Spectroscopic Studies with N-Chloroarylsulphonamides: IR and ^{1}H, ^{13}C and ^{23}Na NMR Spectra of Sodium Salts of N-Chloro-Mono- and Di-Substituted-Benzenesulphonamides, 4-X-$C_6H_4SO_2NaNCl$ (X = H; CH_3; C_2H_5; F; Cl; Br; I or NO_2) and *i*-X, *j*-$YC_6H_3SO_2NaNCl$ (*i*-X, *j*-Y = 2,3-$(CH_3)_2$; 2,4-$(CH_3)_2$; 2,5-$(CH_3)_2$; 2-CH_3, 4-Cl; 2-CH_3, 5-Cl; 3-CH_3, 4-Cl; 2,4-Cl_2 or 3,4-Cl_2)

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In an effort to introduce N-chloroarylsulphonamides of different oxydising strengths, sixteen sodium salts of N-chloro-mono- and di-substituted benzenesulphonamides of the configuration, 4-X-$C_6H_4SO_2NaNCl$ (where X = H; CH_3; C_2H_5; F; Cl; Br; I or NO_2) and *i*-X, *j*-$YC_6H_3SO_2NaNCl$ (where *i*-X, *j*-Y = 2,3-$(CH_3)_2$; 2,4-$(CH_3)_2$; 2,5-$(CH_3)_2$; 2-CH_3,4-Cl; 2-CH_3,5-Cl; 3-CH_3,4-Cl; 2,4-Cl_2 or 3,4-Cl_2) are prepared, characterized through their infrared spectra in the solid state and NMR spectra in solution. The $\nu_{N—Cl}$ frequencies vary in the range 950 – 927 cm^{-1}. Effects of substitution in the benzene ring in terms of electron donating and electron withdrawing groups have been considered, and conclusions drawn. The chemical shifts of aromatic protons and carbon-13 in all the N-chloroarylsulphonamides have been calculated by adding substituent contributions to the shift of benzene. Considering the approximation employed the agreement between the calculated and experimental chemical shift values for different protons or carbon-13 is quite good. Effects of phenyl ring substitution on chemical shift values of both ^{1}H and ^{13}C are also graphically represented in terms of line diagrams.

Key words: Infrared; Nuclear Magnetic Resonance; N-Chloroarylsulphonamides.

1. Introduction

Many sulphonamides and their N-chloro compounds exhibit pharmacological, fungicidal, and herbicidal activities because of their oxidising action in aqueous, partial aqueous and non-aqueous media [1 – 7]. Therefore an understanding of the formation, properties and reactions of sulphonamides is central to future development in such areas as medicinal and redox chemistry. A great deal of work on the spectroscopic aspects of amides needs to be done for correlating the frequencies with the chemical bond parameters. Thus we are interested in spectroscopic studies of amides in their crystalline state [8 – 16]. We have recently reported the infrared and NMR spectra of several arylsulphonamides of the configuration, 4-X-$C_6H_4SO_2NH_2$ and *i*-X, *j*-$YC_6H_3SO_2NH_2$ [16].

In this paper we report the results of infrared and NMR (^{1}H, ^{13}C, and ^{23}Na) spectral studies of sixteen sodium salts of N-chlorosubstituted benzenesulphonamides of the configuration, 4-X-$C_6H_4SO_2NaNCl$ (where X = H; CH_3; C_2H_5; F; Cl; Br; I or NO_2) and *i*-X, *j*-$YC_6H_3SO_2NaNCl$ (where *i*-X, *j*-Y = 2,3-$(CH_3)_2$; 2,4-$(CH_3)_2$; 2,5-$(CH_3)_2$; 2-CH_3,4-Cl; 2-CH_3,5-Cl; 3-CH_3,4-Cl; 2,4-Cl_2 or 3,4-Cl_2).

