Infrared and NMR (^{1}H & ^{13}C) Spectra of Sodium Salts of N-Bromo-Mono and Di-Substituted-Benzenesulphonamides

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Z. Naturforsch. **58a,** 351 – 356 (2003); received February 26, 2003

Fifteen sodium salts of mono and di-substituted N-bromobenzene-sulphonamides of the configuration, 4-X-$C_6H_4SO_2NaNBr$ (where X = H; CH_3; C_2H_5; F; Cl; Br; or NO_2) and i-X,j-$YC_6H_3SO_2NaNBr$ (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 and characterised by measuring their infrared spectra in the solid state and NMR spectra in solution. The N-Br vibrational frequencies, ν_{N-Br} of N-bromoarylsulphonamides vary in the range, 945 – 925 cm^{-1}, while the N-Cl vibrational frequencies, ν_{N-Cl}, are observed in the range 950 – 927 cm^{-1} for the corresponding N-chloroarylsulphonamides. Asymmetric and symmetric SO_2 stretching vibrations appear in the ranges, 1391 – 1352 cm^{-1} and 1148 – 1131 cm^{-1} for the monosubstituted N-bromoarylsulphonamides, while for the disubstituted N-bromocompounds they absorb in the ranges 1391 – 1331 cm^{-1} and 1149 – 1121 cm^{-1}, respectively. The chemical shifts of aromatic protons and carbon-13 in all the N-bromoarylsulphonamides have been calculated by adding substituent contributions to the shift of benzene and compared with the observed values. The agreement between the calculated and experimental chemical shifts for different protons or carbon-13 is quite good.

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

1. Introduction

The chemistry of sulphonamides is of interest as they show distinct physical, chemical and biological properties. Many arylsulphonamides and their N-halo compounds exhibit pharmacological, fungicidal and herbicidal activities due to their oxidising action in aqueous, partial aqueous and non-aqueous media [1 – 9]. In an effort to introduce N-haloarylsulphonamides of different oxidising strengths, we have recently reported the preparation, spectroscopic and structural studies of several arylsulphonamides, N-chloroarylsulphonamides and N,N-dichloroarylsulphonamides [10 – 13]. The present paper reports the results of infrared and NMR (^{1}H and ^{13}C) spectral studies of fifteen sodium salts of N-bromosubstituted-benzenesulphonamides of the configuration, 4- X-$C_6H_4SO_2NaNBr$ (where X = H; CH_3; C_2H_5; F; Cl; Br or NO_2) and *i*-X, *j*-Y $C_6H_3SO_2NaNBr$ (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).

The N-bromosubstitutedbenzenesulphonamides prepared and studied are:

1. N-Bromobenzenesulphonamide,
2. N-Bromo-4-methylbenzenesulphonamide,
3. N-Bromo-4-ethylbenzenesulphonamide,
4. N-Bromo-4-fluorobenzenesulphonamide,
5. N-Bromo-4-chlorobenzenesulphonamide,
6. N-Bromo-4-bromobenzenesulphonamide,
7. N-Bromo-4-nitrobenzenesulphonamide,
8. N-Bromo-2,3-dimethylbenzenesulphonamide,
9. N-Bromo-2,4-dimethylbenzenesulphonamide,
10. N-Bromo-2,5-dimethylbenzenesulphonamide,
11. N-Bromo-2-methyl-4-chlorobenzene-sulphonamide,
12. N-Bromo-2-methyl-5-chlorobenzene-sulphonamide,
13. N-Bromo-3-methyl-4-chlorobenzene-sulphonamide,
14. N-Bromo-2,4-dichlorobenzenesulphonamide and
15. N-Bromo-3,4-dichlorobenzenesulphonamide.

Table 1. Melting points of mono- and disubstituted benzenesulphonamides and the sodium salts of N-bromosubstitutedbenzene-sulphonamides.

