Cl$_2$	1324.9s	1373.1m	1376.9m	1328.7m	1341.3m	1374.0s
2,5-Cl$_2$	1334.5s	1341.3m	1343.2s	1340.3s	1348.0s	1374.0s
2,6-Cl$_2$	1337.4m	1374.0s	1334.5m	1330.6s	1336.4m	1330.6s
3,4-Cl$_2$	1326.8m	1330.6s	1331.6s	1335.5m	1325.8s	1373.1s
i-X	S=O (sym)				
H	1162.9s	1173.5s	1174.4s	1152.3s	1161.9s	1160.9s
2-CH$_3$	1154.2s	1148.4s	1163.8s	1156.1s	1163.8m	1164.8s
3-CH$_3$	1154.2s	1172.5s	–	1154.2s	1156.1s	1154.2s
4-CH$_3$	1155.2s	1174.4s	1159.0s	1152.3s	1164.8s	1165.8s
2-Cl	1168.7s	1173.5s	1148.4s	1155.2s	1167.7s	1166.7s
3-Cl	1155.6s	1161.9s	1158.0s	1177.3s	1160.9s	1150.3s
4-Cl	1163.8s	1160.9s	1157.1s	1161.9s	1159.0s	1160.9s
i,j-X$_2$						
2,3-(CH$_3$)$_2$	1154.2s	1160.0s	1157.1s	1147.4s	1166.7s	1151.3s
2,4-(CH$_3$)$_2$	1157.1s	1160.9s	1160.9s	1153.2s	1161.9s	1166.7s
2,5-(CH$_3$)$_2$	1155.2s	1170.6s	1128.2s	1169.6s	1176.4s	1173.5s
2,6-(CH$_3$)$_2$	1160.9s	1157.1s	1157.1s	1152.3s	1157.1s	1158.0s
2,3-Cl$_2$	1168.7s	1155.2s	1165.8s	1168.7s	1166.7s	1167.7s
2,4-Cl$_2$	1158.0s	1172.5s	1162.9s	1159.0s	1167.7s	1167.7m
2,5-Cl$_2$	1162.9s	1170.8s	1167.9s	1171.5s	1184.1s	1166.7s
2,6-Cl$_2$	1167.7s	1160.9s	1160.9s	1157.1s	1166.7s	1160.9s
3,4-Cl$_2$	1157.1s	1166.7s	1173.5s	1169.6s	1160.9s	1172.5s

s = strong, m = medium, and w = weak.
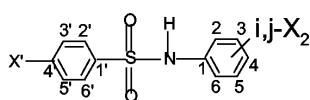
Table 4. Observed chemical shifts (δ, ppm) of various aromatic and other protons in N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides.

