Infrared and NMR Spectra of Arylsulphonamides, 4-X-$C_6H_4SO_2NH_2$ and *i*-X, *j*-$YC_6H_3SO_2NH_2$ (X = H; CH_3; C_2H_5; F; Cl; Br; I or NO_2 and *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 arylsulphonamides of the configuration, 4-X-$C_6H_4SO_2NH_2$ (where X = H; CH_3; C_2H_5; F; Cl; Br; I or NO_2) and *i*-X, *j*-$YC_6H_3SO_2NH_2$ (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) were prepared, and their infrared spectra were measured in the solid state. The NMR spectra were recorded in solution. N–H asymmetric and symmetric stretching vibrations absorb in the ranges, 3390 – 3323 cm^{-1} and 3279 – 3229 cm^{-1}, respectively. Asymmetric and symmetric SO_2 stretching vibrations appear as strong absorption lines in the ranges, 1344 – 1317 cm^{-1} and 1187 – 1147 cm^{-1}, respectively. Sulphonamides exhibit S–N stretching vibrational absorptions in the range, 924 – 906 cm^{-1}. 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. The chemical shift is highly 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 have been discussed. The chemical shifts of aromatic protons and carbons in all the arylsulphonamides have been calculated by adding substituent contributions to the shift of benzene, the principle of substituent addition. Considering the approximation made, the agreement between the calculated and experimental chemical shift values is reasonably good. Generally, electron-withdrawing groups shows high chemical shifts compared to electron-donating groups.

Key words: Infrared; Nuclear Magnetic Resonance; Arylsulphonamides.

Introduction

The amide moiety is an important constituent of many biologically significant compounds. Thus an understanding of the formation, properties and reactions of amides is central to future development in such areas as polypeptide and protein chemistry [1 – 2]. Sulphonamides are of fundamental chemical interest as they show distinct physical, chemical and biological properties. Many sulphonamides and their N-chlorocompounds exhibit pharmacological activity, which has further stimulated recent interest in their chemistry. Many sulphonamides and their N-chlorocompounds exhibit fungicidal and herbicidal activities, because of their oxidizing action in aqueous, partial aqueous and non-aqueous media. A great deal of work on the spectroscopic aspects of amides needs to be done for correlating frequencies with the chemical bond parameters. Thus we are interested in the spectroscopic studies of amides in their crystalline state [3 – 10].

We report herein the infrared and NMR spectra of arylsulphonamides of the configuration, 4-X-$C_6H_4SO_2NH_2$ (where X = H; CH_3; C_2H_5; F; Cl; Br; I or NO_2) and *i*-X, *j*-$YC_6H_3SO_2NH_2$ (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 benzenesulphonamide, 4-methylbenzenesulphonamide, 4-ethylbenzenesulphonamide, 4-fluorobenzenesulphonamide, 4-chlorobenzenesulphonamide, 4-bromobenzenesulphonamide, 4-iodobenzenesulphonamide, 4-nitrobenzenesulphonamide, 2,3-dimethylbenzenesulphonamide, 2,4-dimethylbenzenesulphonamide, 2,5-dimethylbenzenesulphonamide, 2-methyl-4-chlorobenzenesulphonamide, 2-methyl-5-chlorobenzenesulphonamide, 3-methyl-4-chlorobenzenesulphonamide, 2,4-dichlorobenzenesulphonamide and 3,4-dichlorobenzenesulphonamide.

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Table 1. Melting points of arylsulphonamides; [a][11], [12].

Sl. No	Arylsulphonamides	m.p. (°C) obs (lit[a])
1	$4\text{-}C_2H_5C_6H_4SO_2NH_2$	99 – 101
2	$4\text{-}FC_6H_4SO_2NH_2$	125 (124 – 125)
3	$4\text{-}ClC_6H_4SO_2NH_2$	143 (142 – 143)
4	$4\text{-}BrC_6H_4SO_2NH_2$	162 (161.5)
5	$2,3\text{-}(CH_3)_2C_6H_3SO_2NH_2$	138 – 140
6	$2,4\text{-}(CH_3)_2C_6H_3SO_2NH_2$	140 – 142
7	$2,5\text{-}(CH_3)_2C_6H_3SO_2NH_2$	149 – 151
8	$2\text{-}CH_3,4\text{-}ClC_6H_3SO_2NH_2$	180 – 182 (184 – 185)
9	$2\text{-}CH_3,5\text{-}ClC_6H_3SO_2NH_2$	139 – 141 (142 – 143)
10	$3\text{-}CH_3,4\text{-}ClC_6H_3SO_2NH_2$	132 – 134 (126)
11	$2,4\text{-}Cl_2C_6H_3SO_2NH_2$	178 – 180 (179 – 180)
12	$3,4\text{-}Cl_2C_6H_3SO_2NH_2$	141 – 143 (134 – 135)

Experimental

Materials and Methods

Arylsulphonamides were prepared in two steps:

(i) chlorosulphonation of substituted benzenes,

(ii) conversion of arylsulphonylchlorides to amides.

