Infrared, ^{1}H and ^{13}C NMR Spectra of N,N-Dichloroarylsulphonamides, 4-X-$C_6H_4SO_2NCl_2$ (X = H, CH_3, C_2H_5, F, Cl or Br) and *i*-X, *j*-$YC_6H_3SO_2NCl_2$ (*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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Several mono- and di-substituted N,N-dichloroarylsulphonamides of the configuration, 4-X-$C_6H_4SO_2NCl_2$ (where X = H, CH_3, C_2H_5, F, Cl or Br) and *i*-X, *j*-$YC_6H_3SO_2NCl_2$ (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), respectively, were prepared, characterised and their infrared spectra in the solid state and NMR spectra in solution state were measured and correlated. Comparison of the infrared spectra of the N,N-dichloroarylsulphonamides with the corresponding arylsulphonamides and N-chloroarylsulphonamides revealed that the infrared absorption bands in the ranges, 790 – 735 cm^{-1} and 595 – 546 cm^{-1} are due to N-Cl asymmetric and symmetric stretching vibrations, respectively, and that the effect of ring substitution on the N-Cl frequencies is not consistent. The frequencies in the ranges 1384 – 1333 cm^{-1} and 1181 – 1143 cm^{-1} are, respectively, assigned to S=O asymmetric and symmetric modes of vibration. The effect of substitution in the phenyl ring in terms of electron withdrawing and electron donating groups is non-systematic. Since the chemical shift depends on the electron density around the nucleus, empirical correlations relating the chemical shifts to the structures have been considered. The chemical shifts of aromatic protons and carbons in all the N,N-dichloroarylsulphonamides have been calculated by adding substituent contributions to the shift of benzene. Considering the approximation made, the agreement between the calculated and experimental chemical shifts is good.

Key words: Infrared; ^{1}H and ^{13}C NMR Spectra; N, N-Dichloroarylsulphonamides.

1. Introduction

Sulphonamides are of fundamental chemical interest as they show distinct physical, chemical and biological properties. Many sulphonamides and their N-chloro compounds also exhibit pharmacological activity. This has stimulated recent interest in their chemistry. Further, many of these compounds exhibit fungicidal and herbicidal activities due to their oxidising action in aqueous, partial aqueous and non-aqueous media [1 – 6]. Therefore an understanding of the formation, properties and reactions of arylsulphonamides, their N-chloro and N,N-dichloro compounds is of interest in medicinal and redox chemistry. Thus a great deal of work on the spectroscopic and structural aspects of these compounds needs to be done to correlate their reactivities with the chemical bond parameters. Thus we are interested in spectroscopic studies of arylsulphonamides in particular and amides in general [6 – 13].

We have recently reported the spectroscopic studies on a number of arylsulphonamides [12] and their sodium salts of N-chloro compounds [13]. We report herein the infrared and NMR spectra of a number of mono- and di-substituted N,N-dichloroarylsulphonamides of the configuration, 4-X-$C_6H_4SO_2NCl_2$ (where X = H, CH_3, C_2H_5, F, Cl or Br) and *i*-X, *j*-$YC_6H_3SO_2NCl_2$ (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). They are N,N-dichlorobenzenesulphonamide, N,N-dichloro-4-methylbenzenesulphonamide, N,N-dichloro-4-ethylbenzenesulphonamide, N,N-dichloro-4-fluorobenzenesulphonamide, N,N-dichloro-4-chlorobenzenesulphonamide,

Table 1. Melting points of Arylsulphonamides and N,N-dichloroarylsulphonamides.