i,j-X$_2$ =	H-2	H-3	H-4	H-5	H-6	H-2',6'	H-3',5'	H-4'	N-H	Alkyl H
X' = H										
2,3-(CH$_3$)$_2$	–	–	6.96m	7.05m	7.40m	7.74d	7.55t	7.59d	7.26	2.20, 1.94
2,4-(CH$_3$)$_2$	–	6.90t	–	7.14d	7.39m	7.94d	7.55m	7.72d	6.62	2.24, 1.93
2,5-(CH$_3$)$_2$	–	6.96d	6.88d	–	7.40m	7.97m	7.71t	7.93d	6.46	2.27, 1.89
2,6-(CH$_3$)$_2$	–	7.10t	6.98t	7.10t	–	7.72t	7.46d	7.56t	6.39	2.10, 1.94
2,3-Cl$_2$	–	–	7.12m	7.20m	7.43t	7.79t	7.55m	7.60d	7.33	–
2,4-Cl$_2$	–	7.46d	–	7.46d	7.52d	7.95d	7.43d	7.49d	7.54	–
2,5-Cl$_2$	–	7.14d	7.00d	–	7.41m	7.94t	7.67d	7.80d	7.31	–
2,6-Cl$_2$	–	7.30d	7.15t	7.30d	–	7.97d	7.82m	7.93d	7.27	–
3,4-Cl$_2$	7.42t	–	–	7.24t	7.55t	7.97m	7.57t	7.85m	–	–
X' = CH$_3$										
2,3-(CH$_3$)$_2$	–	–	6.98m	7.00m	7.03	7.60d	7.21		6.47	2.39, 2.20, 1.96
2,4-(CH$_3$)$_2$	–	6.90t	–	7.12d	7.19m	7.80d	7.60d		6.59	2.60, 2.24, 1.95
2,5-(CH$_3$)$_2$	–	6.94d	6.86d	–	7.16m	7.63d	7.23m		6.63	2.59, 2.38, 1.92
2,6-(CH$_3$)$_2$	–	6.96t	7.03m	6.96t	–	7.59m	7.25m		6.69	2.53, 2.36, 2.02
2,3-Cl$_2$	–	–	7.11d	7.19d	7.27d	7.66d	7.32m		9.42	2.34
2,4-Cl$_2$	–	7.18d	–	7.23d	7.35t	7.65d	7.44t		7.10	2.37
2,5-Cl$_2$	–	7.00d	6.97d	–	7.17d	7.68t	7.26d		–	2.37
2,6-Cl$_2$	–	7.46d	–	7.46d	–	7.90m	7.85d		–	1.93
3,4-Cl$_2$	7.20t	–	–	6.96d	7.00d	7.73d	7.25t		–	2.35
X' = C$_2$H$_5$										
2,3-(CH$_3$)$_2$	–	–	6.94t	6.99d	7.02d	7.64	7.22		6.88	2.67, 2.19, 1.95, 1.22
2,4-(CH$_3$)$_2$	–	6.89d	–	6.93t	7.14d	7.63d	7.24d		6.68	2.67, 2.24, 1.95, 1.22
2,5-(CH$_3$)$_2$	–	6.94d	6.87d	–	7.14d	7.63d	7.25d		6.44	2.71, 2.26, 1.92, 1.25
2,6-(CH$_3$)$_2$	–	7.08d	6.98d	7.08d	–	7.61d	7.26t		6.25	2.94, 2.69, 2.04, 1.24
2,3-Cl$_2$	–	–	6.94t	7.14t	7.25d	7.86d	7.42d		10.11	2.52, 1.94
2,4-Cl$_2$	–	7.16t	–	7.16t	7.23t	7.65d	7.32t		9.59	2.63, 1.19
2,5-Cl$_2$	–	7.15d	6.94d	–	7.25d	7.73d	7.51m		9.10	2.61, 1.16
2,6-Cl$_2$	–	7.21d	7.11d	7.21d	–	7.82d	7.70t		9.54	2.64, 1.11
3,4-Cl$_2$	7.22d	–	–	7.12d	7.17d	7.76d	7.46d		10.35	2.60, 1.15
X' = F										
2,3-(CH$_3$)$_2$	–	–	6.99d	7.05d	7.13d	7.76d	7.70d		6.59s	2.21, 1.97
2,4-(CH$_3$)$_2$	–	6.92d	–	7.06t	7.10d	7.75t	7.70t		6.59s	2.25, 1.97
2,5-(CH$_3$)$_2$	–	6.98d	6.90d	–	7.07d	7.74m	7.70m		6.32s	2.22, 1.91
2,6-(CH$_3$)$_2$	–	7.09d	7.02d	7.09d	–	7.76t	7.70t		6.49s	2.25, 1.81
2,3-Cl$_2$	–	–	7.09d	7.15d	7.22d	7.81m	7.86m		7.40s	–
2,4-Cl$_2$	–	7.11d	–	7.13d	7.18d	7.40t	7.78m		9.16s	–
2,5-Cl$_2$	–	7.14d	7.00d	–	7.24d	7.85d	7.90d		10.10s	–
2,6-Cl$_2$	–	7.16d	7.04d	7.16d	–	7.82d	7.87d		8.30	–
3,4-Cl$_2$	7.22t	–	–	7.13d	7.16d	7.93t	7.88t		10.58s	–
X' = Cl										
2,3-(CH$_3$)$_2$	–	–	6.99d	7.01t	7.39t	7.63t	7.48d		6.42s	2.22, 1.97
2,4-(CH$_3$)$_2$	–	6.94d	–	7.10d	7.39d	7.86d	7.48d		6.38s	2.27, 1.97
2,5-(CH$_3$)$_2$	–	6.96d	6.90d	–	7.38t	7.87d	7.63t		6.36s	2.23, 1.92
2,6-(CH$_3$)$_2$	–	6.98d	7.07d	6.98d	–	7.67t	7.47d		6.67s	2.03
2,3-Cl$_2$	–	–	7.67d	7.63d	7.66d	7.80d	7.78t		–	–
2,4-Cl$_2$	–	7.11d	–	7.18d	7.20d	7.50d	7.41t		9.45s	–
2,5-Cl$_2$	–	7.20d	6.92d	–	7.25d	7.90d	7.75d		–	–
2,6-Cl$_2$	–	7.59t	7.49d	7.59t	–	8.01d	7.97t		7.91s	–
3,4-Cl$_2$	7.24d	–	–	7.09d	7.15d	7.89m	7.50t		10.25s	–
X' = Br										
2,3-(CH$_3$)$_2$	–	–	6.88d	6.97d	7.06d	7.66t	7.41d		9.19s	2.23, 1.99
2,4-(CH$_3$)$_2$	–	6.90t	–	6.96t	7.09t	7.78d	7.57d		7.25s	2.24, 2.0
2,5-(CH$_3$)$_2$	–	6.96d	6.89d	–	–	7.78d	7.64d		7.12s	2.26, 1.94
2,6-(CH$_3$)$_2$	–	7.09d	7.03d	7.09d	–	7.77t	7.55d		6.32s	2.05, 1.71
2,3-Cl$_2$	–	–	7.13d	7.16d	7.20d	7.77d	7.63t		–	–
2,4-Cl$_2$	–	7.20t	–	7.24d	7.31t	7.60d	7.39d		9.83s	–
2,5-Cl$_2$	–	7.12d	7.09d	–	7.24t	7.82d	7.67t		9.63s	–
2,6-Cl$_2$	–	7.57d	7.54d	7.57d	–	7.90d	7.83d		11.64s	–
3,4-Cl$_2$	7.36d	–	–	7.10d	7.12d	7.82d	7.66d		10.52s	–

