Synthetic, Infrared, ^{1}H and ^{13}C NMR Spectral Studies on N-(*p*-Substituted Phenyl)-*p*-Substituted Benzenesulphonamides, *p*-X'$C_6H_4SO_2$NH-(*p*-XC_6H_4), where X' or X = H, CH_3, C_2H_5, F, Cl or Br

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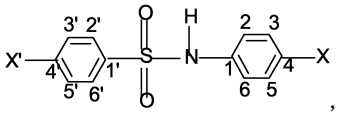
Thirty N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides of the general formula, *p*-X'$C_6H_4SO_2$NH(*p*-XC_6H_4), where X' or X = H, CH_3, C_2H_5, F, Cl or Br, are synthesised and their infrared spectra in the solid state and ^{1}H and ^{13}C NMR spectra in solution are measured. The N-H stretching vibrational frequencies, ν_{N-H} vary in the range 3334 – 3219 cm^{-1}, while the asymmetric and symmetric SO_2 vibrations appear in the ranges 1377 – 1311 cm^{-1} and 1182 – 1151 cm^{-1}, respectively. The compounds exhibit S-N and C-N stretching vibrational absorptions in the ranges 937 – 898 cm^{-1} and 1310 – 1180 cm^{-1}, respectively. There are no particular trends in the variation of these frequencies on substitution with either electron withdrawing or electron donating groups. The ^{1}H and ^{13}C chemical shifts of N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides,



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are assigned to various protons and carbons of the two benzene rings. Further, incremental shifts of the ring protons and carbons due to –SO_2NH(*p*-XC_6H_4) groups in the compounds of the formula, $C_6H_5SO_2$NH(*p*-XC_6H_4), and *p*-X'$C_6H_4SO_2$- and *p*-X'$C_6H_4SO_2$NH- groups in the compounds of the formula, *p*-X'$C_6H_4SO_2$NH(C_6H_5) are computed and used to calculate the ^{1}H and ^{13}C chemical shifts of the parallely substituted compounds of the general formula *p*-X'$C_6H_4SO_2$NH(*p*-XC_6H_4). The computed values agree well with the observed chemical shifts. The above incremental shifts are found to correlate with the Hammett substituent parameters.

Key words: IR; ^{1}H and ^{13}C NMR; N-(*p*-substitutedphenyl)-*p*-substitutedbenzenesulphonamides.

1. Introduction

The chemistry of sulphonamides and their N-halo compounds is of interest due to their distinct physical, chemical and biological properties. They exhibit pharmacological, fungicidal and herbicidal activities due to their oxidising action in aqueous, partial aqueous and non-aqueous media [1 – 7]. In an effort to introduce N-(halo)-arylsulphonamides of different oxidising strengths, we have recently reported the synthetic and spectroscopic studies on several arylsulphonamides, N-(chloro)-arylsulphonamides and N,N-(dichloro)-arylsulphonamides [8 – 13] and employed them as oxidants for studying the kinetics of reactions of several substrates [14 – 18]. This paper reports the synthesis, characterization, infrared, and ^{1}H and ^{13}C NMR spectral studies on thirty N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides of the general formula, *p*-X'$C_6H_4SO_2$NH(*p*-XC_6H_4), where X' or X = H, CH_3, C_2H_5, F, Cl or Br.

2. Experimental

2.1. Materials and Methods

Preparations of N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides (Table 1) involved two steps, (i) chlorosulphonation of substituted benzenes to the corresponding *p*-substituted benzenesulphonylchlorides and (ii) conversion of the latter to the respective sulphonamides [8, 19 – 22].

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

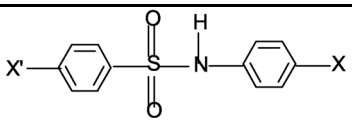
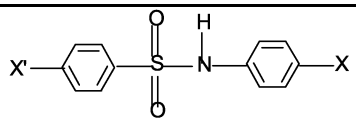
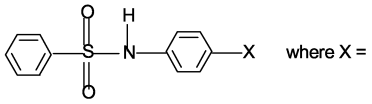
X', X		m. p. (°C)	X', X		m. p. (°C)
H, H	N-(phenyl)-benzenesulphonamide	84	F, H	N-(phenyl)-4-fluorobenzenesulphonamide	62
H, CH_3	N-(4-methylphenyl)-benzenesulphonamide	70	F, CH_3	N-(4-methylphenyl)-4-fluorobenzenesulphonamide	76
H, F	N-(4-fluorophenyl)-benzenesulphonamide	70	F, F	N-(4-fluorophenyl)-4-fluorobenzenesulphonamide	76
H, Cl	N-(4-chlorophenyl)-benzenesulphonamide	142	F, Cl	N-(4-chlorophenyl)-4-fluorobenzenesulphonamide	60
H, Br	N-(4-bromophenyl)-benzenesulphonamide	52	F, Br	N-(4-bromophenyl)-4-fluorobenzenesulphonamide	170
CH_3, H	N-(phenyl)-4-methylbenzenesulphonamide	96	Cl, H	N-(phenyl)-4-chlorobenzenesulphonamide	99
CH_3, CH_3	N-(4-methylphenyl)-4-methylbenzenesulphonamide	30	Cl, CH_3	N-(4-methylphenyl)-4-chlorobenzenesulphonamide	88
CH_3, F	N-(4-fluorophenyl)- 4-methylbenzenesulphonamide	40	Cl, F	N-(4-fluorophenyl)-4-chlorobenzenesulphonamide	82
CH_3, Cl	N-(4-chlorophenyl)- 4-methylbenzenesulphonamide	59	Cl, Cl	N-(4-chlorophenyl)-4-chlorobenzenesulphonamide	148
CH_3, Br	N-(4-bromophenyl)-4-methylbenzenesulphonamide	78	Cl, Br	N-(4-bromophenyl)-4-chlorobenzenesulphonamide	163
C_2H_5, H	N-(phenyl)-4-ethylbenzenesulphonamide	55	Br, H	N-(phenyl)-4-bromobenzenesulphonamide	64
C_2H_5, CH_3	N-(4-methylphenyl)-4-ethylbenzenesulphonamide	56	Br, CH_3	N-(4-methylphenyl)-4-bromobenzenesulphonamide	99
C_2H_5, F	N-(4-fluorophenyl)- 4-ethylbenzenesulphonamide	46	Br, F	N-(4-fluorophenyl)-4-bromobenzenesulphonamide	86
C_2H_5, Cl	N-(4-chlorophenyl)- 4-ethylbenzenesulphonamide	57	Br, Cl	N-(4-chlorophenyl)-4-bromobenzenesulphonamide	138
C_2H_5, Br	N-(4-bromophenyl)- 4-ethylbenzenesulphonamide	86	Br, Br	N-(4-bromophenyl)-4-bromobenzenesulphonamide	133

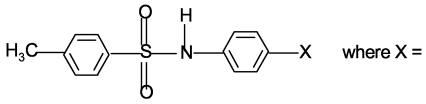
Table 2. Infrared absorption frequencies (cm^{-1}) of N-(*p*-substituted phenyl)-benzenesulphonamides.



Assignment	H	CH_3	F	Cl	Br
N-H(Sym str)	3284.2w	3270.7s	3250.4m	3284.2m	3262.0m
C-H(Ar sym str)	3093.3w	–	3065.3m	3092.3m	–
C-H(Alk str)	–	2920.7m	–	–	–
		2643.9m			
Combination bands	–	1613.2m	1911.1w	1918.8w	–
			1638.2m		
C=C(Ar in plane str)	1575.6m	1583.3m	1592.9m	1576.5m	1584.2w
	1474.3m	1511.0s	1510.0s	1474.3m	1487.8m
		1446.4s	1472.4m		1446.4m
			1444.4m		
N-H(in plane bend)	1396.2m	1394.3m	1394.3m	1397.2m	1388.5w
S=O(Asym str)	1376.9s	1318.1m	1325.8m	1376.0m	1311.4m
C-N(str)	1281.5m	1296.9m	1309.4m	1281.5m	1290.1m
			1294.0m	1180.2s	1186.0m
S=O(Sym str)	1162.9s	1155.2s	1154.2s	1163.8s	1156.1s
C-H(Ar in plane bend)	1091.5s	1068.4m	1131.1s	1094.4s	1091.5m
	1011.5m	1034.6m	1070.3m	–	1073.2m
			1039.4m		1017.3m
			1018.2m		
C-X(Str)	–	–	1232.3s	1012.5m	561.2m
S-N(sym str)	–	921.8m	924.7m	905.4w	920.8w
C-S(str)	836.0m	810.0m	828.3m	832.1m	837.0w
C-H(Ar out of plane bend)	754.0m	756.9s	756.9m	755.0s	756.0m
	600.7m	689.4s	692.3m	635.4w	684.6m
			621.9m		
N-H(out plane bend)	700.0w	728.0s	730.9m	700.0w	723.2m
C=C(Ar out ofplane bend)	470.6m	490.8m	458.0w	470.6m	432.9m
			440.7m		

s = strong, m = medium and w = weak

Table 3. Infrared absorption frequencies (cm^{-1}) of N-(*p*-substituted phenyl)-*p*-methylbenzenesulphonamides.