Sl. No.	Arylsulphonamides	m.p.(°C) obs (lit.)	N,N-Dichloro-arylsulphonamides	m.p.(°C)
1	4-$C_2H_5C_6H_4SO_2NH_2$	99 – 101	4-$C_2H_5C_6H_4SO_2NCl_2$	58
2	4-$FC_6H_4SO_2NH_2$	125 (124 – 125)	4-$FC_6H_4SO_2NCl_2$	55 – 56
3	4-$ClC_6H_4SO_2NH_2$	143 (142 – 143)	4-$ClC_6H_4SO_2NCl_2$	81
4	4-$BrC_6H_4SO_2NH_2$	162 (161.5)	4-$BrC_6H_4SO_2NCl_2$	102
5	2,3-$(CH_3)_2C_6H_3SO_2NH_2$	138 – 140	2,3-$(CH_3)_2C_6H_3SO_2NCl_2$	58
6	2,4-$(CH_3)_2C_6H_3SO_2NH_2$	140 – 142	2,4-$(CH_3)_2C_6H_3SO_2NCl_2$	63
7	2,5-$(CH_3)_2C_6H_3SO_2NH_2$	149 – 151	2,5-$(CH_3)_2C_6H_3SO_2NCl_2$	68
8	2-CH_3,4-$ClC_6H_3SO_2NH_2$	180 – 182 (184 – 185)	2-CH_3,4-$ClC_6H_3SO_2NCl_2$	70
9	2-CH_3,5-$ClC_6H_3SO_2NH_2$	139 – 141 (142 – 143)	2-CH_3,5-$ClC_6H_3SO_2NCl_2$	66
10	3-CH_3,4-$ClC_6H_3SO_2NH_2$	132 – 134 (126) (126)	3-CH_3,4-$ClC_6H_3SO_2NCl_2$	62
11	2,4-$Cl_2C_6H_3SO_2NH_2$	178 – 180 (179 – 180)	2,4-$Cl_2C_6H_3SO_2NCl_2$	67
12	3,4-$Cl_2C_6H_3SO_2NH_2$	141 – 143 (134 – 135)	3,4-$Cl_2C_6H_3SO_2NCl_2$	55

Table 2. Infrared absorption frequencies (cm^{-1}) of N,N-dichloro-*p*-substitutedbenzenesulphonamides. s = strong, m = medium, w = weak.

Assignment	4-X-$C_6H_4SO_2NCl_2$, X =					
	H [18, 21]	CH_3 [18, 21]	C_2H_5	F	Cl	Br
C-H (Ar sym str)	3054.7 w	3066.3 w	3054.7 w	3105.8 w	3095.2 s	3090.4 w
C-H (alk str)	–	2997.5 w 2921.6 w	2967.0 w 2931.3 w	–	–	–
combination bands		1924.6 w 1810.8 w			1918.8 m 1792.5 w	1915.0 m 1792.5 w
C=C (Ar in-plane str)	1636.3 w 1582.3 w 1475.3 w 1447.3 m	1627.6 m 1594.8 s 1490.7 w 1446.4 w	1617.0 s 1597.7 s 1490.7 s	1590.0 s 1538.9 m 1490.7 s	1624.7 m 1582.3 s 1474.3 s	1635.3 m 1571.7 s 1470.5 s
S=O (asym str)	1374.0 w	1373.1 s	1383.7 s	1379.8 m	1377.9 s	1376.9 s
(sym str)	1156.1 s	1157.1 s	1167.7 s	1142.6 s	1172.5 s	1172.5 s
C-X (str)	–	–	–	1240.0 s	1089.6 s	559.3 s
C-H (Ar in-plane bend)	1085.7 s 1024.0 w	1083.8 s 1017.2 m	1087.7 s 1015.3 w	1088.6 s 1014.4 w	1089.6 s 1013.4 s	1081.9 s 1010.5 m
S-N (sym str)	827.3 s	–	862.0 w	834.1 s	826.4 s	910.2 m
N-Cl (asym str)	**785.9 s**	**761.7 s**	**768.5 s**	**789.7 s**	**770.4 s**	**776.2 s**
C-S (str)	749.2 s	813.8 s	803.2 s	–	752.1 s	816.7 s
C-H (Ar out of-plane bend)	720.3 m	665.3 s	736.7 s 716.4 s	727.0 m 681.7 s	702.9 s	737.6 s 698.1 m
N-Cl (sym str)	**557.3 s**	**547.7 s**	**560.2 s**	**545.8 s**	**559.3 s**	**559.3 s**
C=C (Ar out of-plane bend)	468.6 m	487.9 w	459.9 m	453.2 m	483.1 m	421.4 m

N,N-dichloro-4-bromobenzenesulphonamide, N,N-dichloro-2,3-dimethylbenzenesulphonamide, N,N-dichloro-2,4-dimethylbenzenesulphonamide, N,N-dichloro-2,5-dimethylbenzenesulphonamide, N,N-dichloro-2-methyl-4-chlorobenzene-sulphonamide, N,N-dichloro-2-methyl-5-chlorobenzenesulphonamide, N,N-dichloro-3-methyl-4-chlorobenzenesulphonamide, N,N-dichloro-2,4-dichlorobenzenesulphonamide and N,N-dichloro-3,4-dichlorobenzenesulphonamide.