agree also with the assignments of bands in other substituted benzenesulphonamides. The N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides show C-S, S-N and C-N stretching vibrations in the ranges $844 - 800$ cm^{-1}, $945 - 891$ cm^{-1} and $1309 - 1170$ cm^{-1}, respectively. These absorptions in N-(2-/3-/4-substituted phenyl)-4-substituted benzenesulphonamides were observed in the ranges, $838 - 795$ cm^{-1}, $945 - 893$ cm^{-1} and $1310 - 1168$ cm^{-1}, respectively. The assignment of other frequencies to various modes of vibrations of the ring are similar to those in arylsulphonamides [5], N-haloarylsulphonamides [6, 8, 9] and other aromatic organic compounds [19, 20].

The ν_{N-H}, $\nu_{S=O(asym)}$, and $\nu_{S=O(sym)}$ vibrations of all the N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides are compared with those of N-(2-/3-/4-substituted phenyl)-4-substituted benzenesulphonamides [14, 18] (Tables 2 and 3). The variations of these absorption frequencies with substitution in the phenyl ring in N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides had no particular trends, with either electron withdrawing or electron donating groups.

3.2. ^{1}H NMR Spectra

^{1}H chemical shifts of aromatic and alkyl protons of all N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides are shown in Table 4. The aromatic protons and carbon atoms were numbered as shown in the following general structure:
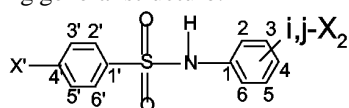

The various chemical shifts were assigned to the protons of two benzene rings in line with similar compounds [5, 14, 15, 19 – 25]. ^{1}H chemical shifts of benzene and substituted benzenes were measured under identical conditions. Further, the incremental shifts due to –SO$_2$NH(i,j-X$_2$C$_6$H$_3$) groups in the compounds with the formula C$_6$H$_5$SO$_2$NH(i,j-X$_2$C$_6$H$_3$) and 4-X'C$_6$H$_4$SO$_2$NH- groups in the compounds of the type 4-X'C$_6$H$_4$SO$_2$NH(C$_6$H$_5$) were computed (Table 5) and used to calculate the ^{1}H chemical shifts of the substituted compounds 4-X'C$_6$H$_4$SO$_2$NH(i,j-X$_2$C$_6$H$_3$) as described below.