2. Experimental

2.1. Materials and Methods

Preparation of arylsulphonamides and sodium salts of N-chloroarylsulphonamides:

The substituted benzenesulphonamides were prepared by chlorosulphonation of substituted benzenes

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Table 1. Melting points of mono- and di-substituted benzenesulphonamides and their N-chloro compounds.

Sl. No	Substituted benzene-sulphonamides	m. p. (°C) obs. [20]	Substituted N-chloro-benzenesulphonamides	m. p. (°C) obs. [20]
1	4-C_2H_5-$C_6H_4SO_2NH_2$	99 – 101	4-C_2H_5-$C_6H_4SO_2NCl(Na).H_2O$	194
2	4-F-$C_6H_4SO_2NH_2$	125(124 – 125)	4-$FC_6H_4SO_2NCl(Na).H_2O$	198
3	4-Cl-$C_6H_4SO_2NH_2$	143(142 – 143)	4-$ClC_6H_4SO_2NCl(Na).H_2O$	191(190)
4	4-Br-$C_6H_4SO_2NH_2$	162(161.5)	4-$BrC_6H_4SO_2NCl(Na).H_2O$	179(178)
5	4-I-$C_6H_4SO_2NH_2$	176(176)	4-$IC_6H_4SO_2NCl(Na).H_2O$	184(185)
6	4-p-NO_2-$C_6H_4SO_2NH_2$	167(167)	4-$NO_2C_6H_4SO_2NCl(Na).H_2O$	188(189)
8	2,3-$(CH_3)_2$-$C_6H_3SO_2NH_2$	138 – 140	2,3-$(CH_3)_2$-$C_6H_3SO_2NCl(Na).H_2O$	167
9	2,4-$(CH_3)_2$-$C_6H_3SO_2NH_2$	140 – 142	2,4-$(CH_3)_2$-$C_6H_3SO_2NCl(Na).H_2O$	154
10	2,5-$(CH_3)_2$-$C_6H_3SO_2NH_2$	149 – 151	2,5-$(CH_3)_2$-$C_6H_3SO_2NCl(Na).H_2O$	192
11	2-CH_3,4-Cl-$C_6H_3SO_2NH_2$	158 – 160 (184 – 185)	2-CH_3,4-Cl-$C_6H_3SO_2NCl(Na).H_2O$	172
12	2-CH_3,5-Cl-$C_6H_3SO_2NH_2$	139 – 141 (142 – 143)	2-CH_3,5-Cl-$C_6H_3SO_2NCl(Na).H_2O$	188
13	3-CH_3,4-Cl-$C_6H_3SO_2NH_2$	132-134(126)	3-CH_3,4-Cl-$C_6H_3SO_2NCl(Na).H_2O$	174
14	2,4-Cl_2-$C_6H_3SO_2NH_2$	178 – 180 (179 – 180)	2,4-Cl_2-$C_6H_3SO_2NCl(Na).H_2O$	210
15	3,4-Cl_2-$C_6H_3SO_2NH_2$	141 – 143 (134 – 135)	3,4-Cl_2-$C_6H_3SO_2NCl(Na).H_2O$	192

Table 2. Infrared spectral frequencies (cm^{-1}) of sodium salts of N-chloro-mono-substituted benzenesulphonamides.

