Synthetic, Infrared, ^{1}H and ^{13}C NMR Spectral Studies on N-(2-/3-Substituted Phenyl)-4-Substituted Benzenesulphonamides, 4-X'$C_6H_4SO_2NH$(2-/3-XC_6H_4), where X' = H, CH_3, C_2H_5, F, Cl or Br, and X = CH_3 or Cl

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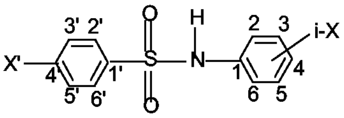
Twenty three N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides of the general formula, 4-X'$C_6H_4SO_2NH$(2-/3-XC_6H_4), where X' = H, CH_3, C_2H_5, F, Cl or Br and X = CH_3 or Cl have been prepared and characterized, and their infrared spectra in the solid state, ^{1}H and ^{13}C NMR spectra in solution were studied. The N-H stretching vibrations, ν_{N-H}, absorb in the range 3285 – 3199 cm^{-1}, while the asymmetric and symmetric SO_2 vibrations vary in the ranges 1376 – 1309 cm^{-1} and 1177 – 1148 cm^{-1}, respectively. The S-N and C-N stretching vibrations absorb in the ranges 945 – 893 cm^{-1} and 1304 – 1168 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 carbons of the two benzene rings. Incremental shifts of the ring protons and carbons due to –SO_2NH(2-/3-XC_6H_4) groups in $C_6H_5SO_2NH$(2-/3-XC_6H_4), and 4-X'$C_6H_4SO_2$- 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 carbons in the substituted compounds, 4-X'$C_6H_4SO_2NH$(2-/3-XC_6H_4). The computed values agree well with the observed chemical shifts.

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

1. Introduction

Sulphonamides exhibit pharmacological, fungicidal and herbicidal activities due to their oxidizing action in aqueous, partial aqueous and non-aqueous media [1 – 19]. Thus we have recently reported the synthesis, characterization, and spectral studies on N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides of the general formula *p*-X'$C_6H_4SO_2NH$(*p*-XC_6H_4), where X' or X = H, CH_3, C_2H_5, F, Cl or Br [16]. This paper reports the synthesis, characterization, infrared, ^{1}H and ^{13}C NMR spectral studies on twenty three N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides of the general formula 4-X'$C_6H_4SO_2NH$(2-/3-XC_6H_4), where X' = H, CH_3, C_2H_5, F, Cl or Br and X = CH_3 or Cl.

2. Experimental

2.1. Materials and Methods

N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides were prepared by the chlorosulphonation of substituted benzenes to substituted benzenesulphonylchlorides and subsequent conversion of the latter to substituted benzenesulphonamides by procedures similar to the ones described in [16, 20 – 23]. N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides so prepared were recrystallized to constant melting points from dilute ethanol (Table 1).

2.2. Spectral Measurements

Infrared spectral measurements were carried out in the solid state as pressed KBr pellets (13 mm) on a

Table 1. The melting points of N-(2-/3-substituted phenyl)-*p*-substituted benzenesulphonamides.

