Synthetic, Infrared and NMR (^{1}H and ^{13}C) Spectral Studies of N-(Substituted Phenyl)-Methanesulphonamides

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Twenty two N-(substituted phenyl)-methanesulphonamides of the general formula, CH_3SO_2NHR, where R = 4-XC_6H_4(X = H, CH_3, F, Cl, Br or NO_2), i-XC_6H_4(X = CH_3, Cl or NO_2 and $i = 2$ or 3) and i,j-$X_2C_6H_3$(i,j-X_2 = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2,6-$(CH_3)_2$, 3,5-$(CH_3)_2$, 2,3-Cl_2, 2,4-Cl_2, 2,5-Cl_2, 2,6-Cl_2 or 3,4-Cl_2) were prepared, characterized and their infrared spectra in the solid state and the NMR (^{1}H and ^{13}C) spectra in solution studied. The N-H stretching vibrations absorb in the range, 3298 – 3232 cm^{-1}. Asymmetric and symmetric SO_2 stretching vibrations appear as strong absorptions in the ranges, 1331 – 1317 cm^{-1} and 1157 – 1139 cm^{-1}, respectively. The sulphonamides exhibit S-N stretching vibrations in the range, 926 – 833 cm^{-1}. The effect of substitution in the phenyl ring in terms of electron withdrawing and electron donating groups is non-systematic. The ^{1}H and ^{13}C chemical shifts of N-(substituted phenyl)-methanesulphonamides are assigned to various protons and carbons of the compounds. Further, incremental shifts of the ring protons and carbons due to CH_3SO_2- and CH_3SO_2NH- groups in the N-(phenyl)-methanesulphonamide are computed and used to calculate the ^{1}H and ^{13}C chemical shifts of various protons and carbons of N-(substituted phenyl)-methanesulphonamides, by adding substituent contributions to the corresponding aromatic proton or carbon chemical shifts of either aniline, substituted anilines, benzene or substituted benzenes, in different ways, as per the principle of substituent addition. The computed values by different procedures agree well with each other and with the experimental chemical shifts. The correlation of these incremental shifts with the Hammett substituent parameters is poor.

Key words: Infrared; ^{1}H and ^{13}C NMR; N-(substituted phenyl)-methanesulphonamides.

1. Introduction

Sulphonamides are of fundamental chemical interest as they show distinct physical, chemical and biological properties. Many sulphonamides exhibit pharmacological, fungicidal and herbicidal activities because of their oxidising action in aqueous, partial aqueous and non-aqueous media [1 – 12]. Thus an understanding of the formation, properties and reactions of sulphonamides is central to future development in areas such as medicinal and redox chemistry [13 – 19]. We report herein the preparation, characterization, IR and NMR spectra of 22 N-(substituted phenyl)-methanesulphonamides of the general formula, CH_3SO_2NHR, where R = 4-XC_6H_4(X = H, CH_3, F, Cl, Br or NO_2); i-XC_6H_4 (X = CH_3, Cl or NO_2 and $i = 2$ or 3) and i,j-$X_2C_6H_3$(i,j-X_2 = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2,6-$(CH_3)_2$, 3,5-$(CH_3)_2$, 2,3-Cl_2, 2,4-Cl_2, 2,5-Cl_2, 2,6-Cl_2 or 3,4-Cl_2).

2. Experimental

2.1. Materials and Methods

The N-(substituted phenyl)-methanesulphonamides were prepared by the reactions of methane sulphonylchloride with the corresponding anilines [20]. The reaction mixtures were heated to about 40 – 50° for a few minutes and allowed to stand for several hours to several days at room temperature. The completion of the reactions with nitro substituted compounds took longer periods, while those of the methyl substituted compounds took longer periods for the precipitation due to crystallization problems. The products were then cooled with ice cold water. The resultant solid sulphonamides were filtered under suction, washed thoroughly with ice cold water and recrystallised to constant melting points from dilute ethanol (Table 1).

Table 1. The melting points of N-(substituted phenyl)-methanesulphonamides.

SI.No	N-(substituted phenyl)-methanesulphonamides	m. p. (°C)
1	$CH_3SO_2NHC_6H_5$	99
2	$CH_3SO_2NH(2\text{-}CH_3C_6H_4)$	44
3	$CH_3SO_2NH(2\text{-}ClC_6H_4)$	56
4	$CH_3SO_2NH(2\text{-}NO_2C_6H_4)$	158 – 160
5	$CH_3SO_2NH(3\text{-}CH_3C_6H_4)$	46 – 49
6	$CH_3SO_2NH(3\text{-}ClC_6H_4)$	38
7	$CH_3SO_2NH(3\text{-}NO_2C_6H_4)$	150 – 152
8	$CH_3SO_2NH(4\text{-}CH_3C_6H_4)$	40
9	$CH_3SO_2NH(4\text{-}FC_6H_4)$	46
10	$CH_3SO_2NH(4\text{-}ClC_6H_4)$	122 – 124
11	$CH_3SO_2NH(4\text{-}BrC_6H_4)$	96 – 98
12	$CH_3SO_2NH(4\text{-}NO_2C_6H_4)$	176 – 178
13	$CH_3SO_2NH(2,3\text{-}(CH_3)_2C_6H_3)$	38 – 40
14	$CH_3SO_2NH(2,4\text{-}(CH_3)_2C_6H_3)$	46 – 48
15	$CH_3SO_2NH(2,5\text{-}(CH_3)_2C_6H_3)$	42
16	$CH_3SO_2NH(2,6\text{-}(CH_3)_2C_6H_3)$	37 – 40
17	$CH_3SO_2NH(3,5\text{-}(CH_3)_2C_6H_3)$	38 – 40
18	$CH_3SO_2NH(2,3\text{-}Cl_2C_6H_3)$	52
19	$CH_3SO_2NH(2,4\text{-}Cl_2C_6H_3)$	78 – 80
20	$CH_3SO_2NH(2,5\text{-}Cl_2C_6H_3)$	126
21	$CH_3SO_2NH(2,6\text{-}Cl_2C_6H_3)$	56 – 58
22	$CH_3SO_2NH(3,4\text{-}Cl_2C_6H_3)$	116 – 118

2.2. Spectral Measurements

Infrared spectra: Infrared spectral measurements were made on a JASCO-430 (Japan) FT-IR spectrometer. The resolution was set to 2 cm^{-1} and the scanning range was 400 to 4000 cm^{-1}. The spectra were measured in the solid state as pressed KBr pellets (13 mm).

^{1}H and ^{13}C NMR spectra: The proton NMR spectra of all the N-(substituted phenyl)-methanesulphonamides 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; 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) of 1.0(sec), acquisition time (AQ) was 1.360(sec), receiver gain (RG) 10, decoupling power (DP) was 63L CPD, filter to suppress noise (LB) 0.0, reference value (SR) was set at 4125.36 ppm for H_2O internally. For ^{13}C NMR spectra, the spectral frequency (SF) was kept at 75.469 MHz, sweep

Table 2. Infrared absorption frequencies (cm^{-1}) of N-(2/3-substituted phenyl)-methanesulphonamides.