2. Experimental

2.1. Materials and Methods

N,N-dichloroarylsulphonamides were prepared as follows:

i) Preparation of arylsulphonamides and N-chloroarylsulphonamides: The arylsulphonamides were prepared and N-chlorinated to get N-chloroarylsulphonamides by the procedures reported in [12 – 18] (Table 1).

ii) Further N-chlorination of N-chloroarylsulphonamides: Pure chlorine gas was bubbled through clear aqueous solutions of the sodium salts of N-chloroarylsulphonamides for about 1 h. The precipitated N,N-dichloroarylsulphonamides were filtered, washed, dried and recrystallised from acetic acid. The purity of all reagents was checked by determining the melting points [13 – 18] (Table 1), and by estimating iodometrically the amounts of active chlorine present in them. All other reagents employed were of analytical grade.

Table 3. Infrared absorption frequencies (cm^{-1}) of N,N-dichloro-disubstitutedbenzenesulphonamides. s = strong, m = medium, w = weak.

Assignment	*i*-X, *j*-Y-$C_6H_3SO_2NCl_2$, *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	3,4-Cl_2
C-H (Ar sym str)	3058.6 w	3104.8 m	3058.6 w	3095.2 m	3099.1 m	3086.5 w	3091.3 w	3064.3 m
C-H (alk str)	2977.6 w 2922.6 w	 2931.3 w	2971.8 m 2925.5 w	2992.0 w 2930.3 w	2976.6 w 2931.3 w	2952.5 w 2922.6 w	–	–
combination bands	1927.5 w 1760.7 w	 1822.4 w 1787.7 w	1941.0 w 1792.5 w	1924.6 w	1932.3 w 1766.5 w	1920.8 w 1762.6 w	1913.0 w 1828.2 w 1776.1 w	1926.5 w 1821.4 w 1775.2 w
C=C (Ar in-plane str)	 1593.9 s 1487.8 m 1449.2 s	1629.6 m 1592.9 m 1450.2 w	1608.3 m 1558.2 m 1492.6 s 1451.2 s	 1585.2 s 1468.5 s 1446.4 s	1624.7 w 1592.1 w 1464.7 s	1635.3 w 1583.3 m 1467.6 s 1446.4 m	1650.8 m 1581.3 m 1473.4 m	1630.5 w 1572.7 m 1454.1 s
S=O (asym str)	1365.4 s	1376.9 s	1332.6 s	1359.6 s	1356.7 s	1373.1 s	1346.1 m	1380.8 s
(sym str)	1167.7 s	1162.9 s	1160.0 s	1176.4 s	1163.8 s	1173.5 s	1164.8 s	1181.2 s
C-H (Ar in-plane bend)	1086.7 s 1023.1 m	1081.9 s 1035.6 w	1060.7 s 1040.4 m	1105.0 s 1031.7 m	1113.7 s	1092.5 s	1141.7 s 1014.4 m	1133.9 s 1091.5 s
C-X (str)	–	–	–	1048.1 s	1055.8 s	1052.9 s	1087.7 s	1033.7 s
S-N (sym str)	892.9 m	927.6 m	885.2 s	879.4 s	885.2 m	884.2 s	931.5 s	890.0 w
C-S (str)	816.7 m	752.1 s	823.5 s	824.4 s	829.2 s	818.6 m	825.4 s	825.4 s
N-Cl (asym str)	**766.6 s**	**779.1 s**	**752.1 s**	**734.8 s**	**750.2 s**	**775.2 s**	**783.0 s**	**769.5 s**
C-H (Ar out of-plane bend)	702.0 m	713.5 s	719.3 m 700.0 s	 697.1 s	 690.4 s	706.8 s	752.1 m 684.6 m	 699.1 m
N-Cl (sym str)	**572.8 s**	**559.3 s**	**582.4 s**	**579.5 s**	**586.3 s**	**585.3 s**	**559.3 s**	**594.9 s**
C=C (Ar out of-plane bend)	482.1 w	455.1 w	463.8 w	489.8 s	498.5 s	460.9 m	482.1 s	472.5 m

Table 4. The observed and calculated ^{1}H chemical shifts (δ, ppm) of N,N-dichloro-*p*-substitutedbenzenesulphonamides (4-X $C_6H_4SO_2NCl_2$).

X	δ (in ppm)				
	H_o (2,6)		H_m (3,5)		alkyl H
	Obs.	Calc.	Obs.	Calc.	
H	8.10 d	–	7.82 m	–	–
CH_3	7.95 d	8.00	7.46 d	7.67	2.45 m
C_2H_5	7.88 d	8.00	7.53 d	7.67	2.72 m 1.85 m
F	8.16 m	8.12	7.39 m	8.12	–
Cl	8.05 m	8.10	7.67 m	7.82	–
Br	7.96 d	8.10	7.83 m	7.82	–

s = singlet, d = doublet, t = triplet and m = multiplet.