X', i-X	4-X'$C_6H_4SO_2NH$(2-/3-XC_6H_4)	M. p. [°C]
H, 2-CH_3	N-(2-methylphenyl)-benzenesulphonamide	76
H, 3-CH_3	N-(3-methylphenyl)-benzenesulphonamide	62
H, 2-Cl	N-(2-chlorophenyl)-benzenesulphonamide	72
H, 3-Cl	N-(3-chlorophenyl)-benzenesulphonamide	89
CH_3, 2-CH_3	N-(2-methylphenyl)-4-methylbenzenesulphonamide	70
CH_3, 3-CH_3	N-(3-methylphenyl)-4-methylbenzenesulphonamide	88
CH_3, 2-Cl	N-(2-chlorophenyl)-4-methylbenzenesulphonamide	87
CH_3, 3-Cl	N-(3-chlorophenyl)-4-methylbenzenesulphonamide	111
C_2H_5, 2-CH_3	N-(2-methylphenyl)-4-ethylbenzenesulphonamide	110
C_2H_5, 2-Cl	N-(2-chlorophenyl)-4-ethylbenzenesulphonamide	90
C_2H_5, 3-Cl	N-(3-chlorophenyl)-4-ethylbenzenesulphonamide	85
F, 2-CH_3	N-(2-methylphenyl)-4-fluorobenzenesulphonamide	92
F, 3-CH_3	N-(3-methylphenyl)-4-fluorobenzenesulphonamide	80
F, 2-Cl	N-(2-chlorophenyl)-4-fluorobenzenesulphonamide	96
F, 3-Cl	N-(3-chlorophenyl)-4-fluorobenzenesulphonamide	96
Cl, 2-CH_3	N-(2-methylphenyl)-4-chlorobenzenesulphonamide	111
Cl, 3-CH_3	N-(3-methylphenyl)-4-chlorobenzenesulphonamide	90
Cl, 2-Cl	N-(2-chlorophenyl)-4-chlorobenzenesulphonamide	87
Cl, 3-Cl	N-(3-chlorophenyl)-4-chlorobenzenesulphonamide	106
Br, 2-CH_3	N-(2-methylphenyl)-4-bromobenzenesulphonamide	119
Br, 3-CH_3	N-(3-methylphenyl)-4-bromobenzenesulphonamide	104
Br, 2-Cl	N-(2-chlorophenyl)-4-bromobenzenesulphonamide	101
Br, 3-Cl	N-(3-chlorophenyl)-4-bromobenzenesulphonamide	119

JASCO-430 (Japan), FT-IR spectrometer. The resolution was set to 4 cm^{-1}. The scanning range was from 400 – 4000 cm^{-1}.

The ^{1}H NMR spectra of all the N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides were recorded in $CDCl_3$ and DMSO with tetramethylsilane (Me_4Si) as internal standard on a BRUKER Ac 300F, 300 MHz FT-NMR spectrometer. The experimental conditions employed were as follows: The spectral frequency (SF) was kept at 300.134 MHz, sweep width (SW) at 6024.096, pulse width (PW) at 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. The reference value (SR) was set at 4125.36 ppm for H_2O internally.

The ^{13}C NMR spectra of all the compounds were also 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: The SF was kept at 75.469 MHz, SW at 22727.273, PW at 5.0, RD of 1.0 s, AQ was 0.360 s, RG 400, DP was 14H CPD, LB 6.0, SR was set at 701.89 ppm for DMSO at 39.5 ppm externally.

3. Results and Discussion

3.1. Infrared Spectra

Table 2. The comparison of N-H stretching, S=O (asym) and S=O (sym) infrared absorption frequencies [cm^{-1}] of N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides.

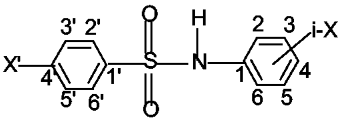
	4-X'$C_6H_4SO_2NH$(i-XC_6H_4) where X' =					
i-X	H	CH_3	C_2H_5	F	Cl	Br
N-H stretching						
H	3284.2w	3254.3w	3278.4w	3218.6s	3259.1m	3257.2m
2-CH_3	3216.7m	3268.8s	3266.8m	3275.5s	3284.2w	3266.8s
3-CH_3	3234.0s	3230.2w	–	3258.1s	3266.8m	3264.9s
4-CH_3	3270.7s	3234.0w	3263.9s	3270.7s	3233.1m	3234.0s
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
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
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

s = strong, m = medium and w = weak

The selected infrared absorption frequencies of all the twenty three N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides have been assigned to various modes of vibrations in conformity with the literature values for similar compounds [7, 8, 10, 11, 15 – 17, 24 – 26], 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.

The N-H stretching vibrational frequencies, ν_{N-H}, of N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides vary in the range 3285 – 3199 cm^{-1}. These are in conformity with the values of N-H symmetric stretching vibrations in the range 3334 – 3219 cm^{-1}, observed for N-(4-substituted phenyl)-4-substituted benzenesulphonamides. Asymmetric and symmetric SO_2 stretching vibrations appear in the ranges 1376 – 1309 cm^{-1} and 1177 – 1148 cm^{-1}, respectively, compared to the ranges of 1377 – 1311 cm^{-1} and 1182 – 1151 cm^{-1}, observed for the N-(4-substituted phenyl)-4-substituted benzenesulphonamides, respectively [16]. These ranges agree also with the assignments of bands in other substituted benzenesulphonamides. The N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides exhibit

Table 3. The observed chemical shifts (δ, ppm) of various aromatic and other protons in N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides.