(i) Chlorosulphonation of substituted benzene 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. After about 20 min, the contents were poured into crushed ice in a beaker. The chloroform layer was separated, washed with cold water and evaporated. The residual crude arylsulphonylchloride was then recrystallised from a

Table 2. Infrared spectral frequencies (cm^{-1}) of monosubstituted benzenesulphonamides.

Assignment	$i\text{-}X\text{-}C_6H_4SO_2NH_2$, $i\text{-}X =$							
	H	$4\text{-}CH_3$	$4\text{-}C_2H_5$	4-F	4-Cl	4-Br	4-I	$4\text{-}NO_2$
N–H (asym str)	3349.7 s	3327.6 s	3338.1 s	3361.3 s	3352.6 s	3329.5 s	3361.3 s	3344.9 s
(sym str)	3247.5 s	3242.7 s	3259.1 s	3261.0 s	3265.8 s	3239.8 s	3256.2 s	3263.9 s
C–H (Ar sym str)	3073.9 w	3030.2 w	3053.7 m	374.9 w	3094.2 w	3020.9 w	3074.9 w	3093.2 m
C–H		2924.9 w	2962.3 m					
(alk str)	–		2930.2 m	–	–	–	–	–
combination bands	1980.5 w	1917.7 w	1912.8 w	1912.4 w	1912.5 w	1912.7 w	1912.2 w	1937.4 w
	1906.3 w	1799.4 w	1799.9 w	1780.2 w	1774.3 w	1774.3 w		1824.3 w
	1768.5 w							
C=C	1683.5 w	1596.7 s	1597.7 s	1587.1 s	1583.2 s	1574.5 s	1571.7 m	1607.3 m
(Ar in-plane str)								
	1558.2 m	1575.5 m	1543.7 s	1493.6 s	1474.3 s	1469.4 s	1514.8 s	1531.2 s
	1541.8 m	1496.4 w	1463.7 s	1408.7 m	1396.2 s	1390.4 s	1471.4 m	1352.8 s
	1474.3 w	1402.0 w	1407.7 s					
S=O (asym str)	1335.5 s	1326.8 s	1327.7 s	1331.6 s	1328.7 s	1327.7 s	1344.0 s	1334.5 s
(sym str)	1157.0 s	1152.2 s	1178.2 s	1150.3 s	1157.0 s	1147.4 s	1157.0 s	1186.9 s
C–H (Ar in-plane bend)	1090.5 m	1094.4 s	1097.3 s	1092.4 s	1088.6 s	1091.5 s	1093.0 s	1085.7 m
	1024.0 w	1016.3 w	1059.6 s	1013.4 m	1068.5 s	1010.5 s	1006.6 s	
S–N (sym str)	905.5 s	907.3 s	947.3 w	914.0 s	913.1 w	910.2 s	923.7 s	907.3 m
C–H (Ar out of-plane bend)	756.9 m	808.9 s	787.7 s	840.8 s	766.5 s	818.6 s	816.7 s	760.7 m
	687.5 m	669.1 s	676.8 s	814.7 m	746.3 m	741.5 s	730.9 s	738.6 m
C–X (str)	–	–	–	1238.1 s	1009.5 s	518.4 s	533.2 s	–
C=C (Ar out of-plane bend)	426.6 m	427.2 m	–	485.3 m	453.2 m	419.4 m	421.4 m	455.1 m

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

sulphonic solvent (chloroform, ethanol or petroleum ether) and dried in vacuum over conc. H_2SO_4.

(ii) Conversion of arylsulphonyl chloride to sulphonamide

The prepared arylsulphonyl chloride (10 g) was boiled for ten minutes with concentrated ammonium hydroxide (100 cc, sp. gr. 0.90). It was cooled to room temperature and added to ice cold water (100 cc). The resultant solid sulphonamide was filtered under suction and thoroughly washed with cold water. It was then recrystallised to constant melting point from dilute ethanol and dried at 105 °C. The purity of all the reagents was checked by determining the melting points (Table 1) [11, 12].