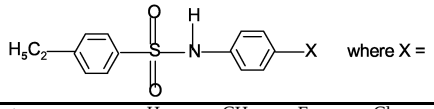


Assignment	H	CH_3	F	Cl	Br
N-H(Sym str)	3254.3w	3234.0w	3258.1s	3305.4s	3334.3s
C-H(Ar sym str)	3091.3w	–	–	–	–
	3058.6w				
C-H(Alk str)	2922.6w	2921.6w	2920.7w	2925.5w	–
		2589.9w		2650.7w	
				2360.4w	
Combination bands	1927.5w	1926.5w	1921.7w	1946.8w	–
C=C(Ar in plane str)	1592.0m	1592.9m	1598.7w	1584.2w	1594.8m
	1486.9w	1510.0m	1505.2s	1542.8w	1494.6w
		1488.8w	1448.3w	1474.3m	1464.7w
		1459.9w		1448.3m	
N-H(in plane bend)	–	1373.1m	1389.5m	1393.3m	–
S=O(Asym str)	1373.1s	1334.5m	1332.6s	1327.8s	1341.3s
C-N(str)	1294.0m	1186.1s	1304.6w	1248.7w	–
	1187.0s		1290.1w	1193.7m	
S=O(Sym str)	1173.5s	1174.4s	1160.9s	1160.9s	1158.0s
C-H(Ar in plane bend)	1120.4m	1079.9m	1091.5m	1090.6s	1090.6m
	1079.9m		1018.2w	1071.3w	
	1045.2w				
	1015.3w				
C-X(Str)	–	–	1236.2w	1025.9w	–
S-N(sym str)	921.8w	912.2w	905.4m	899.6m	909.3m
C-S(str)	810.9m	810.0m	813.8m	826.4w	–
C-H(Ar out of plane bend)	756.0w	767.5w	783.9w	760.8s	667.3m
	651.8s	651.8m	678.8m	688.5s	
N-H(out plane bend)	702.0m	702.0m	708.7m	719.3m	
C=C(Ar out of plane bend)	476.3m	489.3w	442.6w	472.5w	
		476.3w			

s = strong, m = medium and w = weak

(i) Chlorosulphonation of substituted benzenes with chlorosulphonic acid: The substituted benzene (10 g) was dissolved in chloroform (50 cc). The solution was cooled to 0 °C and treated dropwise with chlorosulphonic acid (50 g). After the initial evolution of hydrogen chloride subsided, the reaction mixture was brought to room temperature. The contents were poured into crushed ice in a beaker. The chloroform

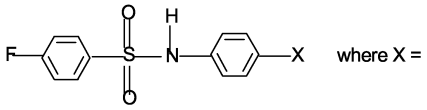
Table 4. Infrared absorption frequencies (cm^{-1}) of N-(*p*-substituted phenyl)-*p*-ethylbenzenesulphonamides.



Assignment	H	CH_3	F	Cl	Br
N-H(Sym str)	3278.4w	3263.9s	3269.7s	3262.0m	3254.3m
C-H(Ar sym str)	3091.3w	–	–	–	–
	3059.5w				
C-H(Alk str)	–	2969.8s	–	2923.6m	2966.0m
		2643.0s		2600.5m	2639.1w
Combination bands	1927.5w	–	–	–	–
C=C(Ar in plane str)	1592.0m	1597.7m	1505.2s	1589.1m	1636.3w
	1488.8w	1534.1m	1442.4m	1542.8m	1560.1w
		1509.0s		1467.6m	1488.8m
		1434.8m			
N-H(in plane bend)	–	1389.5s	1383.7m	1386.6m	1405.9w
S=O(Asym str)	1373.1s	1328.7s	1330.6s	1326.8m	1329.7w
C-N(str)	1304.6w	1298.8m	–	–	–
	1294.0m	1286.3m			
S=O(Sym str)	1174.4s	1159.0s	1160.0s	1157.1s	1182.2s
C-H(Ar in plane bend)	1120.4m	1128.2s	1091.5m	1093.4m	1125.3m
	1079.0m	1091.5s		1067.4m	1068.4w
		1036.6s			1034.6m
					1010.5m
C-X(Str)	–	–	1210.1m	–	565.0m
S-N(sym str)	–	904.5s	902.5m	930.5w	–
C-S(str)	810.9m	810.9s	829.2m	833.1w	832.1m
C-H(Ar out of plane bend)	–	786.8m	781.0m	777.2m	–
	651.8s	680.8s	668.2s	656.3m	678.8m
N-H(out plane bend)	702.0m	–	–	703.9w	709.7w
C=C(Ar out of plane bend)	475.4m	496.6s	–	–	488.9m
					419.4m

s = strong, m = medium and w = weak

Table 5. Infrared absorption frequencies (cm^{-1}) of N-(*p*-substituted phenyl)- *p*-fluorobenzenesulphonamides.



Assignment	H	CH_3	F	Cl	Br
N-H(Sym str)	3218.6s	3270.7s	3250.4s	3284.2m	3264.9m
C-H(Ar sym str)	–	–	3074.0m	–	3067.2m
Combination bands	–	–	1900.5w	–	1915.9w
C=C(Ar in plane str)	1592.0m	1592.0m	1637.3w	1575.6w	1631.5w
	1492.6m	1510.0m	1509.0s	1500.4w	1591.0m
	1464.7w	1493.6m	1470.5m	1474.3w	1513.9w
	1411.6w		1445.4m		1492.6s
					1448.3m
N-H(in plane bend)	–	1395.3w	1393.3m	1379.8m	1388.5m
S=O(Asym str)	1337.4s	1339.3m	1326.8s	1332.6m	1316.2m
C-N(str)	1310.4w	1293.0m	1294.0m	1280.5m	1291.1m
	1295.9w				1271.8w
S=O(Sym str)	1152.3s	1152.3s	1151.3s	1161.9s	1152.3s
C-H(Ar in plane bend)	1091.5m	1090.6w	1091.5m	1089.6m	1092.5m
			1036.6m		1067.4m
			1011.5m		1032.7m
					1011.5m
C-F(Str)	1232.3m	1242.9m	1232.3s	–	1204.3m
C-X(Str)	–	–	–	1011.5m	567.0s
S-N(sym str)	937.2w	925.7w	924.7m	898.7w	907.3m
C-S(str)	818.6w	834.1w	828.3s	824.4m	837.9s
C-H(Ar out of plane bend)	758.9w	–	756.9m	754.0m	689.4m
	603.6w	675.0w	691.4s	635.4m	672.1m
			636.4m		614.2w
N-H(out plane bend)	704.9m	709.7w	720.3m	707.8w	713.5m
C=C(Ar out of plane bend)	481.2w	–	440.7w	470.6m	488.9m

s = strong, m = medium and w = weak

layer was separated, washed with cold water and allowed to evaporate slowly. The residual crude *p*-substituted benzenesulphonylchloride was then recrystallized from sulphonic solvent (choroform, ethanol or petroleum ether) and dried in vacuum over conc. H_2SO_4.

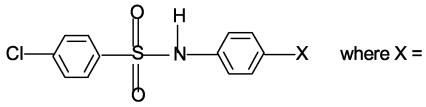
(ii) Conversion of sulphonyl chlorides to sulphonamides with *p*-substituted anilines: The *p*-substituted benzenesulphonylchloride prepared as above was boiled for ten minutes with a *p*-substituted aniline in the stoichiometric ratio. The reaction mixture was cooled to room temperature and added to ice cold water (100 cc). The resultant solid N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamide was filtered under suction and thoroughly washed with cold water. It was then recrystallised to constant melting point from dilute ethanol. The purity of all the reagents was checked by determining their melting points (Table 1).