Sl. No	Substituted benzene-sulphonamides	m.p. (°C) obs ([10])	Sodium salts of N-Bromo-substituted benzenesulphonamides	m.p. (°C)
1	4-C_2H_5-$C_6H_4SO_2NH_2$	99 – 101	4-C_2H_5-$C_6H_4SO_2NaNBr.H_2O$	121
2	4-F-$C_6H_4SO_2NH_2$	125 (124 – 125)	4-F$C_6H_4SO_2NaNBr.H_2O$	220
3	4-Cl-$C_6H_4SO_2NH_2$	143 (142 – 143)	4-Cl$C_6H_4SO_2NaNBr.H_2O$	232
4	4-Br-$C_6H_4SO_2NH_2$	162 (161.5)	4-Br$C_6H_4SO_2NaNBr.H_2O$	211
5	4-p-NO_2-$C_6H_4SO_2NH_2$	167 (167)	4-$NO_2C_6H_4SO_2NaNBr.H_2O$	180 – 182
6	2,3-$(CH_3)_2$-$C_6H_3SO_2NH_2$	138 – 140	2,3-$(CH_3)_2$-$C_6H_3SO_2NaNBr.H_2O$	170
7	2,4-$(CH_3)_2$-$C_6H_3SO_2NH_2$	140 – 142	2,4-$(CH_3)_2$-$C_6H_3SO_2NaNBr.H_2O$	175
8	2,5-$(CH_3)_2$-$C_6H_3SO_2NH_2$	149 – 151	2,5-$(CH_3)_2$-$C_6H_3SO_2NaNBr.H_2O$	135
9	2-CH_3,4-Cl-$C_6H_3SO_2NH_2$	158 – 160 (184 – 185)	2-CH_3,4-Cl-$C_6H_3SO_2NaNBr.H_2O$	158 – 160
10	2-CH_3,5-Cl-$C_6H_3SO_2NH_2$	139 – 141 (142 – 143)	2-CH_3,5-Cl-$C_6H_3SO_2NaNBr.H_2O$	147 – 150
11	3-CH_3,4-Cl-$C_6H_3SO_2NH_2$	132 – 134 (126)	3-CH_3,4-Cl-$C_6H_3SO_2NaNBr.H_2O$	145
12	2,4-Cl_2-$C_6H_3SO_2NH_2$	178 – 180 (179-180)	2,4-Cl_2-$C_6H_3SO_2NaNBr.H_2O$	210
15	3,4-Cl_2-$C_6H_3SO_2NH_2$	141 – 143 (134-135)	3,4-Cl_2-$C_6H_3SO_2NaNBr.H_2O$	182

Table 2. Infrared absorption frequencies (cm^{-1}) of sodium salts of N-bromo-monosubstituted benzene-sulphonamides).

s = strong, m = medium and w = weak.

Assignments	4-X-$C_6H_4SO_2NaNBr.H_2O$, where X =						
	H	CH_3	C_2H_5	F	Cl	Br	NO_2
C-H (Ar sym str)	3056.0w	3256.2w	2965.0w	3059.5w	3090.3w	3090.3w	3095.1w
C-H (Alk str)		– 2847.8w	2915.2w	2929.3w	–	–	2360.4w
Combination bands	–	1913.6w	–	1907.2w	1907.2w	1733.0w	–
C=C (Ar in plane str)	1638.0w 1444.0m	1645.9w 1599.2w 1492.2m	1642.0w 1597.7w 1493.6m	1641.1m 1594.8s 1494.5s	1645.9m 1584.2m 1476.2s	1646.9w 1575.9w 1472.3w	1640.1w 1530.2w 1430.9w
S=O (Asym str)	–	–	1385.6s	1383.0s	1391.3m	1385.6s	1352.8s
(Sym str)	1137.0s	1131.0s	1136.8s	1136.8s	1136.8s	1132.9s	1148.4s
C-H (Ar in plane bend)	1246.2s 1090.0s 1020.0w	1244.0s 1082.5s 1017.5w	1243.8s 1091.5s 1011.6w	1243.8s 1089.5s 1012.0w	1244.8s 1089.8s 1014.2w	1243.8s 1087.6s 1011.2w	1247.7s 1115.6s 1068.3s
C-X(str)	–	–	–	1291.4s	1014.0s	593.2s	–
N-Br(str)	933.3s	925.6s	940.1s	934.3s	941.0s	941.0s	944.9s
S-N (sym str)	756.0s	808.8s	822.0s	831.1s	824.2s	822.0s	874.5s
C-S(str)	717.0m	675.6s	739.5s	680.0m	753.3s	739.3s	735.7w
C-H (Ar out of plane bend)	686.4m	626.7m	656.6m	634.5s	659.4s	655.3s	666.2s
C=C (Ar out of plane bend)	449.0m	465.7m	460.9m	457.0w	456.m	419.4m	460.9w

2. Experimental

2.1. Materials and Methods

Preparation of sodium salts of N-bromoarylsulphonamides

The arylsulphonamides were prepared by the chlorosulphonation of substituted benzenes to the respective sulphonylchlorides and subsequent treatment of the latter with concentrated ammonium hydroxide by the procedures reported in [10 – 17]. The

Table 3. Infrared absorption frequencies (cm^{-1}) of sodium salts of N-bromo-disubstituted benzenesulphonamides.

s = strong, m = medium and w = weak.