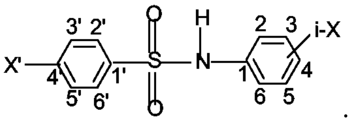
i-X	H-2	H-3	H-4	H-5	H-6	H-2',6'	H-3',5'	H-4'	N-H	Alkyl H
						where X' = H				
H	7.37d	7.17d	7.05d	7.17d	7.37d	7.96d	7.51d	7.81d	7.72	–
2-CH_3	–	7.10m	7.07m	7.16m	7.28t	7.73t	7.51m	7.57m	6.78	1.97
3-CH_3	7.40d	–	6.90m	7.10t	7.47m	7.97t	7.55m	7.79t	7.26	2.25
4-CH_3*	7.42d	6.98d	–	6.98d	7.42d	7.95d	7.52d	7.76m	7.26	2.24
2-Cl	–	7.22d	7.06d	7.15m	7.39d	7.76d	7.53m	7.67d	7.08	–
3-Cl	7.36m	–	7.00m	7.05m	7.18t	7.84d	7.41d	7.48m	8.74	–
4-Cl*	7.37m	7.32m	–	7.32m	7.37m	7.91d	7.75m	7.79m	8.01	–
						CH_3				
H	7.22d	7.11m	7.07m	7.11m	7.22d	7.67d	7.26d	–	6.91	2.37
2-CH_3	–	7.10m	7.04m	7.20m	7.14m	7.62d	7.29d	–	6.43	2.36, 2.00
3-CH_3	7.06t	–	6.86t	6.90t	7.11t	7.68d	7.23m	–	–	2.36, 2.25
4-CH_3*	7.00m	6.93m	–	6.93m	7.00m	7.65d	7.20d	–	7.10	2.37, 2.24
2-Cl	–	–	6.96d	7.02d	7.16t	7.67m	7.21t	–	–	2.31
3-Cl	7.28d	–	7.00d	7.07d	7.19t	7.74d	7.21m	–	7.42	2.31
4-Cl*	7.18d	7.12m	–	7.12m	7.18d	7.68d	7.25d	–	7.41	2.64, 2.29
						C_2H_5				
H	7.16d	7.11d	6.94d	7.11d	7.16d	7.73d	7.43d	–	9.70	2.57, 1.15
2-CH_3	–	7.08d	7.05d	7.12d	7.22d	7.66t	7.32d	–	–	2.64, 2.15,1.20
4-CH_3*	7.20d	6.98d	–	6.98d	7.20d	7.70d	7.25d	–	7.32	2.65, 2.24,1.20
2-Cl	–	7.13d	7.00d	7.06d	7.21d	7.68d	7.42t	–	10.55	2.61, 1.17
3-Cl	7.20t	–	6.96d	7.06d	7.20t	7.80d	7.22t	–	8.14	2.58, 1.13
4-Cl*	7.21d	7.13d	–	7.13d	7.21d	7.71d	7.41d	–	10.04	2.63, 1.19
						F				
H	7.22d	7.10m	7.04m	7.10m	7.22d	7.83m	7.80m		7.70s	–
2-CH_3	–	7.06d	7.09d	7.12d	7.16d	7.73m	7.78m	–	7.26s	2.02
3-CH_3	7.11d	–	6.88t	6.94t	7.03d	7.87d	7.82d	–	7.73s	2.22
4-CH_3*	7.07m	7.00m	–	7.00m	7.07m	7.83m	7.77m	–	7.50s	2.27
2-Cl	–	7.10d	7.02d	7.14d	7.19d	7.88d	7.92d	–	8.11s	–
3-Cl	7.26d	–	7.03d	7.10d	7.21d	7.84t	7.77d	–	7.35s	–
4-Cl*	7.10d	6.78s	–	6.78s	7.10d	7.33d	7.81d	–	10.17s	–
						Cl				
H	7.19m	7.15m	7.06d	7.15m	7.19m	7.76d	7.30d	–	7.94s	–
2-CH_3	–	7.11t	7.08d	7.15d	7.27d	7.88t	7.50t	–	6.75s	2.03
3-CH_3	7.08t	–	6.91t	7.13t	7.38t	7.87d	7.47d	–	7.26s	2.26
4-CH_3*	7.04m	6.96m	–	6.96m	7.04m	7.70d	7.37d	–	7.26s	2.26
2-Cl	–	7.24t	7.06d	7.10d	7.37t	7.67d	7.40t	–	7.18s	–
3-Cl	7.18d	–	7.01d	7.06d	7.11d	7.89d	7.37d	–	7.99s	–
4-Cl*	7.20d	7.04d	–	7.04d	7.20d	7.71d	7.49d	–	7.26s	–
						Br				
H	7.20d	7.12m	7.06	7.12m	7.20d	7.65d	7.47d	–	7.80s	
2-CH_3	–	7.13d	7.10d	7.18t	7.27d	7.79d	7.59d	–	6.63s	2.02
3-CH_3	7.05t	–	6.87d	6.95d	7.11t	7.79t	7.60t	–	–	2.21
4-CH_3*	7.02m	6.95m	–	6.95m	7.02m	7.62d	7.48d	–	9.20s	2.26
2-Cl	–	7.68d	–	7.68d	7.68d	7.83d	7.70d	–	–	–
3-Cl	7.18d	–	7.00d	7.06d	7.14d	7.70t	7.56d	–	7.81s	–
4-Cl*	7.20d	7.04d	–	7.04d	7.20d	7.64d	7.56d	–	7.26s	