The incremental shifts of aromatic protons in N-(substituted phenyl)-benzenesulphonamides due to –SO$_2$NH(i,j-X$_2$C$_6$H$_3$) [where i,j-X$_2$= 2,3-(CH$_3$)$_2$, 2,4-

Table 5. Incremental shifts (ppm) of aromatic protons due to –SO$_2$NH(i,j-X$_2$C$_6$H$_3$) groups in C$_6$H$_5$SO$_2$NH(i,j-X$_2$C$_6$H$_3$) and 4-X'C$_6$H$_4$SO$_2$NH– groups in 4-X'C$_6$H$_4$SO$_2$NH(C$_6$H$_5$).

Group	H-2',6'	H-3',5'	H-4'
–SO$_2$NHC$_6$H$_5$	0.67	0.22	0.52
–SO$_2$NH[(2,3-(CH$_3$)$_2$C$_6$H$_3$]	0.45	0.26	0.30
–SO$_2$NH[(2,4-(CH$_3$)$_2$C$_6$H$_3$]	0.65	0.26	0.43
–SO$_2$NH[(2,5-(CH$_3$)$_2$C$_6$H$_3$]	0.68	0.42	0.64
–SO$_2$NH[(2,6-(CH$_3$)$_2$C$_6$H$_3$]	0.43	0.17	0.27
–SO$_2$NH(2,3-Cl$_2$C$_6$H$_3$)	0.50	0.26	0.31
–SO$_2$NH(2,4-Cl$_2$C$_6$H$_3$)	0.66	0.14	0.20
–SO$_2$NH(2,5-Cl$_2$C$_6$H$_3$)	0.65	0.38	0.51
–SO$_2$NH(2,6-Cl$_2$C$_6$H$_3$)	0.68	0.53	0.64
–SO$_2$NH(3,4-Cl$_2$C$_6$H$_3$)	0.68	0.28	0.56
Group	H-2,6	H-3,5	H-4
C$_6$H$_5$SO$_2$NH–	0.08	−0.12	−0.24
4-CH$_3$C$_6$H$_4$SO$_2$NH–	−0.07	−0.18	−0.22
4-C$_2$H$_5$C$_6$H$_4$SO$_2$NH–	−0.13	−0.18	−0.35
4-FC$_6$H$_4$SO$_2$NH–	−0.07	−0.19	−0.25
4-ClC$_6$H$_4$SO$_2$NH–	−0.10	−0.14	−0.23
4-BrC$_6$H$_4$SO$_2$NH–	−0.09	−0.17	−0.23

(CH$_3$)$_2$, 2,5-(CH$_3$)$_2$, 2,6-(CH$_3$)$_2$, 2,3-Cl$_2$, 2,4-Cl$_2$, 2,5-Cl$_2$, 2,6-Cl$_2$ or 3,4-Cl$_2$] were calculated by comparing the chemical shifts of these protons in C$_6$H$_5$SO$_2$NH(i,j-X$_2$C$_6$H$_3$) with that of the benzene proton value of 7.29 ppm. The calculated values are shown in Table 5. Then the chemical shifts of the H-2',6' and H-3',5' protons in 4-X'C$_6$H$_4$SO$_2$NH(i,j-X$_2$C$_6$H$_3$) were calculated in two ways. In the first method (calc. 1) the chemical shifts of the H-2',6' and H-3',5' protons were calculated by adding the incremental shifts due to –SO$_2$NH(i,j-X$_2$C$_6$H$_3$) [i,j-X$_2$ = 2,3-(CH$_3$)$_2$, 2,4-(CH$_3$)$_2$, 2,5-(CH$_3$)$_2$, 2,6-(CH$_3$)$_2$, 2,3-Cl$_2$, 2,4-Cl$_2$, 2,5-Cl$_2$, 2,6-Cl$_2$ or 3,4-Cl$_2$] and the substituent X' (CH$_3$, C$_2$H$_5$, F, Cl or Br) (Table 5) to the benzene proton value of 7.29 ppm. In the second method (calc. 2) the chemical shifts of the H-2',6' and H-3',5' protons in 4-X'C$_6$H$_4$SO$_2$NH(i,j-X$_2$C$_6$H$_3$) were computed by adding the incremental shifts due to –SO$_2$NH(i,j-X$_2$C$_6$H$_3$) [i,j-X$_2$= 2,3-(CH$_3$)$_2$, 2,4-(CH$_3$)$_2$, 2,5-(CH$_3$)$_2$, 2,6-(CH$_3$)$_2$, 2,3-Cl$_2$, 2,4-Cl$_2$, 2,5-Cl$_2$, 2,6-Cl$_2$ or 3,4-Cl$_2$] to the chemical shifts of the corresponding protons in substituted benzenes. The calculated chemical shifts by the two methods compared well with each other and with the experimental chemical shifts.