Assignments	i-X,j-Y-$C_6H_3SO_2NaNBr.H_2O$, 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	3-CH_3, 4-Cl	2-CH_3, 5-Cl	2,4-Cl_2	3,4-Cl_2
C-H (Ar sym str)	3021.9w	3090.3w	3065.3w	3101.9w	3077.8w	3090.3w	3097.1w	3097.1w
C-H (Alk str)	2972.7w 2920.6w	2928.3w 2859.9w	2978.5w 2924.1w	2987.2w 2928.3w	2928.4w 2854.1w	2984.3w	–	–
Combination Bands	1730.8w	–	–	1931.3w 1714.4w	–	–	–	–
C=C (Ar in plane str)	1637.2w 1449.2s	1645.9m 1476.2s	1637.2w 1484.9m 1450.2w 1447.3s	1635.4m 1558.2s 1466.6m	1637.3w 1466.6m 1447.3m	1638.2w 1560.1w 1465.6s 1454.0s	1633.4m 1573.6s 1555.3s	1638.2w 1453.1w
S=O (Asym str)	1330.6s	1391.3m	–	1382.7m	1383.6w	1381.7w	1369.2s	1370.1w
(Sym str)	1122.3s	1135.8s	1121.4s	1137.8s	1128.5s	1123.3s	1133.9s	1149.3s
C-H (Ar in plane	1243.8s 1089.5s	1244.8s 1089.5s	1236.1s 1064.5s	1237.1s 1099.2s	1243.6s 1095.3s	1240.9s 1058.7s	1240.9s 1098.2s	1240.1m 1094.4s
C-X(str)	–	–	–	1054.8s	1050.0s	-	1040.4s	1033.6
N-Br(str)	940.1s	941.0s	935.3s	929.5s	942.0s	935.3s	936.2s	936.1s
S-N (sym str)	833.1w	824.4w	813.8s	832.1s	833.1s	833.1s	827.3s	830.2m
C-S(str)	703.8w	753.0w	700.0w	706.7s	705.0m	702.9w	678.8m	678.7m
C-H (Ar out of bend)	675.9s 585.2s	658.5s 559.2s	649.8w 598.7s	654.7s 571.7s	660.5s 582.4m	647.9s 585.2	652.7s 573.7s	660.5w5 87.2s
C=C (Ar out of plane bend)	442.5w	479.2w	465.7	460.9s	465.0w	444.5w	494.6m	448.3m

Table 4. ^1H NMR observed and calculated δ (ppm) values of sodium salts of N-bromo-monosubstituted benzenesulphonamides.

i-X-$C_6H_4SO_2$ $NaNBr.H_2O$ where i-X =	δ values (in ppm)				
	H_o (2,6)		H_m (3,5)		Alkyl H
	Obs.	Calc.	Obs.	Calc.	
Parent	8.10(s)	–	7.71(s)	–	–
4-CH_3	8.16(d)	8.00	7.62(d)	7.57	2.72(s) 2.67(d)
4-C_2H_5	7.88(d)	8.00	7.41(d)	7.56	1.23(s)
4-F	8.11(s)	8.12	8.01(s)	7.48	–
4-Cl	7.96(s)	8.10	7.60(s)	7.71*	
4-Br	8.06(d)	8.10	7.90(d)	7.71*	

s = singlet, d = doublet, t = triplet and m = multiplet. * The signal at 7.71 integrates for 3 protons corresponding to 3, 4, 5.

sulphonamides were recrystallised to their constant melting point (Table 1) from dilute ethanol and dried at 105 °C. The purity of all the compounds was checked by recording their infrared spectra. The sulphonamides were then N- chlorinated to obtain sodium salts of N-chloro-arylsulphonamides [11]. Pure chlorine gas was bubbled through solutions of substituted benzenesulphonamides in 4 mol dm^{-3} NaOH at 70 °C for about 1 h. The precipitated sodium salts of N-chloro-substituted benzenesulphonamides (CASB) were filtered, washed, dried and recrystallised from water. The purity of all the reagents was checked by determining the melting points and estimation of the amounts of active chlorine present in them [11, 18].