2.2. Spectral Measurements

Infrared Spectra: Infrared spectral measurements were made on a JASCO-430 (Japan), FT-IR spectrometer. The resolution was set to 4 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-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides were measured on a BRUKER Ac 300F, 300 MHz FT-NMR spectrometer. The spectra were recorded in $CDCl_3$ and DMSO with tetramethylsilane (Me_4Si) as internal standard. 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 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

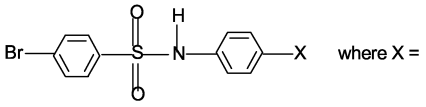
Table 6. Infrared absorption frequencies (cm^{-1}) of N-(*p*-substituted phenyl)-*p*-chlorobenzenesulphonamides.



Assignment	H	CH_3	F	Cl	Br
N-H(Sym str)	3259.1m	3233.1s	3245.6s	3259.1s	3260.1s
C-H(Ar sym str)	3089.4w	–	3094.2w	–	–
C-H(Alk str)	–	2920.7m	–	–	–
Combination bands	–	–	1914.0w	–	–
C=C(Ar in plane str)	1599.7w	1612.2w	1650.8w	1638.2w	1584.2w
	1497.5m	1584.2m	1583.3m	1575.6m	1486.9m
	1480.1m	1509.0m	1503.2s	1487.8m	1431.9w
	1414.5m	1475.3m	1472.4m	1474.3m	
			1444.4m	1431.9w	
N-H(in plane bend)	1396.2w	1397.2m	1393.3m	1379.8m	1395.3m
S=O(Asym str)	1343.2m	1339.3s	1332.6s	1332.6m	1330.6m
C-N(str)	1283.4m	1299.8m	1280.5m	1280.5w	1246.8m
	1178.3m	1276.7m	1205.3m	1227.5m	–
S=O(Sym str)	1161.9s	1164.8s	1159.0s	1159.0s	1160.0s
C-H(Ar in plane bend)	1094.4m	1095.4s	1177.3m	1090.6s	1123.3m
	1030.8w	–	1090.6s	1038.5w	1090.6s
					1071.3m
					1034.6w
C-X(Str)	–	–	–	–	560.2m
C-Cl(Str)	1012.5w	1017.3m	1011.5m	1011.5m	1009.6m
S-N(sym str)	924.7m	915.1s	906.4m	904.6w	905.4w
C-S(str)	826.4w	810.0s	825.4s	825.4m	824.4m
C-H(Ar out of plane bend)	753.1s	754.0s	788.7m	758.9s	759.8m
	621.9m	675.0m	757.9s	690.4w	692.3w
		642.2m	674.0m		655.7m
N-H(out plane bend)	694.3m	705.8w	706.8m	722.2m	715.5w
C=C(Ar out of plane bend)	482.1m	482.1s	478.3m	470.6m	488.9w
			444.5w		

s = strong, m = medium and w = weak

Table 7. Infrared absorption frequencies (cm^{-1}) of N-(*p*-substituted phenyl)-*p*-bromobenzenesulphonamides.



Assignment	H	CH_3	F	Cl	Br
N-H(Sym str)	3257.2m	3234.0s	3251.7s	3258.1w	3259.1s
C-H(Ar sym str)	3090.4m	–	–	3089.4w	–
C=C(Ar in plane str)	1567.8m	1612.2m	1572.7m	1567.8m	1572.7m
	1492.6m	1572.7s	1500.4m	1488.8w	1485.9m
	1468.5m	1509.0s	1465.6w	1467.6m	1468.5w
	1405.9m	1469.5s	1445.4w		1431.9w
N-H(in plane bend)	1389.5m	1395.3s	1387.5m	1389.5m	1388.5m
S=O(Asym str)	1374.0s	1340.3s	1333.5m	1374.0s	1329.7s
C-N(str)	1278.6m	1299.8m	1277.6w	1278.6m	1277.6w
	1187.9m	1275.7m	1204.3w	1187.9s	1216.9w
S=O(Sym str)	1160.9s	1165.8s	1158.0s	1160.9s	1159.0s
C-H(Ar in plane bend)	1087.7m	1089.6m	1086.7m	1065.5s	1101.2w
	1066.4m	1068.4s	1067.4m		1085.7w
	1009.6m	1012.5m			1067.4m
					1008.6m
C-X(Str)	–	–	1238.1w	1007.6s	–
S-N(sym str)	925.7w	917.0s	907.3w	–	904.5w
C-S(str)	820.6m	811.9s	827.3m	819.6m	820.6m
C-H(Ar out of plane bend)	739.6m	738.6s	787.8w	756.0m	751.1m
	–	665.3m	673.0w	696.2w	686.5w
					640.3m
N-H(out plane bend)	698.1m	702.0m	745.4m	738.6s	711.6w
C-Br(Str)	561.2m	565.0m	574.7m	561.2s	558.3m
C=C(Ar out of plane bend)	477.3w	486.0m	413.7w	417.5w	494.7w
	418.5w	420.4m			

s = strong, m = medium and w = weak

to suppress noise (LB) 6.0, reference value (SR) was set at 701.89 ppm for DMSO at 39.5 ppm externally.

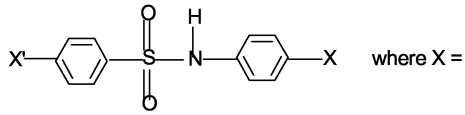
3. Results and Discussion

3.1. Infrared Spectra

The selected infrared absorption frequencies of all the N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides are shown in Tables 2 – 8. The assignment of these important frequencies to various modes of vibrations are also indicated in the tables. The details of assignments of various bands in organic compounds, in general, is described elsewhere [23 – 25]. The range of group absorptions has been assigned based on many compounds in which the groups occur. The precise frequency or wavenumber at which a specific group absorbs is dependent on its environment in the molecule and on its physical state [23, 24].

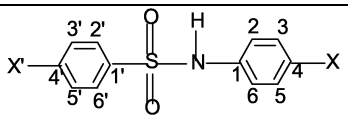
The N-H stretching vibrational frequencies (ν_{N-H}), of N-(*p*-substituted phenyl)-*p*-substituted benzene-

Table 8. The summary of N-H and S=O (sym.and asym) stretching infrared absorption frequencies (cm^{-1}) of N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.



X'	H	CH_3	F	Cl	Br
N-H symmetric stretching					
H	3284.2w	3270.7s	3250.4m	3284.2m	3262.0m
CH_3	3254.3w	3234.0w	3258.1s	3305.4s	3334.3s
C_2H_5	3278.4w	3263.9s	3269.7s	3262.0m	3254.3m
F	3218.6s	3270.7s	3250.4s	3284.2m	3264.9m
Cl	3259.1m	3233.1s	3245.6s	3259.1s	3260.1s
Br	3257.2m	3234.0s	3251.7s	3258.1w	3259.1s
S=O asymmetric					
H	1376.9s	1318.1m	1325.8m	1376.0m	1311.4m
CH_3	1373.1s	1334.5m	1332.6s	1327.8s	1341.3s
C_2H_5	1373.1s	1328.7s	1330.6s	1326.8m	1329.7w
F	1337.4s	1339.3m	1326.8s	1332.6m	1316.2m
Cl	1343.2m	1339.3s	1332.6s	1332.6m	1330.6m
Br	1374.0s	1340.3s	1333.5m	1374.0s	1329.7s
S=O symmetric					
H	1162.9s	1155.2s	1154.2s	1163.8s	1156.1s
CH_3	1173.5s	1174.4s	1160.9s	1160.9s	1158.0s
C_2H_5	1174.4s	1159.0s	1160.0s	1157.1s	1182.2s
F	1152.3s	1152.3s	1151.3s	1161.9s	1152.3s
Cl	1161.9s	1164.8s	1159.0s	1159.0s	1160.0s
Br	1160.9s	1165.8s	1158.0s	1160.9s	1159.0s

Table 9. Observed chemical shifts (δ, ppm) of various aromatic and other protons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.