S-N and C-N stretching vibrations absorbing in the ranges 945 – 893 cm^{-1} and 1304 – 1168 cm^{-1}, respectively. These absorptions in N-(4-substituted phenyl)-4-substituted benzenesulphonamides were observed in the ranges 937 – 898 cm^{-1} and 1310 – 1180 cm^{-1}, respectively [16]. The assignment of other frequencies to various modes of vibrations of the ring (Tables 2 – 5) are similar to those in arylsulphonamides [7], N-haloarylsulphonamides [8, 10, 11, 15] and other aromatic organic compounds [24, 25].

The ν_{N-H}, $\nu_{S=O(asym)}$, and $\nu_{S=O(sym)}$ vibrations of all the N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides are summarised in Table 2 and compared with those of N-(4-substituted phenyl)-4-substituted benzenesulphonamides [16]. The variations of these absorption frequencies with substitution in the phenyl ring in N-(2-/3-substituted 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 the N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides are shown in Table 3. The aromatic protons and carbons 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 those for similar compounds [16, 24–32]. ^{1}H chemical shifts of benzene and substituted benzenes were also measured under identical conditions. Further, the incremental shifts due to –SO_2NH(2-/3-C_6H_4) groups in the compounds of the general formula $C_6H_5SO_2$NH(2-/3-XC_6H_4) and 4-X'$C_6H_4SO_2$NH- groups in the compounds of the type 4-X'$C_6H_4SO_2$NH(C_6H_5) were computed and used to calculate the ^{1}H chemical shifts of the substituted compounds 4-X'$C_6H_4SO_2$NH(2-/3-XC_6H_4) as described below.

The incremental shifts of the aromatic protons in N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides due to –SO_2NH(2-/3-XC_6H_4) (X = CH_3 or Cl) were calculated by comparing the chemical shifts of these protons in $C_6H_5SO_2$NH(2-/3-XC_6H_4) (X = CH_3 or Cl) with that of the benzene proton value of 7.29 ppm. The calculated values are shown in Table 4. Then the chemical shifts of the H-2',6' and H-3',5' protons in 4-X'$C_6H_4SO_2$NH(2-/3-XC_6H_4) were calculated in two ways. In the first way (calc. 1), the chemical shifts of H-2',6' and H-3',5' protons were calculated by adding the incremental shifts due to –SO_2NH(2-/3-XC_6H_4) (Table 4) and of the substituent X' (CH_3, C_2H_5, F, Cl or Br) [24, 25] to the benzene proton value of 7.29 ppm. In the second method (calc. 2), the chemical shifts of H-2',6' and H-3',5' protons in 4-X'$C_6H_4SO_2$NH(2-/3-XC_6H_4) were computed by adding the incremental shifts due to –SO_2NH (2-/3-XC_6H_4) to the chemical shifts of the corresponding protons in substituted benzenes. The good agreement between the two sets of calculated values and the experimental chemical shifts show that the two methods of calculations lead to almost the same values.