The N-bromosubstituted benzensulphonamides were prepared by partial debromination of N,N-dibromosubstituted benzenesulphonamides. The latter were obtained by the bromination of aqueous solution of N-chloro-substituted benzenesulphonamides. About 4 cm^3 of liquid bromine was added dropwise from a microburette to a solution of about 20 gm

Table 5. ^{1}H NMR observed and calculated δ (ppm) values of sodium salts of N-bromo-disubstituted benzenesulphonamides.

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

i-X, *j*-Y-$C_6H_3SO_2$-NaNBr.H_2O where i-X, j-Y =	δ values (in ppm) 2-H		3-H		4-H		5-H		6-H		alkyl H
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
2,3-$(CH_3)_2$	–	–	–	–	7.10d	7.02	7.12d	7.07	7.46d	7.90	1.99 2.10
2,4-$(CH_3)_2$	–	–	7.54d	7.56	–	–	7.41d	7.46	7.94s	7.90	1.84 2.14
2,5-$(CH_3)_2$	–	–	7.36s	7.46	7.32s	7.22	–	–	7.91s	7.85	2.46 2.73
2-CH_3, 4-Cl	–	–	7.71s	7.56	–	–	7.73s	7.61	8.26d	8.00	3.01
2-CH_3, 5-Cl	–	–	7.64t	7.56	7.53d	7.17	–	–	8.15d	8.00	2.61 2.85
3-CH_3, 4-Cl	7.82t	7.95	–	–	–	–	7.50m	7.61	8.02s	8.00	2.49
2,4-Cl_2	–	–	7.94s	7.71	–	–	7.79s	7.71	8.44s	8.10	–
3,4-Cl_2	8.16s	8.10	–	–	–	–	7.92d	7.71	7.75d	7.71	–

of N-chloro-substituted benzenesulphonamides in 400 cm^3 water, with constant stirring of the solution at room temperature. N,N-dibromosubstituted benzenesulphonamides separated out were filtered under suction, washed thoroughly with water until all the bromine adsorbed on the compound was completely eliminated and then dried in a vacuum desiccator for 24 h. N-bromosubstituted benzenesulphonamides were then obtained by dissolving N,N-dibromosubstituted benzenesulphonamides in 4 mol dm^{-3} NaOH. About 20 g of each N,N-dibromosubstituted benzenesulphonamide were dissolved with stirring in 30 cm^3 of 4 mol dm^{-3} NaOH at room temperature. The resultant aqueous solution was cooled in ice. The pale yellow crystals of the N-bromosubstituted benzenesulphonamides were filtered under suction, washed quickly with a minimum of ice cold water and dried over phosphorus pentoxide. The purity of all N-bromosubstituted benzenesulphonamides was checked by determining the melting points (Table 1) and estimating the amounts of active bromine present in them.

2.2. Spectral Measurements

Infrared spectral measurements were made on a JASCO FT-IR-430 spectrophotometer (Japan). 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).

The proton NMR spectra of the compounds were measured on a BRUKER Ac 300F, 300 MHz FT-NMR spectrometer, in D_2O with tetramethylsilane (Me_4Si) as internal standard. The experimental conditions 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 s, acquisition time (AQ) 1.360 s, receiver gain (RG) 10, decoupling power (DP) 63L CPD, filter to suppress noise(LB) 0.0. The reference value (SR) was set at 4125.36 ppm for H_2O internally.

Carbon-13 NMR spectra of the compounds were measured in D_2O. Tetramethylsilane was used as the external reference standard. The following experimen-

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

Substituent	Ortho	Meta	Para
CH_3	−0.15	−0.1	−0.1
COOH	+0.8	+0.15	+0.2
$COOCH_3$	+0.8	+0.15	+0.2
CN	+0.3	+0.3	+0.3
$CONH_2$	+0.5	+0.2	+0.2
-COR	+0.6	+0.3	+0.3
SR	+0.1	−0.1	−0.2
NH_2	−0.8	−0.15	−0.4
I	+0.3	−0.2	−0.1
Br	0.0	0.0	0.0
Cl	0.0	0.0	0.0
F	0.30	0.02	0.22
CHO	+0.7	+0.2	+0.4
NHCOR	+0.4	−0.2	−0.3
NO_2	+1.0	+0.3	+0.4
OH	−0.4	−0.4	−0.4
OCH_3	−0.2	−0.2	−0.2
$OCOCH_3$	+0.2	−0.1	−0.2
SO_3H	+0.4	+0.1	+0.4