Assignments	$CH_3SO_2NH(i\text{-}XC_6H_4)$; i-X =						
	H	$2\text{-}CH_3$	2-Cl	$2\text{-}NO_2$	$3\text{-}CH_3$	3-Cl	$3\text{-}NO_2$
N-H(Sym str)	3256.2s	3280.3s	3283.2s	3282.6s	3249.5s	3232.1s	3298.0s
C-H (Ar sym str)	3018.1w	3025.8w 3010.3w	3012.3w	–	3018.1w	–	3120.6w 3035.7w
C-H(Alk str)	2932.2w	2979.5w 2931.3w	2933.2w	2929.7w	2929.3w	2928.4m	2941.2w
Combination bands	–	1951.6w	1624.7w	–	1610.3w	–	1969.2w 1897.8w 1622.0w
C=C (Ar in plane str)	1595.8w 1495.5w 1472.4w	1583.3m 1496.5m 1467.6w	1588.1w 1479.1s 1456.0w	1487.0m	1589.1w 1492.6m	1594.8w 1554.3w 1505.2w 1474.3m	1527.5s 1483.2m
N-H(in plane bend)	1394.3m	1400.1m	1399.1m	1380.9m	1390.4m	1391.4m	1404.1m
S=O (Asym str)	1323.9s	1317.1s	1318.1s	1323.1s	1317.1s	1318.1s	1328.9s
C-N(str)	1275.7w –	1280.5w 1238.1w	1275.7m 1224.6w	1272.9w	1270.9w 1251.6w	–	1267.1w 1224.7w
S=O(Sym str)	1151.3s	1153.2s	1155.2s	1153.4s	1145.5s	1148.4s	1155.3s
C-H(Ar in plane bend)	1076.1w 1027.9w	1110.8m 1045.2w	1058.7m	1112.9w	–	1080.9w	1080.1w
C-X(str)	–	–	1032.7w	–	–	–	–
S-N(sym str)	895.8w	914.1w	866.9w	867.9w	912.2w	866.9w	883.3s
C-S(str)	774.3w	742.5s	745.4m	759.9m	771.4m	786.8m	738.7m
C-H(Ar out of plane bend)	756.9w 650.3w	833.1m 626.8w	685.6w 619.0w	827.4w 603.7w	742.5m 644.1w	675.9m	815.8m 673.1m
N-H(out of plane bend)	694.3m	709.7w	720.3w	–	692.3m	707.8w	–
C=C(Ar out of plane bend)	490.0w	445.5w 428.1w	457.1w 413.7w	466.7m 432.0w	447.4w 408.8w	–	–

s = strong, m = medium and w = weak

Assignments	$CH_3SO_2NH(i\text{-}XC_6H_4)$; i-X =					
	H	4-CH_3	4-F	4-Cl	4-Br	4-NO_2
N-H(Sym str)	3256.2s	3291.9s	3243.7s	3288.0s	3286.5s	3283.2w
C-H (Ar sym str)	3018.1w	3021.9w	3015.2w	3006.5w	–	–
C-H(Alk str)	2932.2w	2931.3w 2865.7w	2931.3w	2927.4w	–	–
Combination bands	–	1889.9w 1614.1m	1605.5w	–	1668.3w	1631.5 m
C=C (Ar in plane str)	1595.8w 1495.5w 1472.4w	1510.0m 1475.3m	1509.0m 1448.3w	1589.1w 1490.7m 1452.1m	1587.3w 1488.9m 1448.4m	1597.7m 1474.3m
N-H(in plane bend)	1394.3m	1394.3m	1391.4w	1386.6m	1382.9m	–
S=O (Asym str)	1323.9s	1330.6s	1319.1s	1326.8s	1323.1s	1327.6s
C-N(str)	1275.7w –	1282.4w 1230.4w	1243.9w	1294.0w 1218.8w	–	–
S=O(Sym str)	1151.3s	1155.2s	1145.5s	1146.5s	1149.5s	1138.8s
C-H(Ar in plane bend)	1076.1w 1027.9w	1047.2w 1020.2w	1093.4w	1090.6m	1066.6w	1112.7s
C-X(str)	–	–	–	1016.3w	–	–
S-N(sym str)	895.8w	925.7w	898.7w	899.6w	–	841.8w
C-S(str)	774.3w	771.4w	777.2w	773.3m	765.7m	751.1w
C-H(Ar out of plane bend)	756.9w 650.3w	740.5w 642.2w	– 647.0w	696.2w 626.8w	677.0w	–
N-H(out of plane bend)	694.3m	–	–	711.6w	–	–
C=C(Ar out of plane bend)	490.0w	–	–	493.7m 452.2w	–	492.7w

Table 3. Infrared absorption frequencies (cm^{-1}) of N-(4-substituted phenyl)-methanesulphonamides.

s = strong, m = medium and w = weak

Assignments	$CH_3SO_2NH(i\text{-}XC_6H_4)$; i, j-X_2 =				
	2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2,6-$(CH_3)_2$	3,5-$(CH_3)_2$
N-H(Sym str)	3272.6s	3276.5s	3274.5s	3268.8s	3253.3s
C-H (Ar sym str)	3016.1w	–	3016.1w	3010.3w	3037.3w
C-H(Alk str)	2933.2w	2931.3w	2931.3w	2930.3w	2942.8w 2916.8w
Combination bands	1618.0w	–	1618.0w	–	1731.8w 1606.4s
C=C (Ar in plane str) 1411.6m	1577.5w 1508.1w	1502.3w	1577.5w 1508.1w	1470.5w	1505.2m 1437.7m
N-H(in plane bend)	1396.2m	1386.6m	1394.3m	1397.2m	1371.1w
S=O (Asym str)	1319.1s	1322.9s	1319.1s	1318.1s	1327.8s
C-N(str)	1253.5w	1284.4w	1253.5w	1195.7w	1258.3m
S=O(Sym str)	1153.2s	1153.2s	1153.2s	1148.4s	1138.8s
C-H(Ar in plane bend)	1114.7w 1047.2w	1116.6w	1114.7m 1004.7w	–	1048.1s
C-X(str)	–	–	–	–	–
S-N(sym str)	900.6w	889.0w	900.6w	899.6w	873.6s
C-S(str)	757.9m	759.8m	757.9m	769.5s	756.0s
C-H(Ar out of plane bend)	817.7w	827.3m 615.2w	817.7m –	830.2w 690.4w	835.0s 686.5s
N-H(out of plane bend)	703.9w	715.5w	–	732.8w	–
C=C(Ar out of plane bend)	470.6w 455.1w	462.8w	468.6w	489.8w 465.7w	444.5w

Table 4. Infrared absorption frequencies (cm^{-1}) of N-(dimethylsubstituted phenyl)-methanesulphonamides.

s = strong, m = medium and w = weak

Table 5. Infrared absorption frequencies (cm^{-1}) of N-(dichlorosubstituted phenyl)-methanesulphonamides.