Similarly, the incremental shifts of H-2,6; H-3,5 and H-4 protons due to 4-X'C$_6$H$_4$SO$_2$NH- groups (X' = H, CH$_3$, C$_2$H$_5$, F, Cl or Br) in 4-X'C$_6$H$_4$SO$_2$NH(C$_6$H$_5$) were computed by comparing the chemical shifts of H-2,6; H-3,5 and H-4 protons in these compounds with the benzene proton value of 7.29 ppm. The com-
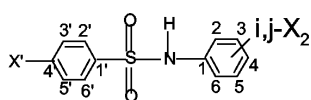
Table 6. Observed chemical shifts (δ, ppm) of aromatic and other carbon atoms in N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides.

	C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2',6'	C-3',5'	C-4'	Alkyl C
i,j-X$_2$ =					X' = H						
2,3-(CH$_3$)$_2$	134.0	131.9	138.0	125.6	126.0	123.6	139.7	127.3	129.0	133.3	20.6, 13.8
2,4-(CH$_3$)$_2$	133.2	131.5	129.3	136.5	127.5	125.5	139.7	127.1	129.0	132.5	20.9, 17.5
2,5-(CH$_3$)$_2$	132.9	127.7	129.3	125.4	130.6	–	133.2	127.1	129.3	132.9	21.0, 17.0
2,6-(CH$_3$)$_2$	137.9	130.0	127.9	127.2	127.9	130.0	140.7	127.2	128.8	132.9	18.7
2,3-Cl$_2$	135.1	127.8	133.5	126.5	127.8	120.2	138.7	127.2	129.2	133.1	–
2,4-Cl$_2$	134.7	129.2	129.2	134.4	127.4	–	141.4	127.4	129.2	134.7	–
2,5-Cl$_2$	138.5	125.9	130.1	123.4	133.5	122.3	141.4	127.1	129.2	133.2	–
2,6-Cl$_2$	135.2	129.0	127.5	127.5	127.5	129.3	141.5	127.7	129.3	133.3	–
3,4-Cl$_2$	133.6	122.8	136.1	130.9	129.4	120.4	138.3	127.2	129.1	133.1	–
					X' = CH$_3$						
2,3-(CH$_3$)$_2$	137.5	130.8	–	124.3	126.3	–	130.8	127.2	129.7	143.9	21.6, 17.6
2,4-(CH$_3$)$_2$	136.3	131.5	129.9	132.2	127.5	125.2	136.8	127.2	129.6	143.6	21.6, 20.9, 17.6
2,5-(CH$_3$)$_2$	136.9	127.2	129.6	125.1	136.7	125.1	130.5	127.0	128.2	143.7	21.6, 21.0, 17.1
2,6-(CH$_3$)$_2$	137.7	129.5	127.6	126.3	127.6	129.5	132.6	127.1	129.1	143.5	21.5, 20.7, 18.7
2,3-Cl$_2$	139.6	128.1	136.5	126.9	128.6	120.2	135.7	127.2	129.5	142.6	21.2
2,4-Cl$_2$	133.6	129.1	130.8	132.9	128.1	123.5	135.6	127.2	129.8	144.5	20.8
2,5-Cl$_2$	135.6	122.9	130.1	125.7	133.5	121.8	134.5	127.2	129.8	144.6	21.6
2,6-Cl$_2$	137.0	129.8	129.1	129.0	129.1	129.8	139.7	129.1	129.8	140.2	20.5
3,4-Cl$_2$	136.3	122.5	135.3	130.8	129.9	120.1	133.0	127.2	128.6	144.5	21.5
					X' = C$_2$H$_5$						
2,3-(CH$_3$)$_2$	136.9	131.7	137.8	127.3	125.8	123.3	134.2	127.3	128.4	149.7	28.7, 20.6, 15.1, 13.7
2,4-(CH$_3$)$_2$	136.2	131.5	131.8	132.2	127.4	125.2	137.0	127.3	128.4	149.8	28.8, 20.9, 17.5, 15.1
2,5-(CH$_3$)$_2$	137.1	125.2	128.4	127.3	136.8	–	130.5	127.0	128.2	149.9	28.9, 21.0, 17.1, 15.2
2,6-(CH$_3$)$_2$	137.8	128.8	127.8	125.7	127.8	128.8	137.0	127.3	128.5	149.9	28.9, 18.7, 15.3