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

i-X-$C_6H_4SO_2$–NaNBr.H_2O where i-X =	δ values (in ppm)								
	C_1		$C_{2,6}$		$C_{3,5}$		C_4		Alkyl C
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
Parent	143.0	–	128.9	–	130.8	–	133.7	–	–
4-CH_3	139.9	140.1	127.0	127.9	131.3	131.3	144.9	143.0	22.6 29.7
4-C_2H_5	139.6	140.4	126.7	126.9	129.7	130.1	150.3	149.3	16.2
4-F	139.5	138.5	131.7	129.8	117.6	116.3	167.6	168.8	–
4-Cl	142.0	141.0	130.4	129.1	130.8	130.8	139.1	140.1	–
4-Br	142.3	142.9	130.6	131.1	133.6	134.0	127.6	128.3	–

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

i-X, *j*-Y-$C_6H_3SO_2$-NaNBr.H_2O where *i*-X, *j*-Y =	δ values (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-$(CH_3)_2$	143.0	143.6	139.2	138.9	139.2	140.6	131.2	134.3	129.0	127.6	125.6	125.9	20.4
2,4-$(CH_3)_2$	140.6	139.4	138.4	138.1	132.7	132.0	140.6	142.9	130.6	128.4	130.6	128.7	20.9
2,5-$(CH_3)_2$	137.2	142.3	135.2	135.3	131.2	131.2	134.0	134.3	137.2	137.0	–	129.5	21.5 20.6
2-CH_3, 4-Cl	141.4	141.7	138.6	139.2	133.8	131.5	138.2	140.0	127.5	127.9	133.1	129.8	21.6
2-CH_3, 5-Cl	137.7	144.7	135.7	136.2	132.5	132.3	133.2	133.8	135.4	134.1	130.7	129.0	21.5
3-CH_3, 4-Cl	141.6	140.9	129.3	130.6	138.7	140.8	139.3	140.8	131.3	130.7	127.7	127.0	21.5
2,4-Cl_2	139.5	141.2	134.5	136.3	133.2	131.0	139.5	141.1	129.0	128.8	129.0	130.9	–
3,4-Cl_2	143.5	142.0	130.9	130.1	134.3	137.2	137.2	140.3	132.7	131.8	128.6	127.9	–

tal 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 s, acquisition time (AQ) was 0.360 s, receiver gain (RG) 400, decoupling power (DP) 14H CPD, filter to suppress noise(LB) 6.0, reference value (SR) 701.89 ppm for DMSO at 39.5 ppm externally.

3. Results and Discussion

3.1. Infrared Spectra

The selected infrared absorption frequencies of the studied salts are shown in Tables 2 and 3. The assignment of various frequencies to different modes of vibrations are indicated in the tables. The N-Br vibrational frequencies, ν_{N-Br}, of the N-bromoarylsulphonamides vary in the range 945 – 925 cm^{-1} in comparison with the N-Cl vibrational frequencies, ν_{N-Cl}, observed in the range of 950 – 927 cm^{-1} for the corresponding N-chloroarylsulphonamides. The asymmetric and symmetric SO_2 stretching vibrations appear in the ranges 1391 – 1352 cm^{-1} and 1148 – 1131 cm^{-1} for the monosubstituted N-bromo-arylsulphonamides and 1391 – 1331 cm^{-1} and 1149 – 1121 cm^{-1} for the disubstituted N- bromocompounds. These stretching vibrations for the N-chloroarylsulphonamides appear in the ranges 1388 – 1303 cm^{-1} and 1150 – 1132 cm^{-1} for the monosubstituted compounds, and 1390 – 1370 cm^{-1} and 1190 – 1130 cm^{-1} for the disubstituted N-chloroarylsulphonamides [11]. The ranges reported for the non-halogenated compounds

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

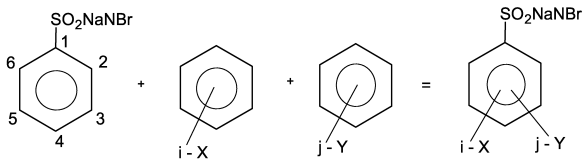
Substituent	C-1 (Att.)	C-2	C-3	C-4	C of substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	–
CH_3	+9.3	+0.7	−0.1	2.9	21.3
CH_2CH_3	+15.6	0.5	0.0	2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	2.0	0.0	2.5	34.4 (CH), 24.1 (CH_3)
C_6H_5	+12.1	−1.8	−0.1	−1.6	–
OH	+26.6	−12.7	+1.6	−7.3	
OCH_3	+31.4	−14.4	+1.0	−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	–

are 1389 – 1327 cm^{-1} and 1187 – 1147 cm^{-1}, respectively [10].