Assignments	$CH_3SO_2NH(i\text{-}XC_6H_4)$; $i, j\text{-}X_2$ =				
	2,3-Cl_2	2,4-Cl_2	2,5-Cl_2	2,6-Cl_2	3,4-Cl_2
N-H(Sym str)	3282.6m	3255.3s	3251.4m	3249.5s	3255.3s
C-H (Ar sym str)	3020.3w	–	–	3018.1w	3012.3w
C-H(Alk str)	2931.6w	2885.0w	2360.5w	2929.3w	2931.3w
Combination bands	–	–	–	1610.3w	–
C=C (Ar in plane str)	1583.4m 1458.1s	1595.8m 1491.7m 1473.4w	1581.3w 1477.2m	1589.1w 1492.6m	1591.0m 1510.0w 1469.5s
N-H(in plane bend)	1380.9m	1395.3w	1390.4m	1392.4m	1376.9m
S=O (Asym str)	1325.0m	1326.8m	1326.8s	1317.1s	1317.1s
C-N(str)	–	1299.4m	1247.7w	1272.8w 1251.6w	1282.4w 1267.0w
S=O(Sym str)	1157.2s	1155.2s	1157.1s	1145.5s	1147.4s
C-H(Ar in plane bend)	–	1092.5s	1093.4w	–	1039.4w
C-X(str)	–	–	1049.1w	–	1025.9w
S-N(sym str)	833.2w	865.9w	889.0w	885.2w	877.5w
C-S(str)	767.6m	779.1m	761.7w	771.4m	754.0w
C-H(Ar out of plane bend)	–	681.7w 623.9w	–	742.5m 642.2w	686.5w 665.3w
N-H(out of plane bend)	–	–	–	692.3m	727.0w
C=C(Ar out of plane bend)	439.7w	–	453.2w	447.4w 412.7w	495.6m 441.6w

s = strong, m = medium and w = weak

Table 6. ^1H NMR observed chemical shifts (δ, ppm) of various aromatic and other protons in N-(mono / di-substituted phenyl)-methanesulphonamides.

	$CH_3SO_2NH(i\text{-}XC_6H_4)$						
i-X	H-2	H-3	H-4	H-5	H-6	N-H	Alkyl H
H	7.34d	7.27t	7.18t	7.27t	7.34d	7.38	3.00
2-CH_3	–	7.13m	7.13m	7.21d	7.43d	6.80	3.00, 2.33
2-Cl	–	7.27m	7.13m	7.27m	7.40m	–	3.02
2-NO_2	–	8.06d	6.66d	7.33d	6.82d	–	3.18
3-CH_3	7.21t	–	6.98d	7.08s	7.21t	7.32	3.00, 2.32
3-Cl	7.46m	–	7.22d	7.37m	7.46m	9.78	2.97
3-NO_2	8.12d	–	7.90d	7.53d	7.64d	10.2	3.04
4-CH_3	7.14m	7.14m	–	7.14m	7.14m	6.35	2.98, 2.34
4-F	7.04m	7.26m	–	7.26m	7.04m	–	3.00
4-Cl	7.25t	7.25t	–	7.25t	7.25t	9.30	2.94
4-Br	7.44t	7.13d	–	7.13d	7.44t	7.21	3.00
4-NO_2	6.63m	8.07m	–	8.07m	6.63m	7.35	3.15
i, j-X_2	$CH_3SO_2NH(i, j\text{-}X_2C_6H_3)$						
2,3-$(CH_3)_2$	–	–	7.05m	7.11d	7.26m	6.67	2.99, 2.30, 2.25
2,4-$(CH_3)_2$	–	7.00s	–	7.02d	7.27d	6.63	2.97, 2.30, 2.29
2,5-$(CH_3)_2$	–	7.09d	6.94d	–	7.25s	6.62	3.00, 2.31, 2.28
2,6-$(CH_3)_2$	–	7.09t	7.09t	7.09t	–	6.36	3.05, 2.40
3,5-$(CH_3)_2$	6.86d	–	6.81s	–	6.86d	6.98	3.00, 2.30
2,3-Cl_2	–	–	7.27m	7.27m	7.59d	7.00	3.05
2,4-Cl_2	–	7.34m	–	7.34m	7.59d	6.85	3.02
2,5-Cl_2	–	7.36d	7.12m	–	7.68d	6.87	3.06
2,6-Cl_2	–	7.41d	7.20t	7.41d	–	6.53	3.30
3,4-Cl_2	7.36d	–	–	7.16d	7.36d	–	3.04

Table 7. ^{1}H chemical shifts of benzene, substituted benzenes, aniline and substituted anilines, measured under identical conditions.

Compound	H-2	H-3	H-4	H-5	H-6
			Substituted benzenes		
C_6H_6	7.29	7.29	7.29	7.29	7.29
$CH_3C_6H_5$	7.06	7.15	7.15	7.15	7.06
$C_2H_5C_6H_5$	7.12	7.23	7.23	7.23	7.12
FC_6H_5	7.50	7.21	7.30	7.21	7.50
ClC_6H_5	7.26	7.26	7.26	7.26	7.26
BrC_6H_5	7.21	7.21	7.21	7.21	7.21
$NO_2C_6H_5$	8.15	7.52	7.68	7.52	8.15
1,2-$(CH_3)_2C_6H_4$	–	7.04	7.04	7.04	7.04
1,3-$(CH_3)_2C_6H_4$	6.88	–	7.06	7.08	7.06
1,4-$(CH_3)_2C_6H_4$	6.98	6.98	–	6.98	6.98
1,2-$Cl_2C_6H_4$	–	7.26	7.26	7.26	7.26
1,3-$Cl_2C_6H_4$	7.08	–	7.08	7.08	7.08
1,4-$Cl_2C_6H_4$	7.24	7.24	–	7.24	7.24
			Substituted anilines		
$C_6H_5NH_2$	6.48	7.05	6.67	7.05	6.48
2-$CH_3C_6H_4NH_2$	–	6.97	6.64	6.97	6.49
2-$ClC_6H_4NH_2$	–	7.13	6.93	7.13	6.59
2-$NO_2C_6H_4NH_2$	–	8.02	6.86	7.28	6.60
3-$CH_3C_6H_4NH_2$	6.33	–	6.51	6.96	6.33
3-$ClC_6H_4NH_2$	6.41	–	6.65	6.95	6.41
3-$NO_2C_6H_4NH_2$	7.46	–	7.55	7.26	7.06
4-$CH_3C_6H_4NH_2$	6.49	6.89	–	6.89	6.49
4-$FC_6H_4NH_2$	6.46	6.80	–	6.80	6.46
4-$ClC_6H_4NH_2$	6.48	7.03	–	7.03	6.48
4-$BrC_6H_4NH_2$	6.49	7.20	–	7.20	6.49
4-$NO_2C_6H_4NH_2$	6.64	7.96	–	7.96	6.64
2,3-$(CH_3)_2C_6H_3NH_2$	–	–	6.53	6.82	6.34
2,4-$(CH_3)_2C_6H_3NH_2$	–	6.74	–	6.74	6.36
2,5-$(CH_3)_2C_6H_3NH_2$	–	6.83	6.44	–	6.27
2,6-$(CH_3)_2C_6H_3NH_2$	–	6.80	6.54	6.80	–
3,5-$(CH_3)_2C_6H_3NH_2$	6.09	–	6.32	–	6.09
2,3-$Cl_2C_6H_3NH_2$	–	–	6.73	6.84	6.47
2,4-$Cl_2C_6H_3NH_2$	–	7.07	–	7.07	6.64
2,5-$Cl_2C_6H_3NH_2$	–	7.05	6.59	–	6.59
2,6-$Cl_2C_6H_3NH_2$	–	7.12	6.87	7.12	–
3,4-$Cl_2C_6H_3NH_2$	6.54	–	–	7.17	6.54