2,3-Cl$_2$	139.8	127.5	133.5	129.0	129.2	120.6	137.9	127.0	129.0	141.4	20.5, 19.5
2,4-Cl$_2$	136.2	127.9	129.6	132.8	127.6	133.3	137.3	127.3	128.9	149.5	39.5, 15.3
2,5-Cl$_2$	136.8	124.7	130.7	125.0	135.1	121.4	137.1	127.3	128.6	150.2	28.8, 15.2
2,6-Cl$_2$	136.2	127.9	127.7	127.2	127.7	127.9	139.1	127.5	128.8	149.3	28.6, 15.3
3,4-Cl$_2$	136.8	121.5	133.0	132.3	130.7	119.6	138.1	127.1	128.6	149.7	28.4, 15.3
					X' = F						
2,3-(CH$_3$)$_2$	135.7	132.0	138.1	126.1	128.7	116.4	133.8	130.0	116.1	–	20.6, 13.8
2,4-(CH$_3$)$_2$	135.8	131.1	130.0	132.5	127.6	125.6	136.8	129.9	116.1	166.9	20.9, 17.6
2,5-(CH$_3$)$_2$	136.9	128.6	130.0	127.5	135.7	125.6	130.7	129.9	116.1	163.5	21.0, 17.1
2,6-(CH$_3$)$_2$	137.8	130.0	128.9	128.1	128.9	130.0	136.8	129.9	116.1	166.9	18.8
2,3-Cl$_2$	134.8	127.8	134.7	126.9	130.1	120.7	133.2	130.0	116.3	167.1	–
2,4-Cl$_2$	132.3	129.3	129.8	131.7	127.7	124.0	135.9	128.3	114.8	164.9	–
2,5-Cl$_2$	137.9	127.5	130.2	127.8	132.9	122.1	136.5	127.0	116.3	166.7	–
2,6-Cl$_2$	139.8	129.2	129.1	128.8	129.1	129.2	141.9	128.8	116.1	165.9	–
3,4-Cl$_2$	135.3	121.4	137.5	130.6	129.7	119.5	131.9	129.5	116.0	166.3	–
					X' = Cl						
2,3-(CH$_3$)$_2$	133.7	132.1	139.4	126.1	126.1	123.6	138.2	128.8	129.8	139.4	20.7, 13.9
2,4-(CH$_3$)$_2$	136.9	131.2	129.8	131.7	127.7	125.5	139.8	128.7	129.2	140.3	20.9, 17.6
2,5-(CH$_3$)$_2$	138.2	129.2	129.3	127.5	137.0	125.4	133.7	128.5	129.8	139.5	21.0, 17.1
2,6-(CH$_3$)$_2$	132.2	129.8	128.9	128.0	128.9	129.8	137.8	128.6	129.3	139.2	18.8
2,3-Cl$_2$	132.2	129.2	128.8	–	128.8	129.2	–	128.8	129.2	140.2	–
2,4-Cl$_2$	135.7	129.2	129.3	132.4	127.8	123.9	138.7	128.7	129.9	139.1	–
2,5-Cl$_2$	134.7	127.3	130.4	127.8	132.7	122.6	138.4	129.0	129.6	144.7	–
2,6-Cl$_2$	139.5	129.5	128.2	129.0	128.2	129.5	141.9	128.2	129.9	142.2	–
3,4-Cl$_2$	137.1	121.8	137.7	132.3	130.5	120.2	138.9	128.3	129.5	139.5	–
					X' = Br						
2,3-(CH$_3$)$_2$	134.0	131.7	137.6	126.1	125.3	121.1	138.4	128.3	132.6	128.5	20.2, 13.6
2,4-(CH$_3$)$_2$	132.7	131.6	131.1	136.7	127.5	125.5	138.7	129.1	132.2	127.5	20.9, 17.6
2,5-(CH$_3$)$_2$	136.8	129.1	130.7	127.9	133.7	125.5	138.7	128.6	132.8	127.5	21.0, 17.2
2,6-(CH$_3$)$_2$	137.8	129.2	129.0	128.2	129.0	129.2	139.7	128.8	132.8	127.9	18.6
2,3-Cl$_2$	134.7	132.5	133.3	126.9	128.7	120.4	137.8	129.2	132.7	127.9	–
2,4-Cl$_2$	133.1	129.3	128.6	132.7	127.3	123.2	139.3	129.8	132.1	128.0	–
2,5-Cl$_2$	138.8	126.1	130.3	126.8	132.5	–	139.7	128.9	131.9	128.3	–
2,6-Cl$_2$	132.7	129.3	127.6	128.0	127.6	129.3	140.3	128.8	132.4	128.4	–
3,4-Cl$_2$	133.1	122.3	133.3	132.5	129.5	120.2	137.7	129.0	131.6	128.0	–