2.2. Infrared Absorption Frequency Measurements

Infrared absorption frequency measurements were made on a JASCO-430 (Japan) FT/IR spectrometer. 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).

2.3. NMR Spectral Measurements

The proton and carbon-13 NMR spectra of the compounds were measured on a BRUKER Ac 300F, 300MHz FT-NMR spectrometer. The spectra were recorded in $CDCl_3$ and DMSO with tetramethylsilane (Me_4Si) as internal standard. The experimental conditions employed for ^{1}H NMR spectra 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

Table 5. The observed and calculated ^{1}H chemical shifts (δ, ppm) of di-substituted N,N-dichlorobenzenesulphonamides (*i*-X, *j*-$YC_6H_3SO_2NCl_2$).

	δ (in ppm)										
i-X, *j*-Y	2-H		3-H		4-H		5-H		6-H		alkyl H
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
2,3-$(CH_3)_2$	–	–	–	–	7.42	7.42	7.69	7.62	7.80	7.90	2.59
											2.41
2,4-$(CH_3)_2$	–	–	7.30	7.52	–	–	7.56	7.57	8.50	7.90	3.26
											2.57
2,5-$(CH_3)_2$	–	–	7.70	7.57	7.43	7.42	–	–	7.99	7.85	2.62
											2.39
2-CH_3, 4-Cl	–	–	7.42	7.67	–	–	7.45	7.72	8.08	8.00	2.68
2-CH_3, 5-Cl	–	–	7.63	7.67	7.48	7.57	–	–	8.04	8.00	2.67
											2.47
3-CH_3, 4-Cl	7.89	7.95	–	–	–	–	7.65	7.72	8.01	8.00	2.46
2,4-Cl_2	–	–	7.52	7.82	–	–	7.67	7.82	8.17	8.10	–
3,4-Cl_2	8.17	8.10	–	–	–	–	7.81	7.82	7.97	8.10	–

Table 6. 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

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.

3. Results and Discussion

3.1. Infrared Spectra

The infrared absorption frequencies of the twelve N,N-dichloroarylsulphonamides, are listed in Tables 2 and 3. The general assignments of the important frequencies to various modes are also indicated in the tables. The infrared absorption frequencies of other reported N,N-dichloroarylsulphonamides were also measured under identical conditions and included for comparison.

The assignment of various bands in various compounds has been done in detail in [19, 20]. A table of characteristic group absorptions is also given there. The range of group absorptions has 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.

Comparison of the infrared spectra of the N,N-dichloroarylsulphonamides with the corresponding arylsulphonamides and N-chloroarylsulphonamides revealed that the infrared absorption bands in the ranges, $790-735$ cm^{-1} and $595-546$ cm^{-1} are due to N-Cl asymmetric and symmetric stretching vibrations, respectively. The effect of ring substitution on the N-Cl frequencies is not systematic. The frequencies in the ranges, $1384-1333$ cm^{-1} and $1181-1143$ cm^{-1} are, respectively, assigned to S=O asymmetric and symmetric modes of vibrations. This agrees with the assignments of bands in N-substitutedarylsulphonamides[21]. Similarly, IR bands in the ranges, $910-826$ cm^{-1} and $829-749$ cm^{-1} are assigned to S-N and C-S modes of vibrations, respectively.

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 and not reported here. There is no regular trend in the variation of the frequencies on substitution either with electron-withdrawing or electron-donating groups.

Table 7. The observed and calculated ^{13}C chemical shifts (δ, ppm) of N,N-dichloro-*p*-substituted benzenesulphonamides (4-X, $C_6H_4SO_2NCl_2$).

X	δ (in ppm) C_1		$C_{2,6}$		$C_{3,5}$		C_4		alkyl C
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
H	136.0	–	131.5	–	129.3	–	127.8	–	–
$CHCH_3$	131.4	133.1	126.2	127.7	129.4	130.0	147.8	140.8	21.7
C_2H_5	132.1	133.1	126.9	127.8	129.0	128.8	147.7	147.1	26.4
									15.2
F	134.6	131.5	124.7	128.7	116.9	115.0	167.4	166.6	–
Cl	132.8	134.0	127.6	128.8	129.6	129.5	143.3	137.9	–
Br	132.8	135.0	130.4	130.0	132.2	132.7	128.2	126.1	–