Table 8. Shifts in the position of benzene protons (δ7.27) caused by the substituents.

Substituent	ortho	meta	para
-CH_3, -R	-0.15	-0.10	-0.10
-COOH, -COOR	$+0.80$	$+0.15$	$+0.20$
-CN	$+0.30$	$+0.30$	$+0.30$
-$CONH_2$	$+0.50$	$+0.20$	$+0.20$
-COR	$+0.60$	$+0.30$	$+0.30$
-SR	$+0.10$	-0.10	-0.20
-NH_2, -NHR	-0.80	-0.15	-0.40
-$N(CH_3)_2$	-0.50	-0.20	-0.50
-I	$+0.30$	-0.20	-0.10
-CHO	$+0.70$	$+0.20$	$+0.40$
-Br	0.00	0.00	0.00
-NHCOR	0.40	-0.20	-0.30
-Cl	0.00	0.00	0.00
-F	$+0.30$	$+0.02$	$+0.22$
-NH_3^+	$+0.40$	$+0.20$	$+0.20$
-OR	-0.20	-0.20	-0.20
-OH	-0.40	-0.40	-0.40
-OCOR	$+0.20$	-0.10	-0.20
-NO_2	$+1.00$	$+0.30$	$+0.40$
-SO_3H, -SO_2NH_2	$+0.40$	$+0.10$	$+0.10$

width (SW) at 22727.273, pulse width (PW) at 5.0, relaxation delay (RD) of 1.0(sec), acquisition time (AQ) was 0.360(sec), receiver gain (RG) 400, decoupling power (DP) was 14H CPD, filter to suppress noise (LB) 6.0, reference value (SR) was set at 701.89 ppm for DMSO at 39.5 ppm externally.

3. Results and Discussion

3.1. Infrared Spectra

The general assignments of the important infrared absorption frequencies of N-(substituted phenyl)-methanesulphonamides are shown in Tables 2 – 5. The infrared absorption frequencies of N-(phenyl)-methanesulphonamide reported earlier [20] were also measured under identical conditions and included in the table for comparison. Assignment of various bands in various compounds, in general, has been dealt with in detail elsewhere [13, 21 – 24], giving a table of characteristic group absorptions. The ranges of group absorptions have been assigned based on many compounds in which the groups occur. Although the ranges are quite well defined, the precise frequency or wavelength at which a specific group absorbs is dependent on its environment within the molecule and on its physical state. N-H stretching vibrations absorb in the ranges, 3298 – 3232 cm^{-1}. Asymmetric and symmetric SO_2 stretching vibrations appear as strong absorptions in the ranges, 1331 – 1317 cm^{-1} and 1157 – 1139 cm^{-1}, respectively. The values reported for N-(phenyl)-methanesulphonamide are 1323 cm^{-1} and 1150 cm^{-1}, respectively. N-(substituted phenyl)-methanesulphonamides exhibit S-N stretching vibrational absorptions in the range, 926 – 833 cm^{-1}. The C-S stretching frequency of the compounds containing the alkyl -SO_2 group is found to be in the region 787 – 739 cm^{-1}. The other discussions are similar to the organic aromatic compounds in general. The effect of substitution in the phenyl ring in terms of electron withdrawing and electron donating groups is non-systematic.

3.2. ^{1}H NMR Spectra

^{1}H chemical shifts of aromatic and alkyl protons of all the N-(substituted phenyl)-methanesulphonamides

Table 9. Calculated and observed chemical shifts (δ, ppm) of various aromatic protons in N-(mono-substituted phenyl)-methanesulphonamides ($CH_3SO_2NH(i\text{-}XC_6H_4)$).

i-X	H-2					H-3					H-4				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
H	–	–	–	–	7.34d	–	–	–	–	7.27t	–	–	–	–	7.18t
2-CH_3	–	–	–	–	–	7.12	7.19	7.12	7.04	7.13m	7.08	7.15	7.08	7.04	7.13m
2-Cl	–	–	–	–	–	7.27	7.35	7.27	7.24	7.27m	7.18	7.44	7.18	7.15	7.13m
2-NO_2	–	–	–	–	–	8.27	8.24	8.27	8.13	8.06d	7.48	7.37	7.48	7.41	6.66d
3-CH_3	7.19	7.19	7.19	7.20	7.21t	–	–	–	–	–	7.03	7.02	7.03	6.95	6.98d
3-Cl	7.34	7.27	7.34	7.31	7.46m	–	–	–	–	–	7.18	7.16	7.18	7.15	7.22d
3-NO_2	8.34	8.32	8.34	8.20	8.12d	–	–	–	–	–	8.18	8.06	8.18	8.04	7.90d
4-CH_3	7.24	7.35	7.24	7.20	7.14m	7.12	7.11	7.12	7.04	7.14m	–	–	–	–	–
4-F	7.36	7.32	7.36	7.26	7.04m	7.57	7.02	7.57	7.48	7.26m	–	–	–	–	–
4-Cl	7.34	7.34	7.34	7.31	7.25t	7.27	7.25	7.27	7.24	7.25t	–	–	–	–	–
4-Br	7.34	7.35	7.34	7.26	7.44t	7.27	7.42	7.27	7.19	7.13d	–	–	–		–
4-NO_2	7.64	7.50	7.64	7.57	6.63m	8.27	8.18	8.27	8.13	8.07m	–	–	–		–

i-X	H-5					H-6				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
H	–	–	–	–	7.27t	–	–	–	–	7.34d
2-CH_3	7.17	7.19	7.17	7.13	7.21d	7.24	7.35	7.24	7.20	7.43d
2-Cl	7.27	7.35	7.27	7.24	7.27m	7.34	7.45	7.34	7.31	7.40m
2-NO_2	7.67	7.50	7.67	7.66	7.33d	7.64	7.46	7.64	7.57	6.82d
3-CH_3	7.17	7.18	7.17	7.18	7.08s	7.24	7.19	7.24	7.29	7.21t
3-Cl	7.27	7.17	7.27	7.24	7.37m	7.34	7.27	7.34	7.31	7.46m
3-NO_2	7.57	7.48	7.57	7.50	7.53d	7.74	7.92	7.74	7.73	7.64d
4-CH_3	7.12	7.11	7.12	7.04	7.14m	7.24	7.35	7.24	7.20	7.14m
4-F	7.57	7.02	7.57	7.48	7.26m	7.36	7.32	7.36	7.25	7.04m
4-Cl	7.27	7.25	7.27	7.24	7.25t	7.34	7.34	7.34	7.31	7.25t
4-Br	7.27	7.42	7.27	7.19	7.13d	7.34	7.35	7.34	7.26	7.44t
4-NO_2	8.27	8.18	8.27	8.13	8.07m	7.64	7.50	7.64	7.57	6.63m