puted incremental shifts are shown in Table 5. Then the chemical shifts of the protons in the substituted compounds $4\text{-}X'C_6H_4SO_2NH(i,j\text{-}X_2C_6H_3)$ were also calculated in two ways (calc. 3 and 4). In method 3, the proton chemical shifts were calculated by adding the incremental shifts due to $4\text{-}X'C_6H_4SO_2NH\text{-}$ ($X' = H$, CH_3, C_2H_5, F, Cl or Br) (Table 5) and the substituents $i,j\text{-}X_2$ [2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2,6-$(CH_3)_2$, 2,3-Cl_2, 2,4-Cl_2, 2,5-Cl_2, 2,6-Cl_2 or 3,4-Cl_2] [19, 20] to the benzene proton chemical shift of 7.29 ppm. In the other method (calc. 4) the chemical shifts of protons were calculated by adding the incremental shifts due to $4\text{-}X'C_6H_4SO_2NH\text{-}$ groups ($X' = H$, CH_3, C_2H_5, F, Cl or Br) (Table 5) to the corresponding proton chemical shifts of the disubstituted benzenes. The agreement between the two sets of calculated chemical shifts and the experimental values showed that the two procedures of calculation lead to almost the same values in most cases, thereby testing the validity of the principle of additivity of substituent effects in these compounds.

The effect of substitution on the chemical shifts of the aromatic protons in N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides have been analysed in terms of line diagrams (figures not shown). These plots have indicated that there are no particular trends in the variation of the chemical shifts with the nature of substitution, either electron withdrawing or electron donating groups. The variation of the chemical shifts of the N-H proton with substitution also did not show regular trends.

3.3. ^{13}C NMR Spectra

The ^{13}C chemical shifts of aromatic and alkyl carbon atoms of all the N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides are shown in Table 6. The various chemical shifts are assigned to the different carbon atoms in the two benzene rings in conformity with the literature for similar compounds [5, 14, 15, 19–25]. The ^{13}C chemical shifts of benzene and substituted benzenes were also measured under identical conditions. Further, the incremental shifts of C-1'; C-2',6'; C-3',5' and C-4' carbon atoms due to $-SO_2NH(i,j\text{-}X_2C_6H_3)$ groups in $C_6H_5SO_2NH(i,j\text{-}X_2C_6H_3)$ were calculated by comparing the chemical shifts of the carbon atoms in these compounds with those of benzene carbon value of 128.4 ppm. Similarly, the incremental shifts of C-1; C-2,6; C-3,5 and C-4 carbon atoms due to $4\text{-}X'C_6H_4SO_2NH\text{-}$

Table 7. Incremental shifts (in ppm) of aromatic carbon atoms due to $-SO_2NH(i,j\text{-}X_2C_6H_3)$ groups in $C_6H_5SO_2NH(i,j\text{-}X_2C_6H_3)$ and $4\text{-}X'C_6H_4SO_2NH\text{-}$ groups in $p\text{-}X'C_6H_4SO_2NH(C_6H_5)$.