X'

H

X	H-2,6	H-3,5	H-4	H-2',6'	H-3',5'	H-4'	N-H	Alkyl H
H	7.37m	7.17m	7.05d	7.96d	7.51m	7.81d	7.72	–
CH_3	7.42m	6.98m	–	7.95m	7.52m	7.76m	–	2.24
F	7.13m	7.41m	–	7.92d	7.55m	7.75d	9.94	–
Cl	7.37m	7.32m	–	7.91d	7.75m	7.79m	8.01	–
Br	7.29d	7.10d	–	7.80d	7.46m	7.54m	10.25	–

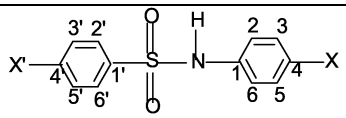
CH_3

	H-2,6	H-3,5	H-4	H-2',6'	H-3',5'	N-H	Alkyl H
H	7.22t	7.11m	7.07m	7.67d	7.26t	6.91	2.37
CH_3	7.00m	6.93m	–	7.65d	7.20d	7.96	2.37, 2.24
F	6.87m	7.06m	–	7.66d	7.23d	–	2.33
Cl	7.18m	7.02m	–	7.68d	7.25t	7.97	2.64, 2.33
Br	7.33m	7.25m	–	7.75m	7.38d	10.92	2.43

C_2H_5

	H-2,6	H-3,5	H-4	H-2',6'	H-3',5'	N-H	Alkyl H
H	7.16m	7.11m	6.94t	7.73m	7.43d	9.70	2.57, 1.15
CH_3	7.20d	6.98d	–	7.70d	7.25d	7.32	2.65, 2.24, 1.20
F	6.93m	7.04m	–	7.65d	7.25d	6.77	2.68, 1.23
Cl	7.21d	7.13d	–	7.71d	7.41d	10.04	2.63, 1.19
Br	7.25m	7.09m	–	7.67m	7.40m	9.96	2.64, 1.20

Table 10. Observed chemical shifts (δ, ppm) of various aromatic and other protons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.



X'

F

X	H-2,6	H-3,5	H-4	H-2',6'	H-3',5'	N-H	Alkyl H
H	7.22m	7.10m	7.04m	7.83m	7.80m	7.70	–
CH_3	7.07m	7.00m	–	7.83m	7.77m	7.50	2.27
F	6.86m	7.08m	–	7.75d	7.45m	9.72	–
Cl	7.10d	6.78s	–	7.33s	7.81s	10.17	–
Br	7.29d	7.07m	–	7.83m	7.44m	10.1	–

Cl

H	7.19m	7.15m	7.06m	7.76d	7.30d	7.94	–
CH_3	7.04m	6.96m	–	7.70d	7.37d	7.89	2.26
F	6.92m	7.07d	–	7.69d	7.37d	7.87	–
Cl	7.20d	7.04d	–	7.71d	7.49d	7.87	–
Br	7.32m	7.07m	–	7.75m	7.48m	10.2	–

Br

H	7.20d	7.12m	7.06m	7.65d	7.47d	7.80	–
CH_3	7.02m	6.95m	–	7.62d	7.48d	9.20	2.26
F	6.92m	7.07m	–	7.64m	7.57m	7.78	–
Cl	7.20d	7.04d	–	7.64d	7.56d	7.80	–
Br	7.34d	6.98d	–	7.64d	7.56d	7.80	–

Table 11. ^{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
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
$C_6H_5NH_2$	6.48	7.05	6.67	7.05	6.48
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

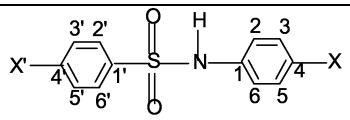
Table 12. The incremental shifts (δ, ppm) of aromatic protons due to -SO_2NH(*p*-XC_6H_4) groups in $C_6H_5SO_2NH$(*p*-XC_6H_4) and *p*-X'$C_6H_4SO_2$- and *p*-X'$C_6H_4SO_2NH$-groups in *p*-X'$C_6H_4SO_2NH(C_6H_5)$ (where X or X' = H, CH_3, C_2H_5, F, Cl or Br).

Groups	H-2',6'	H-3',5'	H-4'
-$SO_2NHC_6H_5$	0.67	0.22	0.52
-SO_2NH(4-$CH_3C_6H_4$)	0.66	0.23	0.47
-SO_2NH(4-FC_6H_4)	0.63	0.26	0.46
-SO_2NH(4-ClC_6H_4)	0.62	0.46	0.50
-SO_2NH(4-BrC_6H_4)	0.57	0.17	0.25
Groups	H-2,6	H-3,5	H-4
$C_6H_5SO_2$–	0.89	0.12	0.38
4-$CH_3C_6H_4SO_2$–	0.74	0.06	0.40
4-$C_2H_5C_6H_4SO_2$–	0.68	0.06	0.27
4-$FC_6H_4SO_2$–	0.74	0.05	0.37
4-$ClC_6H_4SO_2$–	0.71	0.10	0.39
4-$BrC_6H_4SO_2$–	0.72	0.07	0.39
$C_6H_5SO_2NH$–	0.08	−0.12	−0.24
4-$CH_3C_6H_4SO_2NH$–	−0.07	−0.18	−0.22
4-$C_2H_5C_6H_4SO_2NH$–	−0.13	−0.18	−0.35
4-$FC_6H_4SO_2NH$–	−0.07	−0.19	−0.25
4-$ClC_6H_4SO_2NH$–	−0.10	−0.14	−0.23
4-$BrC_6H_4SO_2NH$–	−0.09	−0.17	−0.23

Table 13. Shifts in the position of benzene protons (δ 7.27 ppm) 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

Table 14. Calculated and Observed chemical shifts (δ, ppm) of various aromatic protons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.

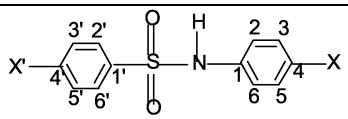


X’

X	CH_3						C_2H_5					
	H-2’,6’			H-3’,5’			H-2’,6’			H-3’,5’		
	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.
H	7.86	7.82	7.67d	7.36	7.28	7.26t	7.86	7.90	7.73m	7.36	7.34	7.43d
CH_3	7.85	7.81	7.65d	7.37	7.29	7.20d	7.85	7.89	7.70d	7.37	7.35	7.25d
F	7.82	7.78	7.66d	7.40	7.32	7.23d	7.82	7.86	7.65d	7.40	7.38	7.25d
Cl	7.81	7.77	7.68d	7.60	7.52	7.25t	7.81	7.85	7.71d	7.60	7.58	7.41d
Br	7.76	7.72	7.75m	7.31	7.23	7.38d	7.76	7.80	7.67m	7.31	7.29	7.40m
	F						Cl					
	H-2’,6’			H-3’,5’			H-2’,6’			H-3’,5’		
	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.
H	7.98	7.88	7.83m	7.81	7.72	7.80m	7.96	7.93	7.76d	7.51	7.48	7.30d
CH_3	7.97	7.87	7.83m	7.82	7.73	7.77m	7.95	7.92	7.70d	7.52	7.49	7.37d
F	7.94	7.84	7.75d	7.85	7.76	7.45m	7.92	7.89	7.69d	7.55	7.52	7.37d
Cl	7.93	7.83	7.33s	8.05	7.96	7.81s	7.91	7.88	7.71d	7.75	7.72	7.49d
Br	7.88	7.78	7.83m	7.76	7.67	7.44m	7.86	7.83	7.75m	7.46	7.43	7.48m

	Br				
	H-2’,6’			H-3’,5’	
	calc.1	calc.2	obs.	calc.1	calc.2	obs.
H	7.96	7.88	7.65d	7.51	7.43	7.47d
CH_3	7.95	7.87	7.62d	7.52	7.44	7.48d
F	7.92	7.84	7.64m	7.55	7.47	7.57m
Cl	7.91	7.83	7.64d	7.75	7.67	7.56d
Br	7.86	7.78	7.64d	7.46	7.38	7.56d

Table 15. Calculated and Observed chemical shifts (δ, ppm) of various aromatic protons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.