Assignment	*i*-X-$C_6H_4SO_2NaNCl{\cdot}H_2O$, *i*-X =							
	Parent	4-CH_3	4-C_2H_5	4-F	4-Cl	4-Br	4-I	4-NO_2
C—H (Ar sym str)	3061.4 w	2930.3 w	3061.4 w	3101.9 w	3118.3 s	3097.1 w	3074.9 w	3081.6 w
C—H (Alk str)		2923.7 w						
	–		2924.3 m	–	–	–	–	–
		2861.8 w						
combination bands	1955.3 w	1912.3 w	1917.7 w	1912.3 w	1912.3 w	1912.7 w	1917.3 w	1987.2 w
	1893.4 w			1768.5 w	1793.2 w			
	1818.5 w							
C==C (Ar in-plane str)	1683.5 w	1679.6 m	1641.1 m	1642.0 m	1644.9 m	1644.9 m	1639.2 m	1606.4 m
	1639.2 s	1599.6 m	1598.7 m	1595.8 s	1573.6 s	1576.5 m	1568.8 m	1530.2 s
	1497.1 w	1493.6 w	1449.2 m	1495.5 s	1476.2 s	1472.3 m	1447.3	
S==O (Asym str)	1309.6 w	1302.6 m	1368.3 w	1380.8 w	1331.6 s	1387.5 m	1382.7 m	1351.8 s
C—H (Ar in-plane bend)	1092.4 s	1084.7 s	1093.4 s	1091.5 s	1090.5 s	1089.5 s	1089.5 s	1117.5 s
	1021.1 w	1017.2 m	1017.3 w	1022.3 w		1010.5 m	1007.6 m	1070.3 s
N—Cl (Str)	**940.1 s**	**926.6 s**	**941.0 s**	**938.0 s**	**929.5 s**	**928.5 s**	**940.1 s**	**949.7 s**
C—H	752.1 s	808.0 s	786.8 w	831.2 s	821.5 s	820.6 s	814.8 s	734.0 s
(Ar out-of-plane-bend)	725.1 s	700.0 s	702.9 s	713.5 s	754.9 s	743.4 s	735.7 s	668.2 s
C—X (Str)	–	–	–	1254.5 s	1013.4 s	598.8 s	594.0 s	–
C==C (Ar out-of-plane bend)	457.1 m	463.8 m	443.6 m	443.6 m	480.2 m	421.4 m	460.9 m	464.8 m

to the corresponding sulphonylchlorides and subsequent conversion of the latter to the respective substituted benzenesulphonamides by procedures reported in [16 – 21]. The sulphonamides were recrystallized to constant melting point (Table 1) from dilute ethanol and dried at 105 °C. The purity of all compounds was further checked by recording their infrared spectra (Tables 2 and 3). The sulphonamides were then N-chlorinated as follows to give sodium salts of N-chloroarylsulphonamides.

Pure chlorine gas was bubbled through clear aqueous solutions of substituted benzenesulphonamides in 4M NaOH at 70 °C for about 1 hr. The precipitated sodium salts of N-chlorosubstituted benzenesulphonamides (CASB) were filtered, washed, dried and recrystallised from water. Purity of all the reagents was checked by determining the melting points[2] (Table 1) and by estimating iodometrically the amounts of active chlorine present in them [2, 3, 17, 21].

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

3. Results and Discussion

3.1. Infrared Spectra

The selected infrared absorption frequencies of sixteen sodium salts of N-chlorosubstituted benzenesul-

Table 3. Infrared spectral frequencies (cm^{-1}) of sodium salts of N-chloro-di-substituted benzenesulphonamides.