The assignment of other frequencies to various modes of vibrations of the ring (Tables 2 and 3) are similar to those in arylsulphonamides [10], N-chloroarylsulphonamides [11] and other aromatic organic compounds [19, 20]. The precise frequency or wavelength at which a specific group absorbs is dependent on its electron environment within the molecule and on its physical state.

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

^{1}H NMR Spectra: The ^{1}H chemical shift values of N-bromoarylsulphonamides are shown in Tables 4 and 5. Since the chemical shift is dependent on the electron density around the nucleus or associated with the atom to which it is bonded, the chemical shifts of aromatic protons in all the N-bromoarylsulphonamides 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_2NaNBr were calculated, comparing the values of the sodium salt of N- bromobenzenesulphonamide (8.10, 7.71) with those of the benzene proton value 7.27 ppm. The values are H_o(2,6) = +0.83 and H_m(3,4,5) = +0.44. The calculated chemical shifts for different protons are shown in Tables 4 and 5. There is good agreement between the calculated and experimental chemical shifts.

^{13}C NMR Spectra: The ^{13}C chemical shifts of sodium salts of N-bromo-substituted benzenesulphonamides are shown in Tables 7 and 8. The chemical shifts of the aromatic carbon-13 in all the N-bromoarylsulphonamides have also been calculated by adding the substituent contribution to the shift of benzene (128.5 ppm), similar to the procedure employed with aromatic protons. These incremental shifts for different substituents [19, 21] are shown in Table 9 and used in the calculation. The shifts in aromatic protons due to -SO_2NaNBr were calculated comparing the values of the sodium salt of N-bromobenzenesulphonamide with those of the benzene carbon-13 value of 128.5 ppm. The values are ^{13}C-1 = +12.89, ^{13}C-4 = +5.22, ^{13}C-2 or 6 = −1.99 and ^{13}C-3 or 5 = +2.03. The calculated chemical shifts for different aromatic carbons are also shown in Tables 7 and 8. The agreement between the calculated and experimental chemical shifts is quite good.

[1] B. T. Gowda and D. S. Mahadevappa, Talanta **30**, 359 (1983).
[2] B. T. Gowda and D. S. Mahadevappa, J. Chem. Soc., Perkin Trans. **2**, 323 (1983).
[3] B. T. Gowda, B. S. Sherigara, and D. S. Mahadevappa, Microchem. J. **34**, 103 (1986).
[4] B. T. Gowda and J. I. Bhat, Tetrahedron **43**, 2119 (1987).
[5] B. T. Gowda and R. V. Rao, J. Chem. Soc., Perkin Trans. **2**, 355 (1988).
[6] B. T. Gowda and B. S. Sherigara, Int. J. Chem. Kinet. **21**, 31 (1989).
[7] B. T. Gowda and P. Ramachandra, J. Chem. Soc., Perkin Trans. **2**, 1067 (1989).
[8] B. T. Gowda and B. H. A. Kumar, Indian J. Chem. **42A**, xxx (2003).
[9] B. T. Gowda, J. D. D'Souza, and K. R. Bhat, J. Indian Chem. Soc. **78**, 412 (2002).
[10] B. T. Gowda, K. Jyothi and J. D. D'Souza, Z. Naturforsch. **57a**, 967 (2002).
[11] B. T. Gowda, J. D. D'Souza, and B. H. A. Kumar, Z. Naturforsch. **58a**, 51 (2003).
[12] B. T. Gowda, K. Jyothi and N. Damodara, Z. Naturforsch. **58a** (2003), in press.
[13] B. T. Gowda, K. Jyothi, J. Kožıšek, and H. Fuess, Z. Naturforsch. **58a** (2003), in press.
[14] F. D. Chattway, J. Chem. Soc. **87**, 145 (1905).
[15] H. D. Dakin, J. B. Cohen, M. Dufrence, and Kenyon, J. Proc. Roy. Soc. (B) **89**, 232 (1917).
[16] A. I. Vogel, Quantitative Organic Analysis; Longman, London 1958.
[17] R. B. Baxter and F. D. Chattway, J. Chem. Soc. **107**, 1814 (1915).
[18] B. T. Gowda and D. S. Mahadevappa, Microchem. J. **28**, 374 (1983).
[19] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, Spectrometric Identification of Organic Compounds; John Wiley and Sons, New York 1991.
[20] W. Kemp, Organic Spectroscopy; MacMillan, London 1996.
[21] D. E. Ewing, Org. Magn. Reson. **12**, 499 (1979).