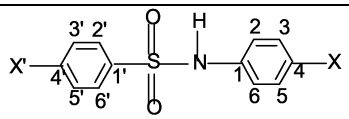


X

X’ CH_3

	H-2,6					H-3,5				
	calc.3	calc.4	calc.5	calc.6	obs.	calc.3	calc.4	calc.5	calc.6	obs.
H	7.27	7.38	7.27	7.23	7.42m	7.02	7.01	7.02	6.94	6.98m
CH_3	7.12	7.23	7.12	7.08	7.00m	6.96	6.95	6.96	6.98	6.93m
C_2H_5	7.06	7.17	7.06	7.02	7.20d	6.96	6.95	6.96	6.88	6.98d
F	7.12	7.23	7.12	7.08	7.07m	6.95	6.94	6.95	6.87	7.00m
Cl	7.09	7.20	7.09	7.05	7.04m	7.00	6.99	7.00	6.92	6.96m
Br	7.10	7.21	7.10	7.06	7.02m	6.97	6.96	6.97	6.89	6.95m
	F									
H	7.39	7.35	7.39	7.29	7.13m	7.47	6.92	7.47	7.38	7.41m
CH_3	7.24	7.20	7.24	7.14	6.87m	7.41	6.86	7.41	7.32	7.06m
C_2H_5	7.18	7.14	7.18	7.08	6.93m	7.41	6.86	7.41	7.32	7.04m
F	7.24	7.20	7.24	7.14	6.86m	7.40	6.85	7.40	7.31	7.08m
Cl	7.21	7.17	7.21	7.11	6.92m	7.45	6.90	7.45	7.36	7.07d
Br	7.22	7.18	7.22	7.12	6.92m	7.42	6.87	7.42	7.33	7.07m

Table 16. Calculated and Observed chemical shifts (δ, ppm) of various aromatic protons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.

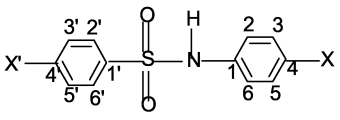


X

X’ Cl

	H-2,6					H-3,5				
	calc.3	calc.4	calc.5	calc.6	obs.	calc.3	calc.4	calc.5	calc.6	obs.
H	7.37	7.37	7.37	7.34	7.37m	7.17	7.15	7.17	7.14	7.32m
CH_3	7.22	7.22	7.22	7.19	7.18m	7.11	7.09	7.11	7.08	7.02m
C_2H_5	7.16	7.16	7.16	7.13	7.21d	7.11	7.09	7.11	7.08	7.13d
F	7.22	7.22	7.22	7.19	7.10d	7.10	7.08	7.10	7.07	6.78s
Cl	7.19	7.19	7.19	7.16	7.20d	7.15	7.13	7.15	7.12	7.04d
Br	7.20	7.20	7.20	7.17	7.20d	7.12	7.10	7.12	7.09	7.04d
	Br									
H	7.37	7.38	7.37	7.29	7.29d	7.17	7.32	7.17	7.09	7.10d
CH_3	7.22	7.23	7.22	7.14	7.33m	7.11	7.26	7.11	7.03	7.25m
C_2H_5	7.16	7.17	7.16	7.08	7.25m	7.11	7.26	7.11	7.03	7.09m
F	7.22	7.23	7.22	7.14	7.29d	7.10	7.25	7.10	7.02	7.07m
Cl	7.19	7.20	7.19	7.11	7.32m	7.15	7.30	7.15	7.07	7.07m
Br	7.20	7.21	7.20	7.12	7.34d	7.12	7.27	7.12	7.04	6.98d

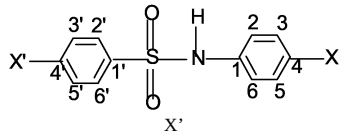
Table 17. Observed chemical shifts (δ, ppm) of various aromatic and other carbons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.



X' / X

X	C-1	C-2,6	C-3,5	C-4	C-1'	C-2',6'	C-3',5'	C-4'	Alkyl C
					X' = H				
H	136.5	121.5	129.0	125.2	138.8	127.6	129.3	133.3	–
CH_3	133.3	122.4	129.8	135.4	139.1	127.7	129.3	133.3	20.8
F	132.3	123.1	115.4	160.9	139.2	127.1	129.1	133.5	–
Cl	133.4	124.7	129.4	130.3	139.1	127.9	129.4	133.4	–
Br	136.9	126.5	131.5	121.8	139.3	127.7	129.1	133.1	–
					CH_3				
H	137.2	121.7	129.4	125.4	135.9	127.4	129.7	144.0	21.6
CH_3	133.9	122.2	130.1	135.3	136.1	127.4	129.7	143.8	20.8, 20.4
F	132.5	124.4	116.0	162.1	135.7	127.3	129.8	144.0	21.5
Cl	135.4	122.7	129.4	132.8	137.1	127.3	130.6	144.2	21.5, 20.4
Br	136.0	124.5	129.4	117.5	136.0	126.7	129.3	143.5	20.9
					C_2H_5				
H	137.8	120.5	129.6	125.9	137.1	127.5	128.9	149.2	28.5, 15.5, 15.0
CH_3	133.9	122.0	129.8	135.1	136.3	127.4	128.5	149.8	26.8, 20.8, 15.0
F	132.5	124.8	116.2	160.1	136.3	127.5	128.6	150.2	28.9, 15.0
Cl	133.7	121.6	129.4	130.0	136.6	128.2	128.7	149.2	28.3, 15.4, 14.8
Br	136.4	124.7	131.4	121.6	136.7	126.6	127.9	148.9	28.1, 15.1, 14.5

Table 18. Observed chemical shifts (δ, ppm) of various aromatic and other carbons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.



X' / X

X	C-1	C-2,6	C-3,5	C-4	C-1'	C-2',6'	C-3',5'	C-4'	Alkyl C
					X' = F				
H	136.3	121.7	129.4	125.6	134.9	130.1	116.2	166.7	–
CH_3	133.5	122.4	130.1	135.6	134.8	129.9	116.2	166.8	20.8
F	132.2	123.3	115.5	157.9	133.3	128.5	114.5	161.1	–
Cl	135.4	123.3	129.5	132.9	136.2	128.7	115.8	162.7	–
Br	136.7	125.1	131.7	122.2	135.4	129.5	114.7	166.2	–
					Cl				
H	136.1	121.6	129.1	125.5	137.1	128.6	129.7	139.4	–
CH_3	133.3	122.5	129.9	135.8	137.4	128.8	129.2	139.5	20.9
F	132.0	124.7	116.4	159.2	137.1	128.7	129.4	139.7	–
Cl	134.7	123.2	129.2	131.4	137.0	128.7	129.7	139.9	–
Br	136.5	125.0	132.3	122.1	137.8	128.8	129.4	138.3	–
					Br				
H	136.0	121.6	128.5	125.5	137.6	129.2	132.5	128.0	–
CH_3	134.2	121.7	129.5	134.5	138.6	131.8	132.6	128.6	20.6
F	131.9	124.8	116.1	159.2	137.6	129.0	132.4	128.3	–
Cl	134.6	123.2	129.2	131.4	137.5	129.6	132.6	128.6	–
Br	135.2	123.4	132.5	119.1	137.6	129.2	132.8	128.7	–

sulphonamides vary in the range, 3334 – 3219 cm^{-1}. These are in conformity with the range, 3266 – 3240 cm^{-1}, reported for the N-H symmetric stretching vibrations of *p*-substituted benzenesulphonamides [8]. Asymmetric and symmetric SO_2 stretching vibrations of N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides appear in the ranges, 1377 – 1311 cm^{-1} and 1182 – 1151 cm^{-1}, respectively, compared to the ranges of 1344 – 1327 cm^{-1} and 1187 – 1147 cm^{-1}, observed for the *p*-substituted benzenesulphonamides,

Table 19. ^{13}C chemical shifts of benzene, substituted benzenes, aniline and substituted anilines measured under identical conditions.

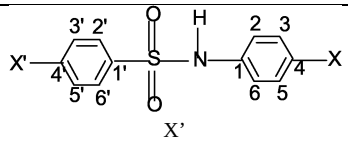
Compound	C-1	C-2	C-3	C-4	C-5	C-6
C_6H_6	128.4	128.4	128.4	128.4	128.4	128.4
$CH_3C_6H_5$	137.7	129.0	128.2	125.3	128.2	129.0
$C_2H_5C_6H_5$	144.3	127.9	128.4	125.7	128.4	127.9
FC_6H_5	164.6	115.4	130.1	124.1	130.1	115.4
ClC_6H_5	134.4	128.7	129.8	126.5	129.8	128.7
BrC_6H_5	122.5	131.5	130.0	126.8	130.0	131.5
$C_6H_5NH_2$	146.2	114.6	128.8	117.8	128.8	114.6
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

Table 20. The incremental shifts (δ, ppm) of aromatic carbons due to -SO_2NH(*p*-XC_6H_4) groups in $C_6H_5SO_2NH$(*p*-XC_6H_4) and *p*-X'$C_6H_4SO_2$- and *p*-X'$C_6H_4SO_2NH$- groups in *p*-X'$C_6H_4SO_2NH(C_6H_5)$ (where X or X' = H, CH_3, C_2H_5, F, Cl or Br).