Assignment	*i*-X,*j*-Y-$C_6H_4SO_2$ NaNCl·H_2O, *i*-X,*j*-Y =							
	2,3-$(CH_3)_2$	2,4-$(CH_3)_2$	2,5-$(CH_3)_2$	2-CH_3, 4-Cl	2-CH_3, 5-Cl	3-CH_3, 4-Cl	2,4-CH_2	3,4-CH_2
C—H (Ar sym str)	3016.1 w	3007.4 m	3021.9 m	3062.2 w	3073.9 w	3068.2 m	3099.0 s	3068.1 s
C—H (Alk. str)	2974.2 w	3007.2 w	3023.4 w					
	2942.2 w	2980.0 w	2987.3 w	2987.0 w	2987.0	2980.2 w	–	–
	2920.2 w	2931.3 w	2931.2 w	2930.0 w	2937.3 w	2924.1 w		
combination bands	1924.2 w	1937.2 w	1857.0 w	1930.0 w	–	1917.7 w	1930.4 w	1924.2 w
	1755.4 w	1843.4 w				1930.0 w	1811.0 w	1861.2 w
C==C (Ar in-plane str)	1638.2 s	1633.4 s	1638.2 m	1635.3 m	1639.0 m	1639.2 s	1633.4 s	1639.2m
	1449.2 s	1602.5 s	1486.8 m	1588.3 m	1562.1 w	1568.8 m	1574.5 s	1569.7 w
		1480.1 s	1458.1 w	1468.5 m	1467.7 s	1468.5 s	1556.2 s	1454.0 s
		1454.0 s		1450.2 m		1443.4 s	1455.0 s	
S==O (Asym str)	1390.4 m	1386.5 w	1370.1 w	1381.7 m	1381.7 m	1384.6 s	1370.1 s	1371.5 s
S==O (Sym str)	1189.8 m	1169.6 s	1147.4 s	1139.1 s	1147.4 s	1132.0 s	1137.8 s	1130.0 s
C—H (Ar in-plane bend)	1126.2 s	1123.2 s	1125.2 s	1100.1 s	1128.3 s	1096.3 s	1098.2 s	1095.3 s
S—N (Sym str)	995.0 m	971.9 w	912.2 m	–	907.3 m	944.9 m	–	–
N—Cl (Str)	**944.9 s**	**936.2 s**	**937.2 s**	**930.4 s**	**939.1 s**	**944.9 s**	**937.2 s**	**942.0 s**
C—H (Ar out-of-plane bend)	816.7 m	827.3 s	815.7 s	833.1 m	814.8 m	817.6 s	860.1 s	832.1 s
	696.1 s	693.2 s	703.8 s	711.6 m	702.9 m	771.4 s	819.6 s	817.7 s
C-X (Str)	–	–	–	1056.8 s	1059.7 s	1050.0 s	1040.4 s	1033.6 s
C==C (Ar out-of-plane bend)	447.4 s	461.9 s	469.6 m	463.8 m	463.8 m	448.4 s	459.9 s	451.3 s

* The signal at 7.53 integrates for 3 protons corresponding to 3, 4, 5.

Table 4. ^{1}H NMR observed and calculated δ (ppm) values of sodium salts of N-chloro-mono-substituted benzenesulphonamides *i*-X-$C_6H_4SO_2$ NaNCl·H_2O.

	δ Values (in ppm)						
	H_o (2,6)		H_m (3,5)		H_p (4)		alkyl H
i-X	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
Parent	7.82(d)	–	7.53(d)	–	*	–	
4-CH_3	7.69(d)	7.72	7.20(d)	7.38	–	–	2.25 (d)
							0.91(m)
4-C_2H_5	7.64(d)	7.72	7.08(d)	7.38	–	–	2.30(m)
4-F	7.76(m)	7.84	7.17(m)	7.83	–	–	
4-Cl	7.92(m)	7.82	7.58(m)	7.53	–	–	
4-Br	7.69(s)	7.82	7.54(d)	7.53	–	–	
4-I	7.41(d)	7.62	7.62(d)	7.83	–	–	
4-NO_2	8.20(m)	8.12	8.45(s)	8.53	–	–	

* The signal at 7.53 integrates for 3 protons corresponding to 3, 4, 5.

Table 5. ^{1}H NMR observed and calculated δ (ppm) values of sodium salts of N-chloro-di-substituted benzenesulphonamides *i*-X,*j*-Y-$C_6H_4SO_2$NaNCl·H_2O.