Similarly, the incremental shifts of H-2,6; H-3,5 and H-4 protons due to 4-X'$C_6H_4SO_2$NH- (X' = H, CH_3, C_2H_5, F, Cl or Br) groups in 4-X'$C_6H_4SO_2$NH(C_6H_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 computed incremental shifts are also shown in Table 4. The chemical shifts of the H-2,6 and H-3,5 protons in the substituted compounds 4-X'$C_6H_4SO_2$NH(2-/3-XC_6H_4) were also calculated in two ways (calc. 3 and 4). In the method 3, the chemical shifts of H-2,6 and H-3,5 protons were calculated by adding the incremental shifts due to 4-X'$C_6H_4SO_2$NH- (X' = H, CH_3, C_2H_5, F, Cl or Br) (Table 4) and of the substituent 2-/3-X (X = CH_3 or Cl) [24, 25] to the benzene proton chemical shift of 7.29 ppm. In the other method (calc. 4), the chemical shifts of H-2,6 and H-3,5 protons were calculated by adding the incremental shifts due to 4-X'$C_6H_4SO_2$NH- (X' = H, CH_3, C_2H_5, F, Cl or Br) groups (Table 4) to the corresponding proton chemical shifts of the substituted benzenes. The comparisons between the values calculated by the methods 3 and 4 and the experimental values revealed that there is a good agreement between the two sets of calculated chemical shifts and the experimental values, indicating the validity of the principle of additivity of the substituent effects in these compounds.

Table 4. The incremental shifts (δ, ppm) of aromatic protons due to -SO_2NH(*i*-XC_6H_4) groups in $C_6H_5SO_2$NH(*i*-XC_6H_4) and 4-X'$C_6H_4SO_2$NH- groups in 4-X'$C_6H_4SO_2$NH(C_6H_5).

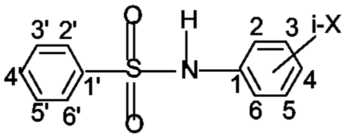
Group	H-2',6'	H-3',5'	H-4'
-$SO_2NHC_6H_5$	0.67	0.22	0.52
-SO_2NH(2-$CH_3C_6H_4$)	0.44	0.22	0.28
-SO_2NH(3-$CH_3C_6H_4$)	0.68	0.26	0.50
-SO_2NH(4-$CH_3C_6H_4$)	0.66	0.23	0.47
-SO_2NH(2-ClC_6H_4)	0.47	0.24	0.38
-SO_2NH(3-ClC_6H_4)	0.55	0.12	0.19
-SO_2NH(4-ClC_6H_4)	0.62	0.46	0.50
Group	H-2,6	H-3,5	H-4
$C_6H_5SO_2$NH–	0.08	−0.12	−0.24
4-$CH_3C_6H_4SO_2$NH–	−0.07	−0.18	−0.22
4-$C_2H_5C_6H_4SO_2$NH–	−0.13	−0.18	−0.35
4-F$C_6H_4SO_2$NH–	−0.07	−0.19	−0.25
4-Cl$C_6H_4SO_2$NH–	−0.10	−0.14	−0.23
4-Br$C_6H_4SO_2$NH–	−0.09	−0.17	−0.23

It is evident from the analysis of the chemical shifts of the N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides that there are no particular trends in the variation of the chemical shifts with the nature of substitution, either the electron withdrawing or electron donating groups.

3.3. ^{13}C NMR Spectra

The measured ^{13}C chemical shifts of the aromatic and alkyl carbons of all the N-(2-/3-substituted

Table 5. Observed chemical shifts (δ, ppm) of various aromatic and other carbons in N-(2-/3-substituted phenyl)-4-substituted benzenesulphonamides.