Groups	C-1'	C-2',6'	C-3',5'	C-4'
-$SO_2NHC_6H_5$	10.44	−0.8	0.86	4.90
-SO_2NH(4-$CH_3C_6H_4$)	10.67	−0.72	0.93	4.85
-SO_2NH(4-FC_6H_4)	10.84	−1.3	0.69	5.07
-SO_2NH(4-ClC_6H_4)	10.70	−0.53	0.99	4.95
-SO_2NH(4-BrC_6H_4)	10.86	−0.71	0.74	4.69
Groups	C-1	C-2,6	C-3,5	C-4
$C_6H_5SO_2$–	−9.68	6.87	0.21	7.43
4-$CH_3C_6H_4SO_2$–	−9.0	7.05	0.59	7.60
4-$C_2H_5C_6H_4SO_2$–	−9.1	5.91	0.84	8.13
4-$FC_6H_4SO_2$–	−9.9	7.13	0.6	7.78
4-$ClC_6H_4SO_2$–	−10.1	6.97	0.33	7.70
4-$BrC_6H_4SO_2$–	−10.2	6.99	−0.27	7.72
$C_6H_5SO_2NH$–	8.12	−6.93	0.61	−3.17
4-$CH_3C_6H_4SO_2NH$–	8.80	−6.75	0.99	−3.0
4-$C_2H_5C_6H_4SO_2NH$–	9.40	−7.89	1.24	−2.47
4-$FC_6H_4SO_2NH$–	7.92	−6.67	1.0	−2.82
4-$ClC_6H_4SO_2NH$–	7.70	−6.83	0.73	−2.9
4-$BrC_6H_4SO_2NH$–	7.62	−6.81	0.13	−2.88

Table 21. 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	C-1 (Attachment)	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	–



X'

Table 22. Calculated and Observed chemical shifts (δ, ppm) of various aromatic carbons in N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides.

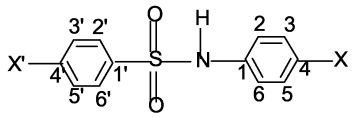
X	C-1'			C-2',6'			C-3',5'			C-4'		
	calc.1	calc.2	obs	calc.1	calc.2	obs	calc.1	calc.2	obs	calc.1	calc.2	obs
						CH_3						
H	135.9	135.7	135.9	127.5	127.4	127.4	130.0	130.0	129.7	142.6	142.6	144.0
CH_3	136.2	136.0	136.1	127.6	127.5	127.4	130.0	129.9	129.7	142.6	142.6	143.8
F	136.3	136.1	135.7	127.0	126.9	127.3	129.8	129.7	129.8	142.8	142.8	144.0
Cl	136.2	136.0	137.1	127.8	127.7	127.3	130.1	130.0	130.6	142.7	142.7	144.2
Br	136.4	136.2	136.0	127.6	127.5	126.7	129.8	129.7	129.3	142.4	142.4	143.5
						C_2H_5						
H	136.2	136.1	137.8	127.6	127.6	127.5	128.8	128.8	128.9	148.9	149.2	149.2
CH_3	136.5	136.4	136.3	127.7	127.7	127.4	128.8	128.8	128.5	148.9	149.2	149.8
F	136.6	136.5	136.3	127.1	127.1	127.5	128.6	128.6	128.6	149.1	149.4	150.2
Cl	136.5	136.4	136.6	127.9	127.9	128.2	128.9	128.9	128.7	149.0	149.3	149.2
Br	136.7	136.6	136.7	127.7	127.7	126.6	128.6	128.6	127.9	148.7	149.0	148.9
						F						
H	134.3	134.5	134.9	128.5	129.3	130.1	115.0	116.3	116.2	168.4	169.5	166.7
CH_3	134.6	134.8	134.8	128.6	129.4	129.9	115.0	116.3	116.2	168.4	169.5	166.8
F	134.7	134.9	133.3	128.0	128.8	128.5	114.8	116.1	114.5	168.6	169.7	161.1
Cl	134.6	134.8	136.2	128.8	129.6	128.7	115.1	116.4	115.8	168.5	169.6	162.7
Br	134.8	135.0	135.4	128.6	129.4	129.5	114.8	116.1	114.7	168.2	169.3	166.2
						Cl						
H	136.8	136.9	137.1	128.6	129.0	128.6	129.5	129.6	129.7	139.7	139.3	139.4
CH_3	137.1	137.2	137.4	128.7	129.1	128.8	129.5	129.6	129.2	139.7	139.3	139.5
F	137.2	137.3	137.1	128.1	128.5	128.7	129.3	129.4	129.4	139.9	139.5	139.7
Cl	137.1	137.2	137.0	128.9	129.3	128.7	129.6	129.7	129.7	139.8	139.4	139.9
Br	137.3	137.4	137.8	128.7	129.1	128.8	129.3	129.4	129.4	139.5	139.1	138.3
						Br						
H	137.8	137.2	137.6	129.8	129.2	129.2	132.7	132.4	132.5	127.9	127.4	128.0
CH_3	138.1	137.5	138.6	130.0	129.3	131.8	132.7	132.4	132.6	127.9	127.4	128.6
F	138.2	137.6	137.6	129.3	128.7	129.0	132.5	132.2	132.4	128.1	127.6	128.3
Cl	138.1	137.5	137.5	130.1	129.5	129.6	132.8	132.5	132.6	128.0	127.5	128.6
Br	138.3	137.7	137.6	129.9	129.3	129.2	132.5	132.2	132.8	127.7	127.2	128.7

respectively [8]. The S-N and C-N stretching absorptions were observed in the ranges, 937 – 898 cm^{-1} and 1310 – 1180 cm^{-1}, respectively, in agreement with the assignments of bands in literature.

The assignment of other frequencies to various modes of vibrations of the ring (Tables 2 – 8) are similar to those in arylsulphonamides, N-(chloro)-arylsulphonamides and other aromatic organic compounds [8, 9, 11, 13, 23, 24]. There are no particular trends in the variation of the frequencies on substitution with either electron withdrawing or electron donating groups.

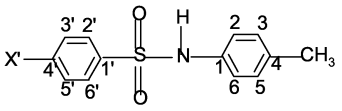
3.2. ^{1}H NMR Spectra

^{1}H chemical shifts of aromatic and alkyl protons of all the N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides are shown in Tables 9 and 10. The aromatic protons and carbons are numbered as shown in the following general structure



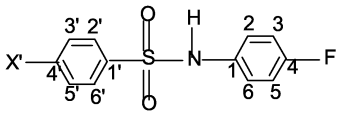
The various chemical shifts are assigned to the protons of two benzene rings in line with those for similar compounds [8, 23, 24, 26 – 31]. ^{1}H chemical shifts of benzene, substituted benzenes, aniline and substituted anilines were measured under identical conditions and included in Table 11. Further, the incremental shifts due to –SO_2NH(*p*-XC_6H_4)groups in the compounds of the formula, $C_6H_5SO_2NH$(*p*-XC_6H_4), and *p*-X'$C_6H_4SO_2$- and *p*-X'$C_6H_4SO_2NH$-groups in the compounds of the type, *p*-X'$C_6H_4SO_2NH(C_6H_5)$, were computed and used to calculate the ^{1}H chemi-

Table 23. Calculated and Observed chemical shifts (δ, ppm) of various aromatic carbons in N-(4-methyl phenyl)-*p*-substituted benzenesulphonamides.



X'	C-1					C-2,6				
	calc.3	calc.4	calc.5	calc.6	obs.	calc.3	calc.4	calc.5	calc.6	obs.
H	133.6	134.1	133.6	133.4	133.7	121.4	121.9	121.4	121.3	122.4
CH_3	134.3	134.8	134.3	134.1	133.9	121.6	122.1	121.6	121.5	122.2
C_2H_5	134.9	135.4	134.9	134.7	133.9	120.4	120.9	120.4	120.3	122.0
F	133.4	133.9	133.4	133.2	133.5	121.6	122.1	121.6	121.5	122.4
Cl	133.2	133.7	133.2	133.0	133.3	121.5	122.0	121.5	121.4	122.5
Br	133.1	133.6	133.1	132.9	134.2	121.5	122.0	121.5	121.4	121.7
			C-3,5					C-4		
H	129.7	129.7	129.7	129.6	129.8	134.5	134.6	134.5	134.5	135.4
CH_3	130.1	130.1	130.1	130.0	130.1	134.7	134.8	134.7	134.7	135.3
C_2H_5	130.3	130.3	130.3	130.2	129.8	135.2	135.3	135.2	135.2	135.1
F	130.1	130.1	130.1	130.0	130.1	134.9	135.0	134.9	134.9	135.6
Cl	129.8	129.8	129.8	129.7	129.9	134.8	134.9	134.8	134.8	135.8
Br	129.2	129.2	129.2	129.1	129.5	134.8	134.9	134.8	134.8	134.5

Table 24. Calculated and Observed chemical shifts (δ, ppm) of various aromatic carbons in N-(4-fluoro phenyl)-*p*-substituted benzenesulphonamides.