Table 10. Calculated and observed chemical shifts (δ, ppm) of various aromatic protons in N-(mono-substituted phenyl) methanesulphonamides ($CH_3SO_2NH(i,j\text{-}X_2C_6H_3)$).

i-X	H-2					H-3					H-4				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
2,3-$(CH_3)_2$	–	–	–	–	–	–	–	–	–	–	6.93	7.04	6.93	6.93	7.05m
2,4-$(CH_3)_2$	–	–	–	–	–	6.97	6.96	6.97	6.86	7.00s	–	–	–	–	–
2,5-$(CH_3)_2$	–	–	–	–	–	7.02	7.05	7.02	6.96	7.09d	6.93	6.95	6.93	6.87	6.94d
2,6-$(CH_3)_2$	–	–	–	–	–	7.02	7.02	7.02	6.86	7.09t	6.98	7.05	6.98	6.97	7.09t
3,5-$(CH_3)_2$	7.09	6.95	7.09	7.11	6.86d	–	–	–	–	–	6.88	6.83	6.88	6.77	6.81s
2,3-Cl_2	–	–	–	–	–	–	–	–	–	–	7.18	7.24	7.18	7.15	7.27m
2,4-Cl_2	–	–	–	–	–	7.27	7.29	7.27	7.06	7.34m	–	–	–	–	–
2,5-Cl_2	–	–	–	–	–	7.27	7.27	7.27	7.22	7.36d	7.18	7.10	7.18	7.13	7.12m
2,6-Cl_2	–	–	–		–	7.27	7.34	7.27	7.06	7.41d	7.18	7.38	7.18	6.97	7.20t
3,4-Cl_2	7.34	7.40	7.34	7.31	7.36d	–	–	–	–	–	–	–	–	–	–

i,j-X_2	H-5					H-6				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
2,3-$(CH_3)_2$	7.07	7.04	7.07	7.02	7.11d	7.14	7.20	7.14	7.09	7.26m
2,4-$(CH_3)_2$	7.02	6.96	7.02	7.04	7.02d	7.14	7.22	7.14	7.13	7.27d
2,5-$(CH_3)_2$	–	–	–	–	–	7.09	7.13	7.09	7.03	7.25s
2,6-$(CH_3)_2$	7.02	7.02	7.02	7.04	7.09t	–	–	–	–	–
3,5-$(CH_3)_2$	–	–	–	–	–	7.09	6.95	7.09	7.11	6.86d
2,3-Cl_2	7.27	7.06	7.27	7.24	7.27m	7.34	7.33	7.34	7.31	7.59d
2,4-Cl_2	7.27	7.29	7.27	7.06	7.34m	7.34	7.50	7.34	7.13	7.59d
2,5-Cl_2	–	–	–	–	–	7.34	7.45	7.34	7.29	7.68d
2,6-Cl_2	7.27	7.34	7.27	7.06	7.41d	–	–	–	–	–
3,4-Cl_2	7.27	7.39	7.27	7.24	7.16d	7.34	7.40	7.34	7.31	7.36d

Table 11. ^{13}C NMR observed chemical shifts (δ, ppm) of various aromatic and other carbons in N-(mono / disubstituted phenyl)-methanesulphonamides.

	$CH_3SO_2NH(i\text{-}XC_6H_4)$						
i-X	C-1	C-2	C-3	C-4	C-5	C-6	Alkyl C
H	136.9	120.9	129.6	125.4	129.6	120.9	39.1
2-CH_3	134.8	131.2	131.2	126.2	127.1	123.4	39.8, 18.0
2-Cl	133.4	126.2	129.6	125.4	127.9	123.0	39.8
2-NO_2	132.1	144.8	123.6	126.2	135.6	119.3	40.8
3-CH_3	136.8	121.4	139.7	126.1	129.4	117.8	39.0, 21.3
3-Cl	139.3	123.4	132.6	128.0	130.4	121.6	39.5
3-NO_2	139.5	113.3	148.3	117.9	130.0	125.0	39.3
4-CH_3	134.2	121.7	130.2	135.5	130.2	121.7	39.0, 20.8
4-F	132.6	123.9	116.5	159.1	116.5	123.9	39.8
4-Cl	136.5	121.5	129.1	129.4	129.1	121.5	39.3
4-Br	136.0	122.4	132.1	121.6	132.8	132.0	39.5
4-NO_2	126.4	125.8	113.5	152.6	113.5	125.8	–
i,j-X_2	$CH_3SO_2NH(i,j\text{-}X_2C_6H_3)$						
2,3-$(CH_3)_2$	134.4	131.4	138.4	126.3	128.5	122.6	39.8, 20.7, 14.2
2,4-$(CH_3)_2$	136.4	131.9	132.0	136.4	127.7	124.4	39.6, 20.8, 18.0
2,5-$(CH_3)_2$	137.1	127.7	131.0	126.9	134.6	123.9	39.8, 21.0, 17.5
2,6-$(CH_3)_2$	137.5	132.9	128.9	128.0	128.9	132.9	41.8, 19.2
3,5-$(CH_3)_2$	136.7	118.5	139.6	127.2	139.6	118.5	39.2, 21.3
2,3-Cl_2	135.4	126.8	133.7	123.6	128.2	120.0	40.3
2,4-Cl_2	132.4	128.6	129.6	131.4	126.0	123.7	40.1
2,5-Cl_2	134.7	122.6	130.6	126.1	134.2	121.6	40.3
2,6-Cl_2	135.0	131.5	129.2	129.0	129.2	131.5	43.4
3,4-Cl_2	130.8	116.5	131.3	122.1	119.8	114.7	39.8

Table 12. ^{13}C chemical shifts of benzene, substituted benzenes, aniline and substituted anilines measured under identical conditions.