i-X	C-1	C-2	C-3	C-4	C-5	C-6	C-1’	C-2’,6’	C-3’5’	C-4’	Alkyl C
H											
H	136.5	121.5	129.0	125.2	129.0	121.5	138.8	127.6	129.3	133.3	–
2-CH_3	134.4	130.8	129.7	124.8	126.4	124.8	139.7	126.9	129.0	131.8	17.6
3-CH_3	133.1	122.4	133.3	129.3	127.7	118.6	139.4	127.7	129.0	133.3	21.4
4-CH_3*	133.3	122.4	129.8	135.4	129.8	122.4	139.1	127.7	129.3	133.7	20.8
2-Cl	133.3	127.7	129.1	125.4	126.1	122.8	138.8	127.2	127.9	129.4	–
3-Cl	138.2	120.6	134.6	124.7	130.2	118.7	138.8	127.0	129.0	133.0	–
4-Cl*	133.4	124.7	129.4	130.3	129.4	124.7	139.1	127.9	129.4	133.4	–
CH_3											
H	137.2	121.7	129.4	125.4	129.4	121.7	135.9	127.4	129.7	144.0	–
2-CH_3	136.7	131.4	130.8	126.2	127.2	124.4	134.6	127.0	129.7	143.8	21.6, 17.7
3-CH_3	139.3	122.0	139.3	126.0	129.1	118.3	136.5	127.3	129.7	143.8	21.6, 21.4
4-CH_3*	133.9	122.2	130.1	135.3	130.1	122.2	136.1	127.4	129.7	143.8	21.5, 20.4
2-Cl	135.8	127.1	129.5	125.1	125.8	122.4	133.4	127.7	129.3	144.1	21.4
3-Cl	138.0	120.7	134.8	125.0	130.3	118.8	135.6	127.3	129.8	144.3	20.9
4-Cl*	135.4	122.7	129.4	132.8	129.4	122.7	137.1	127.3	130.6	144.2	21.5
C_2H_5											
H	137.8	120.5	129.6	125.9	129.6	120.5	137.1	127.5	128.9	149.2	–
2-CH_3	136.9	130.7	131.7	126.1	126.8	124.4	134.5	127.2	128.4	149.8	28.7, 17.6, 15.0
4-CH_3*	133.9	122.0	129.8	135.1	129.8	122.0	136.3	127.4	128.5	149.8	26.8, 20.8
2-Cl	137.4	126.1	129.8	126.8	127.6	125.6	133.9	127.3	127.8	146.6	28.7, 15.4
3-Cl	138.0	120.5	134.6	124.8	130.8	118.6	135.6	127.3	128.6	150.2	28.6, 14.7
4-Cl*	133.7	121.6	129.4	130.0	129.4	121.6	136.6	128.2	128.7	149.2	28.3, 15.4
F											
H	136.3	121.7	129.4	125.6	129.4	121.7	134.9	130.1	116.2	166.9	–
2-CH_3	135.7	131.0	130.0	125.0	126.6	116.0	134.2	129.9	116.1	166.9	17.6
3-CH_3	136.2	122.2	139.4	126.3	130.0	118.5	134.9	129.1	116.1	163.5	21.2
4-CH_3*	133.5	122.4	130.1	135.6	130.1	122.4	134.8	129.9	116.2	166.8	20.8
2-Cl	137.5	130.1	130.4	125.4	–	121.1	134.8	130.0	116.3	163.6	–
3-Cl	134.8	123.5	130.3	125.9	130.0	116.7	133.0	127.9	116.0	166.9	–
4-Cl*	135.4	123.3	129.5	132.9	129.5	123.3	136.2	128.7	115.8	162.7	–
Cl											
H	136.1	121.6	129.1	125.5	129.1	121.6	137.1	128.6	129.7	139.4	–
2-CH_3	138.2	131.0	129.8	126.7	127.0	124.8	139.5	128.6	129.3	140.2	17.6
3-CH_3	136.0	122.4	139.5	126.5	129.2	118.6	137.5	128.7	129.3	140.3	21.4
4-CH_3*	133.3	122.5	129.9	135.8	129.9	122.5	137.4	128.8	129.2	139.5	20.9
2-Cl	132.9	129.1	129.3	126.5	127.9	123.3	137.3	128.7	129.5	139.8	–
3-Cl	137.4	121.1	134.9	125.5	130.4	119.1	136.8	128.6	129.5	139.9	–
4-Cl*	134.7	123.2	129.2	131.4	129.2	123.2	137.0	128.7	129.7	139.9	–
Br											
H	136.0	121.6	128.5	125.5	128.5	121.6	137.6	129.2	132.5	128.0	–
2-CH_3	134.0	131.0	128.7	126.8	127.1	124.7	138.7	129.2	132.8	126.8	17.7
3-CH_3	136.0	122.1	139.4	128.0	128.4	118.4	137.8	128.7	132.7	126.3	21.3
4-CH_3*	134.2	121.7	129.5	134.5	129.5	121.7	138.6	131.8	132.6	128.6	20.6
2-Cl	132.3	128.2	128.7	–	–	–	139.6	128.7	132.3	128.2	–
3-Cl	137.5	121.2	135.1	125.6	130.5	119.2	137.7	128.8	132.6	128.6	–
4-Cl*	134.6	123.2	129.2	131.4	129.2	123.2	137.6	129.2	132.5	128.0	–