Group	C-1'	C-2',6'	C-3',5'	c-4'
$-SO_2NHC_6H_5$	10.40	−0.80	0.90	4.90
$-SO_2NH(2\text{-}CH_3C_6H_4)$	11.30	−1.50	0.60	3.40
$-SO_2NH(3\text{-}CH_3C_6H_4)$	11.00	−0.70	0.60	4.90
$-SO_2NH(4\text{-}CH_3C_6H_4)$	10.70	−0.70	0.90	5.30
$-SO_2NH(2\text{-}ClC_6H_4)$	10.40	−1.20	1.00	4.90
$-SO_2NH(3\text{-}ClC_6H_4)$	10.40	−1.40	0.60	4.60
$-SO_2NH(4\text{-}ClC_6H_4)$	10.70	−0.50	1.00	5.00
$-SO_2NH[2,3\text{-}(CH_3)_2C_6H_3]$	11.30	−1.10	0.60	4.90
$-SO_2NH[2,4\text{-}(CH_3)_2C_6H_3]$	11.30	−1.30	0.60	4.10
$-SO_2NH[2,5\text{-}(CH_3)_2C_6H_3]$	4.80	−1.30	0.90	4.50
$-SO_2NH[2,6\text{-}(CH_3)_2C_6H_3]$	12.30	−1.20	0.40	4.50
$-SO_2NH(2,3\text{-}Cl_2C_6H_3)$	10.30	−1.20	0.80	4.70
$-SO_2NH(2,4\text{-}Cl_2C_6H_3)$	13.0	−1.00	0.80	6.30
$-SO_2NH(2,5\text{-}Cl_2C_6H_3)$	13.0	−1.30	0.80	4.80
$-SO_2NH(2,6\text{-}Cl_2C_6H_3)$	13.1	−0.70	0.90	4.90
$-SO_2NH(3,4\text{-}Cl_2C_6H_3)$	9.90	−1.20	0.70	4.70

Group	C-1	C-2,6	C-3,5	C-4
$C_6H_5SO_2NH\text{-}$	8.10	−6.90	0.60	−3.20
$4\text{-}CH_3C_6H_4SO_2NH\text{-}$	8.80	−6.70	1.00	−3.00
$4\text{-}C_2H_5C_6H_4SO_2NH\text{-}$	9.40	−7.90	1.20	−2.50
$4\text{-}FC_6H_4SO_2NH\text{-}$	7.90	−6.70	1.0	−2.80
$4\text{-}ClC_6H_4SO_2NH\text{-}$	7.70	−6.80	0.70	−2.90
$4\text{-}BrC_6H_4SO_2NH\text{-}$	7.60	−6.80	0.10	−2.90

groups in $4\text{-}X'C_6H_4SO_2NH(C_6H_5)$ were computed by comparing the chemical shifts of the carbon atoms in these compounds with the benzene carbon value of 128.4 ppm. The calculated incremental shifts of C-1'; C-2',6'; C-3',5' and C-4' carbon atoms due to $-SO_2NH(i,j\text{-}X_2C_6H_3)$ groups in $C_6H_5SO_2NH(i,j\text{-}X_2C_6H_3)$ and those of C-1; C-2,6; C-3,5 and C-4 carbon atoms due to $4\text{-}X'C_6H_4SO_2NH\text{-}$ groups in $4\text{-}X'C_6H_4SO_2NH(C_6H_5)$ are shown in Table 7.

These incremental shifts due to the above groups (Table 7) and those of the substituents [19, 20] were used to calculate the chemical shifts of C-1'; C-2',6'; C-3',5' and C-4' and those of C-1, C-2, C-3, C-4, C-5 and C-6 carbon atoms in the substituted compounds $4\text{-}X'C_6H_4SO_2NH(i,j\text{-}X_2C_6H_3)$ by methods similar to the ones described under ^1H NMR spectra. The calculated shifts have also revealed that the different procedures of calculation lead to almost the same values in most cases, indicating the validity of the principle of additivity of the substituent effects with ^{13}C chemical shifts.

The effect of substitution on the chemical shifts of the aromatic carbon atoms in N-(i,j-disubstituted phenyl)-4-substituted benzenesulphonamides have also been analysed through line diagrams (figures not

shown). There are no particular trends in the variation of these chemical shifts with the substitution.

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