Compound	C-1	C-2	C-3	C-4	C-5	C-6
	Substituted benzenes					
C_6H_6	128.4	128.4	128.4	128.4	128.4	128.4
$CH_3C_6H_5$	137.7	129.0	128.2	125.3	128.2	129.0
$C_2H_5C_6H_5$	144.3	127.9	128.4	125.7	128.4	127.9
FC_6H_5	164.6	115.4	130.1	124.1	130.1	115.4
ClC_6H_5	134.4	128.7	129.8	126.5	129.8	128.7
BrC_6H_5	122.5	131.5	130.0	126.8	130.0	131.5
$NO_2C_6H_5$	147.5	122.5	128.8	134.2	128.8	122.5
1,2-$(CH_3)_2C_6H_4$	136.4	136.4	129.6	125.9	125.9	129.6
1,3-$(CH_3)_2C_6H_4$	137.6	129.9	137.6	126.1	128.2	126.1
1,4-$(CH_3)_2C_6H_4$	134.6	128.9	128.9	134.6	128.9	128.9
1,2-$Cl_2C_6H_4$	132.5	132.5	130.5	127.7	127.7	130.5
1,3-$Cl_2C_6H_4$	135.0	128.6	135.0	126.7	130.2	126.7
1,4-$Cl_2C_6H_4$	132.6	129.9	129.9	132.6	129.9	129.9
	Substituted anilines					
$C_6H_5NH_2$	146.2	114.6	128.8	117.8	128.8	114.6
2-$CH_3C_6H_4NH_2$	144.3	124.6	129.7	117.7	126.2	114.3
2-$ClC_6H_4NH_2$	142.7	118.6	129.0	118.6	127.4	115.7
2-$NO_2C_6H_4NH_2$	144.9	135.4	125.4	118.7	135.4	116.3
3-$CH_3C_6H_4NH_2$	146.4	115.6	138.6	119.0	128.8	112.0
3-$ClC_6H_4NH_2$	147.6	114.5	134.2	117.8	130.1	113.0
3-$NO_2C_6H_4NH_2$	148.8	108.0	148.9	111.1	129.4	120.3
4-$CH_3C_6H_4NH_2$	143.8	115.0	129.5	127.2	129.5	115.0
4-$FC_6H_4NH_2$	142.6	115.7	115.2	154.3	115.2	115.7
4-$ClC_6H_4NH_2$	144.9	116.1	128.9	122.6	128.9	116.1
4-$BrC_6H_4NH_2$	145.6	116.7	132.0	110.1	132.0	116.7
4-$NO_2C_6H_4NH_2$	154.4	112.4	125.9	136.7	125.9	112.4
2,3-$(CH_3)_2C_6H_3NH_2$	144.3	125.5	136.4	120.0	125.5	112.7
2,4-$(CH_3)_2C_6H_3NH_2$	141.8	121.8	130.7	130.7	126.8	114.6
2,5-$(CH_3)_2C_6H_3NH_2$	144.2	118.8	129.9	118.8	136.0	115.3
2,6-$(CH_3)_2C_6H_3NH_2$	146.5	124.5	127.5	117.3	127.5	124.5
3,5-$(CH_3)_2C_6H_3NH_2$	146.8	113.3	138.7	120.3	138.7	113.3
2,3-$Cl_2C_6H_3NH_2$	144.4	119.0	132.4	116.8	127.3	113.5
2,4-$Cl_2C_6H_3NH_2$	141.7	119.5	128.9	122.8	127.7	116.4
2,5-$Cl_2C_6H_3NH_2$	143.7	118.5	129.9	117.8	132.8	115.1
2,6-$Cl_2C_6H_3NH_2$	146.9	123.5	129.0	121.0	129.0	123.5
3,4-$Cl_2C_6H_3NH_2$	146.1	116.3	132.5	120.8	130.6	114.6

are shown in Table 6. ^{1}H chemical shifts of benzene, substituted benzenes, aniline and substituted anilines were also measured under identical conditions and included in Table 7. The various chemical shifts were assigned to the aromatic and aliphatic protons in line with those for similar compounds [13, 21, 22, 25–28]. Further, the incremental shifts of the aromatic protons due to the CH_3SO_2- group in the compound $CH_3SO_2NH(C_6H_5)$ were calculated by comparing the chemical shifts of the aromatic protons in this compound with the aniline proton values of H-2,6 = 6.48 ppm, H-3,5 = 7.05 ppm and H-4 = 6.67 ppm. The computed incremental shifts are H-2,6 = 0.86, H-3,5 = 0.22 and H-4 = 0.51. Then the chemical shifts of the aromatic protons in the substituted compounds of the general formula CH_3SO_2NHR, where R = 4-XC_6H_4(X = CH_3, F, Cl, Br or NO_2), i-XC_6H_4(X = CH_3, Cl or NO_2 and $i = 2$ or 3) and i,j-$X_2C_6H_3$(i,j-X_2 = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2,6-$(CH_3)_2$, 3,5-$(CH_3)_2$, 2,3-Cl_2, 2,4-Cl_2, 2,5-Cl_2, 2,6-Cl_2 or 3,4-Cl_2) were computed in two ways (calc. 1 and calc. 2), by using the calculated incremental shifts of aromatic protons due to the CH_3SO_2- group. In the first method (calc. 1), the chemical shifts of the protons in the N-(substituted phenyl)-methanesulphonamides were calculated by adding the incremental shifts due to the CH_3SO_2- group and the substituent X (CH_3, F, Cl, Br or NO_2) (Table 8) to the chemical shifts of the aniline protons (H-2,6 = 6.48 ppm, H-3,5 = 7.05 ppm and H-4 = 6.67 ppm). In the second method (calc. 2), the chemical shifts of the aromatic protons in CH_3SO_2NHR were evaluated by adding the incremental shifts due to the CH_3SO_2- group to the chemical shifts of the corresponding protons of the substituted anilines (Table 7). The calculated chemical shifts by the methods 1 and 2, compared with the observed chemical shifts, are shown in Tables 9 and 10. There is a good agreement between the two sets of calculated values and the experimental chemical shifts, showing that the two methods of cal-

Table 13. Incremental Shifts of the aromatic atoms of monosubstituted benzenes (ppm from benzene at 128.5 ppm, +downfield, -upfield) carbon atom of substituents from TMS.

Substituent (Attachment)	C-1	C-2	C-3	C-4	C of substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	–
CH_3	+9.3	+0.7	−0.1	−2.9	21.3
CH_2CH_3	+15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
C_6H_5	+12.1	−1.8	−0.1	−1.6	–
OH	+26.6	−12.7	+1.6	−7.3	–
OCH_3	+31.4	−14.4	+1.0	−7.7	54.1
COOH	+2.9	+1.3	+0.4	+4.3	168.0
NH_2	+19.2	−12.4	1.3	−9.5	–
NO_2	+19.6	−5.3	+0.9	+6.0	–
F	+35.1	−14.3	+0.9	−4.5	–
Cl	+6.4	+0.2	+1.0	−2.0	–
Br	−5.4	+3.4	+2.2	−1.0	–
I	−32.2	+9.9	+2.6	−7.3	–
SO_2NH_2	+15.3	−2.9	+0.4	+3.3	–

culations lead to almost the same values in most cases.