X'	C-1					C-2,6				
	calc.3	calc.4	calc.5	calc.6	obs.	calc.3	calc.4	calc.5	calc.6	obs.
H	132.0	132.9	132.0	132.2	132.3	122.4	122.6	122.4	123.2	123.1
CH_3	132.7	133.6	132.7	132.9	132.5	122.6	122.8	122.6	123.4	124.4
C_2H_5	133.3	134.2	133.3	133.5	132.5	121.4	121.6	121.4	122.2	124.8
F	131.8	132.7	131.8	132.0	132.3	122.6	122.8	122.6	123.4	123.3
Cl	131.6	132.5	131.6	131.8	132.0	122.5	122.7	122.5	123.3	124.7
Br	131.5	132.4	131.5	131.7	131.9	122.5	122.7	122.5	123.3	124.8
			C-3,5					C-4		
H	114.7	115.4	114.7	116.0	115.4	160.3	161.7	160.3	161.4	160.9
CH_3	115.1	115.8	115.1	116.4	116.0	160.5	161.9	160.5	161.6	162.1
C_2H_5	115.3	116.0	115.3	116.6	116.2	161.0	162.4	161.0	162.1	161.2
F	115.1	115.8	115.1	116.4	115.5	160.7	162.1	160.7	161.8	157.9
Cl	114.8	115.5	114.8	116.1	116.4	160.6	162.0	160.6	161.7	159.2
Br	114.2	114.9	114.2	115.5	116.1	160.6	162.0	160.6	161.7	159.2

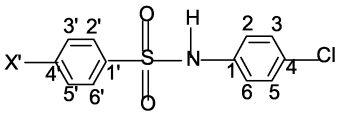
cal shifts of the parallely substituted compounds of the general formula *p*-X'$C_6H_4SO_2NH$(*p*-XC_6H_4) as described below.

The incremental shifts of aromatic protons in N-(*p*-substituted phenyl)-benzenesulphonamides due to –SO_2NH(*p*-XC_6H_4) (X = H, CH_3, F, Cl or Br) were calculated by comparing the chemical shifts of these protons in $C_6H_5SO_2NH$(*p*-XC_6H_4) (X = H, CH_3, F, Cl or Br) with that of benzene proton value of 7.27 ppm. The calculated values are shown in Table 12. Then the chemical shifts of the H-2',6' and H-3',5' protons in *p*-X'$C_6H_4SO_2NH$(*p*-XC_6H_4) were calculated in two ways. In the first method, the chemical shifts of H-2',6' and H-3',5' protons were calculated by adding the incremental shifts due to –SO_2NH(*p*-XC_6H_4) (X = H, CH_3, F, Cl or Br) and the substituent X' (CH_3, C_2H_5, F, Cl or Br) (Table 13) to the benzene proton value of 7.27 ppm (calc. 1). In the second method (calc. 2), the chemical shifts of H-2',6' and H-3',5' protons in *p*-X'$C_6H_4SO_2NH$(*p*-XC_6H_4) were computed by adding the incremental shifts due to –SO_2NH(*p*-XC_6H_4) (X = H, CH_3, F, Cl or Br) to the chemical shifts of the corresponding protons in substituted benzenes (Table 11). The calculated chemical shifts by methods 1 and 2 compared with the observed values are shown in Table 14. There is a good agreement between the two sets of calculated values and the experimental chemical shifts, showing that the two methods of calculations lead to almost the same values in most cases.

Similarly, the incremental shifts of H-2,6; H-3,5 and H-4 protons due to *p*-X'$C_6H_4SO_2$- (X' = H, CH_3, C_2H_5, F, Cl or Br) groups, in *p*-X'$C_6H_4SO_2NH(C_6H_5)$ were calculated by comparing the chemical shifts of H-2,6; H-3,5 and H-4 protons in these compounds with the aniline proton values: H-2,6 = 6.48 ppm, H-3,5 = 7.05 ppm and H-4 = 6.67 ppm. The computed incremental shifts are shown in Table 12. Then the chemical shifts of H-2,6 and H-3,5 protons in the parallely substituted compounds, *p*-X'$C_6H_4SO_2NH$(*p*-XC_6H_4) were calculated in two ways (calc. 3 and calc. 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 *p*-X'$C_6H_4SO_2$- (X'= H, CH_3, C_2H_5, F, Cl or Br) (Table 12) and the substituent X (CH_3, F, Cl or Br) (Table 13) to the chemical shifts of the corresponding aniline proton values (H-2,6 = 6.48 ppm and H-3,5 = 7.05 ppm). In the other method (calc. 4), H-2,6 and H-3,5 chemical shifts were evaluated by adding the incremental shifts due to *p*-X'$C_6H_4SO_2$- (X'= H, CH_3, C_2H_5, F, Cl or Br) to the chemical shifts of the corresponding protons of the substituted anilines (Table 13). The calculated chemical shifts by methods 3 and 4 compared with the observed chemical shifts are shown in Tables 15 and 16.

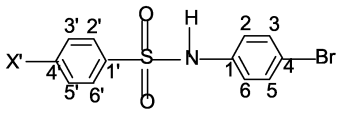
Further, the incremental shifts of H-2,6; H-3,5 and H-4 protons due to *p*-X'$C_6H_4SO_2NH$- (X' = H, CH_3, C_2H_5, F, Cl or Br) groups, in *p*-X'$C_6H_4SO_2NH(C_6H_5)$ were computed by comparing the chemical shifts of H-2,6; H-3,5 and H-4 protons in these compounds with the benzene proton value of 7.27 ppm. The computed incremental shifts are shown in Table 12. Then the chemical shifts of the H-2,6 and H-3,5 protons in the parallely substituted compounds, *p*-X'$C_6H_4SO_2NH$(*p*-XC_6H_4) were also calculated in

Table 25. Calculated and Observed chemical shifts (δ, ppm) of various aromatic carbons in N-(4-chloro phenyl)-*p*-substituted benzenesulphonamides.



X'	C-1					C-2,6				
	calc.3	calc.4	calc.5	calc.6	obs.	calc.3	calc.4	calc.5	calc.6	obs.
H	134.5	135.2	134.5	134.6	133.4	122.5	123.0	122.5	122.9	124.7
CH_3	135.2	135.9	135.2	135.3	135.4	122.7	123.2	122.7	123.1	122.7
C_2H_5	135.8	136.5	135.8	135.9	133.7	121.5	122.0	121.5	121.9	121.6
F	134.3	135.0	134.3	134.4	135.4	122.7	123.2	122.7	123.1	123.3
Cl	134.1	134.8	134.1	134.2	134.7	122.6	123.1	122.6	123.0	123.2
Br	134.0	134.7	134.0	134.1	134.6	122.6	123.1	122.6	123.0	123.2
			C-3,5					C-4		
H	129.2	129.1	129.2	129.3	129.4	131.6	130.0	131.6	131.2	130.3
CH_3	129.6	129.5	129.6	129.7	129.4	131.8	130.2	131.8	131.4	132.8
C_2H_5	129.8	129.7	129.8	129.9	129.4	132.3	130.7	132.3	131.9	130.0
F	129.6	129.5	129.6	129.7	129.5	132.0	130.4	132.0	131.6	132.9
Cl	129.3	129.2	129.3	129.4	129.2	131.9	130.3	131.9	131.5	131.4
Br	128.7	128.6	128.7	128.8	129.2	131.9	130.3	131.9	131.5	131.4

Table 26. Calculated and Observed chemical shifts (δ, ppm) of various aromatic carbons in N-(4-bromo phenyl)-*p*-substituted benzenesulphonamides.