	δ Values (in ppm)										
	2-H		3-H		4-H		5-H		6-H		alkyl
i-X, *j*-Y	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	H
2,3-$(CH_3)_2$	–	–	–	–	7.15	7.02	7.62	7.33	7.64	7.62	2.16
2,4-$(CH_3)_2$	–	–	6.76	7.23	–	–	7.61	7.28	7.64	7.62	2.38
2,5-$(CH_3)_2$	–	–	7.29	7.28	–	7.02	–	–	7.96	7.57	2.77
2-CH_3,4-Cl	–	–	7.71	7.38	–	–	7.74	7.43	8.26	7.72	2.98
2-CH_3,5-Cl	–	–	7.42	7.38	7.31	7.17	–	–	8.06	7.72	2.72
3-CH_3,4-Cl	7.55	7.67	–	–	–	–	7.48	7.43	8.08	7.72	2.31
2,4-Cl_2	–	–	7.48	7.53	–	–	7.61	7.53	8.12	7.82	–
3,4-Cl_2	–	–	7.55	7.53	7.41	7.27	–	–	8.21	7.82	–

Table 6. Shifts in the position of benzene protons (δ7.27) caused by substituents.

Substituent	ortho	meta	para
CH_3	0.17	0.09	0.18
COOH	−0.80	−0.14	−0.20
$COOCH_3$	−0.74	−0.07	−0.20
CN	−0.27	−0.11	−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	0.75	0.24	0.63
I	−0.40	0.26	0.03
Br	−0.22	0.13	0.03
Cl	−0.02	0.06	0.04
F	0.30	0.02	0.22
CHO	−0.58	−0.21	−0.27
NHCOR	0.40	−0.20	−0.30
NO_2	0.50	0.14	0.40
OH	−0.95	−0.17	−0.33
OCH_3	0.43	0.09	0.37
$OCOCH_3$	0.21	0.02	–
Ph	−0.18	0.00	0.08
COCl	−0.83	−0.16	−0.30

phonamides are shown in Tables 2 and 3. The assignments of various frequencies to different modes of vibrations are indicated in the tables. The discussion is similar to the ones described under arylsulphonamides, except for the assignment of frequencies to N-Cl vibrations.

Table 7. ^{13}C NMR observed and calculated δ (ppm) values of sodium salts of N-chloro-mono-substituted benzenesulphonamides.

i-X-	δ Values (in ppm)								
-$C_6H_4SO_2$ NaNCl·H_2O	C_1		$C_{2,6}$		$C_{3,5}$		C_4		alkyl C
where *i*-X =	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	
Parent	133.6	–	130.3	–	128.3	–	141.1	–	–
4-CH_3	139.5	138.2	130.8	130.2	128.3	128.9	144.2	142.8	21.8 29.4
4-C_2H_5	138.7	138.5	129.4	130.3	128.6	127.8	149.8	149.1	15.9
4-F	137.5	136.6	131.1	131.2	117.3	114.0	167.4	168.6	–
4-Cl	138.9	139.1	130.2	131.3	129.9	128.5	139.8	139.8	–
4-Br	166.4	140.1	133.4	132.5	130.3	131.7	128.8	128.1	–
4-I	130.4	133.8	128.5	132.9	140.4	138.2	101.3	101.3	–
4-NO_2	143.5	147.1	131.9	131.2	123.6	123.0	149.1	153.1	–

Table 8. ^{13}C NMR observed and calculated δ (ppm) values of sodium salts of N-chloro-di-substituted benzenesulphonamides.