Similarly, the incremental shifts of aromatic protons due to the CH_3SO_2NH- group in the compound, N-(phenyl)-methanesulphonamide, $CH_3SO_2NH(C_6H_5)$, was computed by comparing the chemical shifts of the protons in this compound with the benzene proton value of 7.29 ppm. The calculated values are H-2,6 $=$ 0.05, H-3,5 $=$ 0.02 and H-4 $= -0.11$. Then the chemical shifts of the aromatic protons in the N-(substituted phenyl)-methanesulphonamides, CH_3SO_2NHR, where R = 4-XC_6H_4(X = CH_3, F, Cl, Br or NO_2), *i*-XC_6H_4(X = CH_3, Cl or NO_2 and $i = 2$ or 3) and i,j-$X_2C_6H_3$(i,j-X_2 = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2,6-$(CH_3)_2$, 3,5-$(CH_3)_2$, 2,3-Cl_2, 2,4-Cl_2, 2,5-Cl_2, 2,6-Cl_2 or 3,4-Cl_2) were computed in two more ways by using the calculated incremental shifts of aromatic protons due to the CH_3SO_2NH- group. In the first method 3 (calc. 3), the chemical shifts of aromatic protons were calculated by adding the incremental shifts due to the CH_3SO_2NH- and the substituent X at different benzene positions (CH_3, F, Cl, Br or NO_2) (Table 8) to the benzene proton value of 7.29 ppm. In the other method (calc. 4), the chemical shifts of aromatic protons in the N-(substituted phenyl)-methanesulphonamides were computed by adding the incremental shifts due to the CH_3SO_2NH- group to the chemical shifts of the corresponding protons in substituted benzenes (Table 7). The calculated chemical shifts by the methods 3 and 4 are also shown in Tables 9 and 10.

The comparisons revealed that generally the four sets of calculated chemical shifts agree well with the experimental values. Thus it is evident from these that the different procedures of calculation lead to almost the same values in most cases, confirming the validity of the principle of additivity of the substituent effects in these compounds.

3.3. ^{13}C NMR Spectra

The ^{13}C chemical shifts of aromatic and alkyl carbons of all the N-(substituted phenyl)-methanesulphonamides are shown in Table 11. The ^{13}C chemical shifts of benzene, substituted benzenes, aniline and substituted anilines were also measured under identical conditions and included in Table 12. The various chemical shifts are assigned to the different carbons in the compounds, in conformity with the literature for similar compounds [13, 21, 22, 25–28]. Further, the incremental shifts of C-1; C-2,6; C-3,5 and C-4 carbons due to the CH_3SO_2- group in N-(phenyl)-methanesulphonamide, $CH_3SO_2NH(C_6H_5)$ were computed by comparing the chemical shifts of the aromatic carbons in this compound with the corresponding aniline carbons (C-1 $=$ 146.2 ppm; C-2,6 $=$ 114.6 ppm; C-3,5 $=$ 128.8 ppm and C-4 $=$ 117.8 ppm). The computed incremental shifts of the C-1; C-2,6; C-3,5 and C-4 carbons are -9.3; 6.3; 0.8 and 7.6, respectively. The incremental shifts due to the CH_3SO_2- group and those of the substituents (Table 13) were used to calculate the chemical shifts of the aromatic carbons in the N-(substituted phenyl)-methanesulphonamides, CH_3SO_2NHR, where R = 4-XC_6H_4(X = CH_3, F, Cl, Br or NO_2), *i*-XC_6H_4(X = CH_3, Cl or NO_2 and $i = 2$ or 3) and i,j-$X_2C_6H_3$(i,j-X_2 = 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 2,6-$(CH_3)_2$, 3,5-$(CH_3)_2$, 2,3-Cl_2, 2,4-Cl_2, 2,5-Cl_2, 2,6-Cl_2 or 3,4-Cl_2), by the methods 1 and 2, similar to the ones described under the ^{1}H NMR spectra. The various calculated chemical shifts, compared with the experimental chemical values, are shown in Tables 14 and 15. There is good agreement between the two sets of calculated values and the experimental chemical shifts.

Similarly, the incremental shifts of the aromatic carbons due to the CH_3SO_2NH- group in the compound $CH_3SO_2NH(C_6H_5)$ was calculated by comparing the chemical shifts of the carbons in this compound with that of the benzene carbon value of 128.4 ppm. The calculated values are C-1 $=$ 8.5; C-2,6 $= -7.5$;

Table 14. Calculated and observed chemical shifts (δ, ppm) of various aromatic carbons in N-(mono-substituted phenyl)-methanesulphonamides ($CH_3SO_2NH(i\text{-}XC_6H_4)$).

i-X	C-1					C-2					C-3				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
H	–	–	–	–	136.9	–	–	–	–	120.9	–	–	–	–	129.6
2-CH_3	137.6	135.0	137.6	137.4	134.8	130.2	130.9	130.2	130.1	131.2	130.3	130.5	130.3	130.1	131.2
2-Cl	137.1	133.4	137.1	137.1	133.4	127.3	124.9	127.3	126.8	126.2	129.8	129.8	129.8	129.8	129.6
2-NO_2	131.6	135.6	131.6	130.9	132.1	140.5	141.7	140.5	139.9	144.8	124.3	126.2	124.3	123.6	123.6
3-CH_3	136.8	137.1	136.8	136.6	136.8	121.6	121.9	121.6	121.4	121.4	138.9	139.4	138.9	138.8	139.7
3-Cl	137.9	138.3	137.9	138.2	139.3	121.1	120.8	121.1	121.1	123.4	136.0	135.0	136.0	135.5	132.6
3-NO_2	137.8	139.5	137.8	137.2	139.5	115.6	114.3	115.6	114.9	113.3	149.2	149.7	149.2	148.6	148.3
4-CH_3	134.0	134.5	134.0	133.7	134.2	120.8	121.3	120.8	120.6	121.7	130.3	130.3	130.3	130.1	130.2
4-F	132.4	133.3	132.4	132.5	132.6	121.8	122.0	121.8	122.5	123.9	115.3	116.0	115.3	116.5	116.5
4-Cl	134.9	135.6	134.9	134.9	136.5	121.9	122.4	121.9	122.2	121.5	129.8	129.7	129.8	129.8	129.1
4-Br	135.9	136.3	135.9	135.2	136.0	123.1	123.0	123.1	122.4	122.4	133.0	132.8	133.0	132.6	132.1
4-NO_2	142.9	145.1	142.9	142.6	126.4	121.8	118.7	121.8	121.2	125.8	124.3	126.7	124.3	123.6	113.5