Table 8. The observed and calculated ^{13}C chemical shifts (δ, ppm) of N,N-dichloro-disubstitutedbenzenesulphonamides (*i*-X, *j*-$YC_6H_3SO_2NCl_2$).

i-X, *j*-Y	δ (in ppm) C_1		C_2		C_3		C_4		C_5		C_6		alkyl C
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
2,3-$(CH_3)_2$	138.4	136.6	132.0	137.8	146.7	139.3	130.4	132.1	129.3	126.3	125.7	124.8	20.1
2,4-$(CH_3)_2$	136.8	133.8	138.5	137.0	133.8	130.7	149.4	140.7	127.5	127.1	128.0	129.0	21.3
2,5-$(CH_3)_2$	141.8	136.6	136.0	134.2	129.5	129.9	132.4	132.1	138.6	135.7	128.1	128.4	20.4
													16.5
2-CH_3, 4-Cl	135.0	134.7	143.2	138.1	133.2	130.2	142.6	137.8	127.0	126.6	128.0	128.7	21.0
2-CH_3, 5-Cl	139.7	137.7	137.9	135.1	132.6	131.0	134.4	131.6	135.7	132.8	130.0	127.9	20.4
3-CH_3, 4-Cl	133.2	133.9	131.5	129.5	143.2	138.8	137.9	138.6	129.7	129.4	126.7	125.9	20.3
2,4-Cl_2	136.1	134.2	136.5	135.2	132.9	129.7	143.4	138.9	127.2	127.5	127.9	129.8	–
3,4-Cl_2	132.8	135.0	130.3	129.0	134.2	135.9	141.5	138.1	131.3	130.5	128.2	126.8	–

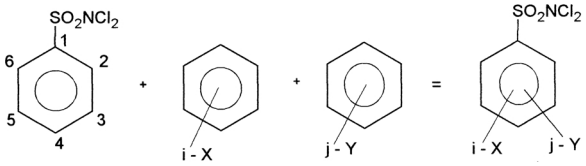
Table 9. Incremental shifts of the aromatic carbon atoms of monosubstituted benzenes (ppm from benzene at 128.5 ppm, +downfield, −upfield).

Sub-stituent	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	–

3.2. ^{1}H and ^{13}C NMR Spectra

The ^{1}H chemical shifts of the twelve N,N-dichloroarylsulphonamides are listed in Tables 4 and 5. The ^{1}H chemical shifts of N,N-dichlorobenzenesulphonamide and N,N-dichloro-4-methylbenzene-sulphonamide reported earlier [18] were also obtained under identical conditions and included in the tables for comparison.

The chemical shift depends on the electron density around the nucleus. Thus the chemical shifts of aromatic protons in all the N,N-dichloroarylsulphonamides 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 that of the benzene proton of 7.27) for different substituents are listed in Table 6 and are used in the calculations. The shifts in aromatic protons due to $-SO_2NCl_2$ were calculated comparing the values of N,N-dichlorobenzenesulphonamide (8.10, 7.82) with those of the benzene proton of 7.27 ppm. The values are $H_o(2,6) = +0.83$ and $H_m(3,4,5) = +0.55$.

The calculated chemical shift for different protons compared with the experimental values are given in Tables 4 and 5. Considering the approximation used, the agreement between the calculated and experimental chemical shifts is reasonably good.

The ^{13}C chemical shifts are tabulated in Tables 7 and 8. Since the chemical shifts of aromatic carbon are also dependent on the electron density around the nucleus, the chemical shifts of aromatic carbons in all the N,N-dichloroarylsulphonamides have been calculated by adding the substituent contributions (Table 9) to the

shift of benzene (128.5 ppm), similar to the procedure employed for aromatic protons. The shifts in aromatic protons due to $-SO_2NCl_2$ were calculated comparing the values of N,N-dichlorobenzenesulphonamide with that of benzene carbon-13 of 128.5 ppm [19, 22]. The values are ^{13}C-1 = +7.473, ^{13}C-4 = +3.022, ^{13}C-3 or 5 = +0.814 and ^{13}C-2 or 6 = −0.656.

The calculated chemical shifts for different aromatic carbons compared with the experimental values are listed in Tables 7 and 8. The agreement between the calculated and experimental chemical shift values is reasonably good. The ^{1}H and ^{13}C chemical shifts are also compared with those of the corresponding arylsulphonamides and sodium salts of N-chloroarylsulphonamides. The effect of substitution in the phenyl ring in terms of electron-withdrawing and electron-donating groups could not be generalised, as the effect is non-systematic.

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