i-X, *j*-Y-C_6H_3-SO_2	δ Values (in ppm)												
-NaNCl·H_2O	C_1		C_2		C_3		C_4		C_5		C_6		alkyl C
where *i*-X, *j*-Y =	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
2,3-$(CH_3)_2$	142.5	141.7	138.8	140.2	138.5	138.3	131.0	134.1	125.9	125.3	129.1	127.3	20.2
2,4-$(CH_3)_2$	137.6	138.9	138.4	139.5	131.2	129.7	143.6	142.7	127.6	126.1	134.3	130.1	21.8
2,5-$(CH_3)_2$	139.3	141.7	137.2	136.7	131.5	128.9	134.1	134.1	135.5	134.7	133.9	130.9	21.6
2-CH_3, 4-Cl	141.2	141.8	139.2	140.6	132.8	129.2	138.5	139.8	127.3	125.6	133.5	131.2	21.2
2-CH_3, 5-Cl	142.1	142.8	137.8	137.6	129.6	129.9	133.3	133.6	132.5	131.8	130.9	130.4	20.9
3-CH_3, 4-Cl	141.0	141.0	131.3	131.4	127.9	127.9	139.1	138.7	127.4	127.4	129.5	129.5	21.3
2,4-Cl_2	139.2	139.3	138.6	137.7	128.6	128.7	139.9	140.9	128.2	126.5	132.6	132.3	–
3,4-Cl_2	142.1	140.1	131.0	131.5	134.4	134.9	141.8	140.1	130.2	129.5	128.7	129.3	–

The various vibrations in N-chloroarylsulphonamides and their characteristic absorption frequencies are discussed below.

The N—Cl vibrational frequencies, $\nu_{N—Cl}$, vary in the range 950 – 927 cm^{-1}. Asymmetric and symmetric SO_2 stretching vibrations appear in the ranges, 1388 – 1303 cm^{-1} and 1150 – 1132 cm^{-1} for the mono-substituted N-chloroarylsulphonamides and 1390 – 1370 cm^{-1} and 1190 – 1130 cm^{-1} for the di-substituted N-chlorocompounds, respectively. The ranges reported for the non-chlorinated compounds are 1389 – 1327 cm^{-1} and 1187 – 1147 cm^{-1}, respectively [16].

The other frequencies are assigned to various other vibrations of the ring (Tables 2 and 3). The discussions are similar to those of other organic aromatic compounds, dealt in detail in [22, 23]. The ranges of group absorptions are assigned based on many compounds in which the groups occur. The precise frequency or wavelength at which a specific group absorbs is dependent on its environment within the molecule and on its physical state.

As may be seen in the Tables, like with non-N-chlorinated sulphonamides, there is no regular trend in the variation of the frequencies on substitution with either electron withdrawing or donating groups.

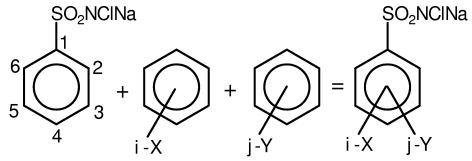
3.2. NMR (^{1}H, ^{13}C, *and* ^{23}Na) *Spectra*

^{1}H NMR Spectra

The proton NMR spectra of the compounds were measured on a BRUKER Ac 300F, 300 MHz FT-NMR spectrometer. ^{1}H spectra were recorded in D_2O with tetramethylsilane (Me_4Si) as internal standard. The experimental conditions employed are 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) 1.360 sec, 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 ^{1}H spectra of N-chloro-arylsulphonamides and the chemical shifts are shown in Tables 4 and 5. The chemical shift is dependent on the electron density around the nucleus, or associated with the atom to which it is bonded. Hence empirical correlations relating the chemical shifts to the structures are discussed.

Thus the chemical shifts of aromatic protons in all the N-chloroarylsulphonamides have been calculated by adding substituent contributions (Table 6) to the shift of benzene (7.27 ppm), as per the principle of substituent addition:



The incremental shifts of the aromatic protons (ppm from those of benzene proton values of 7.27) for different substituents are shown in Table 6 and are used in the calculation. The shifts in aromatic protons due to SO_2NaNCl were calculated comparing the values of the sodium salt of N-chlorobenzenesulphonamide (7.82, 7.53) with those of benzene proton value of 7.27 ppm. The values are $H_o(2,6) = +0.55$ and $H_m(3,4,5) = +0.26$. The calculated chemical shifts for different protons compared with the experimental values are shown in Tables 4 and 5. Considering the approximation employed, the agreement between the calculated and experimental chemical shifts is quite good.