i-X	C-4					C-5					C-6				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
H	–	–	–	–	125.4	–	–	–	–	129.6	–	–	–	–	120.9
2-CH_3	125.3	125.3	125.3	125.1	126.2	126.7	127.0	126.7	126.4	127.1	120.8	120.6	120.8	120.6	123.4
2-Cl	126.4	126.2	126.4	126.7	125.4	127.6	128.2	127.6	127.6	127.9	121.9	122.0	121.9	122.2	123.0
2-NO_2	126.3	126.3	126.3	125.7	126.2	135.6	136.2	135.6	135.3	135.6	121.8	122.6	121.8	121.2	119.3
3-CH_3	126.1	126.6	126.1	125.9	126.1	129.5	129.6	129.5	129.3	129.4	118.0	118.3	118.0	117.7	117.8
3-Cl	125.6	125.4	125.6	125.6	128.0	130.6	130.9	130.6	130.9	130.4	118.9	119.3	118.9	118.9	121.6
3-NO_2	120.1	118.7	120.1	119.4	117.9	130.5	130.2	130.5	129.9	130.0	126.9	126.6	126.9	126.6	125.0
4-CH_3	134.7	134.8	134.7	134.6	135.5	130.3	130.3	130.3	130.1	130.2	120.8	121.3	120.8	120.6	121.7
4-F	160.5	161.9	160.5	161.5	159.1	115.3	116.0	115.3	116.5	116.5	121.8	122.0	121.8	122.5	123.9
4-Cl	131.8	130.2	131.8	131.3	129.4	129.8	129.7	129.8	129.8	129.1	121.9	122.4	121.9	122.2	121.5
4-Br	120.0	117.7	120.0	119.4	121.6	133.0	132.8	133.0	132.6	132.8	123.1	123.0	123.1	122.4	132.0
4-NO_2	145.0	144.3	145.0	144.4	152.6	124.3	126.7	124.3	123.6	113.5	121.8	118.7	121.8	121.2	125.8

Table 15. Calculated and observed chemical shifts (δ, ppm) of various aromatic carbons in N-(di-substituted phenyl)-methanesulphonamides ($CH_3SO_2NH(i,j\text{-}X_2C_6H_3)$).

i,j-X_2	C-1					C-2					C-3				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
2,3-$(CH_3)_2$	137.5	135.0	137.5	138.0	134.4	130.9	131.8	130.9	128.8	131.4	139.6	137.2	139.6	137.5	138.4
2,4-$(CH_3)_2$	134.7	132.5	134.7	134.5	136.4	130.1	128.1	130.1	130.0	131.9	131.0	131.5	131.0	131.0	132.0
2,5-$(CH_3)_2$	137.7	134.9	137.7	137.3	137.1	127.3	125.1	127.3	127.0	127.7	130.2	130.7	130.2	130.0	131.0
2,6-$(CH_3)_2$	138.3	137.2	138.3	138.3	137.5	130.1	130.8	130.1	130.0	132.9	127.4	128.3	127.4	127.2	128.9
3,5-$(CH_3)_2$	136.9	137.5	136.9	136.6	136.7	118.7	119.6	118.7	118.5	118.5	138.8	139.5	138.8	138.7	139.6
2,3-Cl_2	138.1	135.1	138.1	138.9	135.4	127.5	125.3	127.5	124.9	126.8	136.2	133.2	136.2	133.6	133.7
2,4-Cl_2	135.1	132.4	135.1	135.1	132.4	128.3	125.8	128.3	127.4	128.6	130.0	129.7	130.0	129.7	129.6
2,5-Cl_2	138.1	134.4	138.1	138.3	134.7	125.3	124.8	125.3	125.0	122.6	130.8	130.7	130.8	131.0	130.6
2,6-Cl_2	137.3	137.6	137.3	137.0	137.5	128.3	129.8	128.3	127.4	131.5	127.8	129.8	127.8	127.8	129.2
3,4-Cl_2	135.9	136.8	135.9	136.1	130.8	122.1	122.6	122.1	122.9	116.5	136.2	133.3	136.2	133.6	131.3

i,j-X_2	C-4					C-5					C-6				
	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.	calc.1	calc.2	calc.3	calc.4	obs.
2,3-$(CH_3)_2$	126.0	127.6	126.0	126.5	126.3	126.6	126.3	126.6	127.0	128.5	117.9	119.0	117.9	118.3	122.6
2,4-$(CH_3)_2$	134.6	138.3	134.6	134.5	136.4	127.4	127.6	127.4	127.2	127.7	120.7	120.9	120.7	120.6	124.4
2,5-$(CH_3)_2$	126.0	126.4	126.0	125.8	126.9	136.0	136.8	136.0	135.7	134.6	121.5	121.6	121.5	121.3	123.9
2,6-$(CH_3)_2$	125.2	124.9	125.2	125.1	128.0	127.4	128.3	127.4	127.2	128.9	130.1	130.8	130.1	130.0	132.9
3,5-$(CH_3)_2$	126.8	127.9	126.8	126.8	127.2	138.8	139.5	138.8	138.7	139.6	118.7	119.6	118.7	118.5	118.5
2,3-Cl_2	126.6	124.4	126.6	127.4	123.6	128.6	128.1	128.6	128.8	128.2	119.9	119.8	119.9	120.1	120.0
2,4-Cl_2	132.8	130.4	132.8	131.9	131.4	127.8	128.5	127.8	127.8	126.0	122.9	122.7	122.9	122.6	123.7
2,5-Cl_2	126.6	125.4	126.6	126.8	126.1	134.0	133.6	134.0	133.7	134.2	122.1	121.4	122.1	122.3	121.6
2,6-Cl_2	127.4	128.6	127.4	127.1	129.0	127.8	129.8	127.8	127.8	129.2	128.3	129.8	128.3	127.4	131.5
3,4-Cl_2	132.0	128.4	132.0	129.4	122.1	130.8	131.4	130.8	131.6	119.8	119.9	120.9	119.9	120.1	114.7

C-3,5 = 1.2 and C-4 = −3.0. Then these incremental shifts due to the CH_3SO_2NH- group and of the substituents X (Table 13) were used to calculate the chemical shifts of the aromatic carbons in the N-(substituted phenyl)-methanesulphonamides, by two more methods similar to the ones described under ^1H NMR spectra (calc. 3 and calc. 4). In the method 3, the chemical shifts of aromatic carbons were computed by adding the incremental shifts due to the CH_3SO_2NH-group and of the substituents X (Table 13) to the benzene carbon value of 128.4 ppm. In the other method (calc. 4), the chemical shifts of the aromatic carbons in all N-(substituted phenyl)-methanesulphonamides were computed by adding the incremental shifts due to the CH_3SO_2NH- group to the chemical shifts of the corresponding carbons in substituted benzenes (Table 12). The calculated chemical shifts by methods 3 and 4 are also shown in Tables 14 and 15.

It is evident from the comparison of the 4 sets of calculated shifts that the different procedures of calculation lead to almost the same values in most cases, showing the validity of the principle of additivity of the substituent effects in the case of ^{13}C chemical shifts. The correlation between the incremental shifts of either the aromatic protons or carbons due to the groups CH_3SO_2– and CH_3SO_2NH- with the corresponding Hammett substituent parameters was poor.

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