X'	C-1					C-2,6				
	calc.3	calc.4	calc.5	calc.6	obs.	calc.3	calc.4	calc.5	calc.6	obs.
H	135.5	135.9	135.5	134.9	136.9	123.7	123.6	123.7	123.1	125.3
CH_3	136.2	136.6	136.2	135.6	136.0	123.9	123.8	123.9	123.3	124.5
C_2H_5	136.8	137.2	136.8	136.2	136.4	122.7	122.6	122.7	122.1	124.7
F	135.3	135.7	135.3	134.7	136.7	123.9	123.4	123.9	123.3	125.1
Cl	135.1	135.5	135.1	134.5	136.5	123.8	123.7	123.8	123.2	125.0
Br	135.0	135.4	135.0	134.4	135.2	123.4	123.7	123.4	123.2	123.4
			C-3,5					C-4		
H	132.4	132.2	132.4	132.1	132.4	119.8	117.5	119.8	119.3	121.8
CH_3	132.8	132.6	132.8	132.5	129.4	120.0	117.7	120.0	119.5	117.5
C_2H_5	133.0	132.8	133.0	132.7	131.4	120.5	118.2	120.5	120.0	121.6
F	132.8	132.6	132.8	132.5	131.7	120.2	117.9	120.2	119.7	122.2
Cl	132.5	132.3	132.5	132.2	132.3	120.1	117.8	120.1	119.6	122.1
Br	131.9	131.7	131.9	131.6	132.5	120.1	117.8	120.1	119.6	119.1

two more ways (calc. 5 and 6). In method 5, the H-2,6 and H-3,5 proton chemical shifts were calculated by adding the incremental shifts due to *p*-X'$C_6H_4SO_2NH$- (X' = H, CH_3, C_2H_5, F, Cl or Br) and the substituent X (CH_3, F, Cl or Br) (Tables 12 and 13) to the benzene proton chemical shift of 7.27 ppm. In the other method (calc. 6), the chemical shifts of H-2,6 and H-3,5 protons were calculated by adding the incremental shifts due to *p*-X'$C_6H_4SO_2NH$- (X' = H, CH_3, C_2H_5, F, Cl or Br) to the corresponding proton chemical shifts of the substituted benzenes (Table 11). The values calculated by the methods 5 and 6 are also shown in Tables 15 and 16. The comparisons revealed that there is a good agreement between the four sets of calculated chemical shifts and the experimental values. 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*

^{13}C chemical shifts of aromatic and alkyl carbons of all the N-(*p*-substituted phenyl)-*p*-substituted benzenesulphonamides are shown in Tables 17 and 18. The various chemical shifts are assigned to the different carbons in the two benzene rings in conformity with the literature for similar compounds [8, 23 – 31]. ^{13}C chemical shifts of benzene, substituted benzenes, aniline and substituted anilines were measured under identical conditions and included in Table 19. Further, the incremental shifts of C-1'; C-2',6'; C-3',5' and C-4' carbons due to –SO_2NH(*p*-XC_6H_4) groups in $C_6H_5SO_2NH$(*p*-XC_6H_4) were calculated by comparing the chemical shifts of the carbons in these compounds with that of benzene carbon value of 128.5 ppm. Similarly, the incremental shifts of C-1; C-2,6; C-3,5 and C-4 carbons due to *p*-X'$C_6H_4SO_2$- groups in *p*-X'$C_6H_4SO_2NH(C_6H_5)$ compounds were computed by comparing the chemical shifts of the carbons in these 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). Further, the incremental shifts of C-1; C-2,6; C-3,5 and C-4 carbons due to *p*-X'$C_6H_4SO_2NH$- groups in *p*-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 128.5 ppm. The computed incremental shifts of C-1'; C-2',6'; C-3',5' and C-4' carbons due to –SO_2NH(*p*-XC_6H_4) groups in $C_6H_5SO_2NH$(*p*-XC_6H_4) and those of C-1; C-2,6; C-3,5 and C-4 carbons due to *p*-X'$C_6H_4SO_2$-, *p*-X'$C_6H_4SO_2NH$- groups in *p*-X'$C_6H_4SO_2NH(C_6H_5)$ are shown in Table 20.

The incremental shifts due to these groups and those of the substituents (Table 21) 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-2,6; C-3,5 and C-4 carbons in the parallely substituted compounds *p*-X'$C_6H_4SO_2NH$(*p*-XC_6H_4) by methods similar to the ones described under ^{1}H NMR. The various calculated chemical shifts compared with the experimental chemical values are

shown in Tables 22 – 26. It is evident from the calculated shifts 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 with ^{13}C chemical shifts also.

The incremental shifts of the aromatic carbons due to the groups –SO_2NH(*p*-XC_6H_4), *p*-X'$C_6H_4SO_2$- and *p*-X'$C_6H_4SO_2NH$- are found to reasonably correlate with the corresponding Hammett meta and para substituent parameters. Further, the chemical shifts of C-1 and C-4; C-1' and C-4'; C-1 and C-4'; and C-1' and C-4; are found to intercorrelate with each other.

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[1] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York 1988.
[2] M. M. Campbell and G. Johnson, Chem. Rev. **78**, 65 (1978).
[3] B. T. Gowda and D. S. Mahadevappa, Talanta **30**, 359 (1983).
[4] B. T. Gowda and D. S. Mahadevappa, J. Chem. Soc., Perkin Trans. **2**, 323 (1983).
[5] B. T. Gowda, B. S. Sherigara, and D. S. Mahadevappa, Microchem. J. **34**, 103 (1986).
[6] K. K. Banerji, B. Jayaram, and D. S. Mahadevappa, J. Sci. Ind. Res. **46**, 65 (1987).
[7] M. C. Agrawal and S. K. Upadhyay, J. Sci. Ind. Res. **49**, 13 (1990).
[8] B. T. Gowda, K. Jyothi, and J. D. D'Souza, Z. Naturforsch. **57a**, 967 (2002).
[9] B. T. Gowda, J. D. D'Souza, and B. H. A. Kumar, Z. Naturforsch. **58a**, 51 (2003).
[10] B. T. Gowda and K. M. Usha, Z. Naturforsch. **58a**, 351 (2003).
[11] B. T. Gowda, K. Jyothi, and N. Damodara, Z. Naturforsch. **58a**, 563 (2003).
[12] B. T. Gowda, K. Jyothi, J. Kožíšek, and H. Fuess, Z. Naturforsch. **58a**, 656 (2003).
[13] K. Jyothi and B. T. Gowda Z. Naturforsch. **59a**, xxx (2004).
[14] B. T. Gowda, J. D. D'Souza, and K. R. Bhat, J. Indian Chem. Soc. **78**, 412 (2002).
[15] B. T. Gowda and B. H. A. Kumar, Oxid. Commun. **26**, 403 (2003).
[16] B. T. Gowda, K. L. Jayalakshmi, and K. Jyothi, Z. Naturforsch. **58b**, 787 (2003).
[17] B. T. Gowda and M. Shetty, J. Phys. Org. Chem. **17**, xxx (2004)
[18] M. Shetty and B. T. Gowda, Z. Naturforsch. **59b**, 63 (2004).
[19] R. R. Baxter and F. D. Chattway, J. Chem. Soc. **107**, 1814 (1915).
[20] H. D. Dakin, J. B. Cohen, M. Dufrence, and Kenyon, J. Proc. Roy Soc. (B) **89**, 232 (1917).
[21] E. H. Huntress and F. H. Carten, J. Org. Chem. **62**, 511 (1940).
[22] A. I. Vogel, Quantitative Organic Analysis; Longman, London 1958.
[23] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, Spectrometric Identification of Organic Compounds; John Wiley and Sons, New York 1991.
[24] W. Kemp, Organic Spectroscopy; MacMillan, London 1996.
[25] M. Goldstein, M. A. Russell, and H. A. Willis, Spectrochim. Acta **25A**, 1275 (1969).
[26] H. Kalova, R. Slechtova, J. Socha, Jaromir, and V. Bekarck, Acta Univ. Palacki. Olomuc. Fac. Rerum Nat. **49**, 143 (1976).
[27] V. L. Levashova, V. F. Mandyuk, and R. V. Vizgert, Visn. L'viv. Politekh Inst. **130**, 64 (1979).
[28] D. E. Ewing, Org. Magn. Reson. **12**, 499 (1979).
[29] A. M. Hakkinen, P. Ruostesuo, and R. Kivekas, J. Chem. Soc. Perkin Trans. **2**, 815 (1988).
[30] R. Minkwitz, P. Garzarek, and H. Preut, Z. Naturforsch. **52b**, 88 (1997).
[31] E. Kolehmainen, H. Janota, R. Gawinecki, K. Laihia, and R. Kauppinen, Magn. Reson. Chem. **38**, 384 (2000).