phenyl)-4-substituted benzenesulphonamides are shown in Table 5. The various chemical shifts are assigned to the different carbons in the two benzene rings in conformity with the literature for similar compounds [16, 24–32]. The ^{13}C chemical shifts of benzene and substituted benzenes were measured under identical conditions. Further, the incremental shifts of C-1’; C-2’,6’; C-3’,5’ and C-4’ carbons due to –SO_2NH(2-/3-XC_6H_4) groups in $C_6H_5SO_2NH$ (2-/3-XC_6H_4) were calculated by comparing the chemical shifts of the carbons in these compounds with that of the benzene carbon value of 128.4 ppm. Similarly, the incremental shifts of C-1; C-2,6; C-3,5 and C-4 carbons due to 4-X’$C_6H_4SO_2NH$- groups in 4-X’$C_6H_4SO_2NH$ (C_6H_5) were computed by comparing the chemical shifts of the carbons 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’

Table 6. The incremental shifts (δ, ppm) of aromatic carbons due to -SO_2NH (i-XC_6H_4) groups in C_6H_5 SO_2NH (i-XC_6H_4) and 4-X'$C_6H_4SO_2$ NH- groups in 4-X'$C_6H_4SO_2$ NH (C_6H_5).

Group	C-1'	C-2',6'	C-3',5'	C-4'	Group	C-1	C-2,6	C-3,5	C-4
-$SO_2NHC_6H_5$	10.40	−0.80	0.90	4.90	$C_6H_5SO_2$NH-	8.10	−6.90	0.60	−3.20
-SO_2NH(2-$CH_3C_6H_4$)	11.30	−1.50	0.60	3.40	4-$CH_3C_6H_4SO_2$NH-	8.80	−6.70	1.00	−3.00
-SO_2NH(3-$CH_3C_6H_4$)	11.00	−0.70	0.60	4.90	4-$C_2H_5C_6H_4SO_2$NH-	9.40	−7.90	1.20	−2.50
-SO_2NH(4-$CH_3C_6H_4$)	10.70	−0.70	0.90	5.30	4-$FC_6H_4SO_2$NH-	7.90	−6.70	1.0	−2.80
-SO_2NH(2-ClC_6H_4)	10.40	−1.20	1.00	4.90	4-$ClC_6H_4SO_2$NH-	7.70	−6.80	0.70	−2.90
-SO_2NH(3-ClC_6H_4)	10.40	−1.40	0.60	4.60	4-$BrC_6H_4SO_2$NH-	7.60	−6.80	0.10	−2.90
-SO_2NH(4-ClC_6H_4)	10.70	−0.50	1.00	5.00					

and C-4' carbons due to –SO_2NH(2-/3-XC_6H_4) groups in $C_6H_5SO_2$NH(2-/3-XC_6H_4) and those of C-1; C-2,6; C-3,5 and C-4 carbons due to 4-X'$C_6H_4SO_2$NH- groups in 4-X'$C_6H_4SO_2$NH(C_6H_5) are shown in Table 6. These incremental shifts due to the above groups (Table 6) and those of the substituents [24, 25] were used to calculate the chemical shifts of C-1'; C-2',6'; C-3',5' and C-4' carbons and those of C-1; C-2,6; C-3,5 and C-4 carbons in the substituted compounds 4-X'$C_6H_4SO_2$NH(2-/3-XC_6H_4) by the methods similar to the ones described under ^{1}H NMR spectra. The good agreement between the various calculated ^{13}C chemical shifts and the experimental values showed that the different procedures of calculation lead to almost the same values in most cases, testing the validity of the principle of additivity of the substituent effects. Further, the analysis of the experimental ^{13}C chemical shifts revealed that there are no particular trends in the variation of the chemical shifts with the nature of substitution, as in the case of ^{1}H NMR.

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