^{13}C NMR Spectra

The Carbon-13 NMR spectra of the compounds were measured in D_2O. Tetramethylsilane was used as the external reference standard. The following experimental conditions were employed in the spectral measurement of carbon-13: 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 to suppress noise (LB) 6.0, reference value (SR) was set at 701.89 ppm for DMSO at 39.5 ppm externally.

The ^{13}C spectra of the sodium salts of N-chlorosubstituted benzenesulphonamides are shown in Tables 7 and 8.

As in the case of ^{1}H NMR, the chemical shifts of aromatic carbon are also dependent on the electron density around the nucleus or associated with the atom to which it is bonded. The chemical shifts of aromatic carbon-13 in all the N-chloroarylsulphonamides have been calculated by adding a substituent contribution (Table 9) to the shift of benzene (128.5 ppm), similar to the procedure employed with aromatic protons.

Table 9. Incremental shifts of the aromatic carbon atoms of mono-substituted benzenes (ppm from benzene at 128.5 ppm, +downfield, −upfield).

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	–

The incremental shifts of the aromatic carbon-13 (ppm from those of benzene carbon-13 values of 128.5) for different substituents [22, 24] are shown in Table 9 and are used in the calculation. The shifts in aromatic protons due to $-SO_2NaNCl$ were calculated by comparing the values of the sodium salt of N-chlorobenzenesulphonamide with those of benzene carbon-13 of 128.5 ppm. The values are ^{13}C-1 = + 4.959, ^{13}C-4 = +12.616, ^{13}C-2 or 6 = +1.764 and ^{13}C-3 or 5 = −0.23.

The calculated chemical shifts for different aromatic carbons compared with the experimental values are shown in Tables 7 and 8. The agreement between the calculated and experimental chemical shifts is quite good.

^{23}Na NMR Spectra

Sodium-23 NMR spectra of the compounds were measured using a BRUKER Ac 300F, 300MHz FT-NMR spectrometer ^{23}NaCl, dissolved in D_2O, was used as the external reference standard. The experimental conditions employed for the measurement of ^{23}Na NMR spectra are as follows: The spectral frequency (SF) 79.391 MHz, sweep width (SW) 22727.273, pulse width (PW) 5.0, relaxation delay (RD) 1.0 sec, acquisition time (AQ) 0.360 sec, receiver gain (RG) 20, decoupling power (DP) 14H DO, filter to suppress noise (LB) 0.0, the reference value (SR) was set at 3262.03 ppm for NaCl externally.

Table 10. ^{23}Na NMR δ (ppm) values of sodium salts of N-chloro-mono- and di-substituted benzenesulphonamides.

i-X-$C_6H_4SO_2$ $NaNCl{\cdot}H_2O$, *i*-X =	^{23}Na δ values (in ppm)	*i*-X, *j*-Y-$C_6H_3SO_2$ $NaNCl{\cdot}H_2O$, *i*-X, *j*-Y =	^{23}Na δ values (in ppm)
Parent	−0.8267	2,3-$(CH_3)_2$	−0.8893
4-CH_3	−0.9598	2,4-$(CH_3)_2$	−0.8014
4-C_2H_5	−0.7937	2,5-$(CH_3)_2$	−1.2062
4-F	−0.8035	2-CH_3, 4-Cl	−1.0479
4-Cl	−1.0216	2-CH_3, 5-Cl	−1.2218
4-Br	−0.7584	3-CH_3, 4-Cl	−1.3267
4-I	−0.7912	2,4-Cl_2	−1.0126
4-NO_2	−0.8802	3,4-Cl_2	−1.4352

The chemical shifts of ^{23}Na NMR spectra of sodium salts of N-chlorosubstituted benzenesulphonamides are tabulated in Table 10. As may be seen, there is no specific trend in the chemical shifts of ^{23}Na on substitution in the phenyl ring.

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