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 was measured in the solid state as pressed KBr pellets (13 mm).

Results and Discussion

Infrared Spectra

The infrared absorption frequencies of nine arylsulphonamides, 4-ethylbenzenesulphonamide, 2,3-dimethylbenzenesulphonamide, 2,4-dimethylbenzenesulphonamide, 2,5-dimethylbenzenesulphonamide, 2-methyl-4-chlorobenzenesulphonamide, 2-methyl-5-chlorobenzenesulphonamide, 3-methyl-4-chlorobenzenesulphonamide, 2,4-dichlorobenzenesulphonamide and 3,4-dichlorobenzenesulphonamide are shown in Tables 2 and 3. The general assignments of the important frequencies to various

Table 3. Infrared spectral frequencies (cm^{-1}) of disubstituted benzenesulphonamides.

Assignment	i-X,j-Y-$C_6H_4SO_2NH_2$, 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
N–H								
(asym str)	3337.2 s	3366.1 s	3390.2 s	3360.3 s	3386.3 s	3322.7 s	3363.2 s	3322.7 s
(sym str)	3243.6 s	3261.0 s	3279.3 s	3252.3 s	3274.5 s	3229.2 s	3254.2 s	3229.2 s
C–H								
(Ar sym str)	3110.6 m	3110.6 m	3103.8 m	3105.8 w	3097.1 m	3074.9 m	3094.2 m	3087.4 m
C–H								
(alk str)	2980.0 m	2967.0 m	2974.2 w	2967.1 w	2967.2 w	2992.0 w	–	–
	2949.0 m	2924.2 w	2924.0 w	2924.2 w	2992.3 w	2949.0 w		
		2861.0 w	2868.3 w			2918.2 w		
combination bands	1968.3 w	1924.5 w	1937.4 w	1786.8 w	1917.0 w	1899.3 w	1917.0 w	1905.1 w
	1912.3 w	1780.8 w	1861.3 w	1912.2 w	1856.3 w	1774.2 w	1780.0 w	1767.2 w
	1774.2 w		1793.3 w		1780.2 w			
C=C		1602.5 s		1664.2 m				
(Ar in-plane str)	1566.8 s	1565.9 s	1563.9 s	1559.1 s	1561.0 s	1554.3 s	1554.3 s	1553.3 s
	1487.8 s	1480.1 s	1491.6 s	1466.6	1463.7 s	1473.3 s	1455.9 s	1455.9 s
	1448.2 s	1446.3 m	1453.1 s				1438.6 m	
S=O								
(asym str)	1330.6 s	1317.1 s	1323.9 s	1322.9 s	1333.5 s	1332.6 s	1338.3 s	1334.5 s
(sym str)	1159.0 s	1172.5 s	1154.1 s	1153.2 s	1157.0 s	1159.0 s	1159.0 s	1164.7 s
C–H								
(Ar in-plane bend)	1094.4 s	1133.9 s	1065.4 m	1105.0 m	1108.8 s	1103.0 s	1103.0 s	1102.2 s
S–N								
(sym str)	923.7 s	932.4 s	919.8 s	919.8 m	921.8 s	915.0 s	923.7 s	909.2 s
C–H								
(Ar out of-plane bend)	824.4 s	823.4 s	827.3 s	876.5 m	826.3 s	887.1 s	867.8 s	884.2 s
	704.4 s	661.4 s	799.0 s	825.4 m	717.4 m	721.5 s	819.6 s	820.5 s
C–X								
(str)	–	–	–	1059.6 s	1064.5 s	1048.1 s	1042.3 s	1031.7 s
C=C								
(Ar out of-plane bend)	431.0 m	468.3 m	436.7 m	456.2 m	480.2 m	434.9 m	436.7 w	442.8 s

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

Table 4. The observed and calculated ^{1}H chemical shifts (δ, ppm) of *p*-substituted benzenesulphonamides (4-$XC_6H_4SO_2NH_2$).

X	δ (in ppm)				
	$H_o(2,6)$		$H_m(3,5)$		alkyl H
	Obs.	Calc.	Obs.	Calc.	
H	7.87 m	–	7.46 m	–	–
CH_3	7.73 m	7.57	7.22 d	7.52	2.34 s
C_2H_5	7.77 d	7.57	7.24 d	7.52	2.63 m 1.17 m
F	7.90 m	7.65	7.14 m	7.67	–
Cl	7.83 m	7.67	7.45 m	7.37	–
Br	7.80 m	7.67	7.67 m	7.37	–
I	7.60 t	7.47	7.83 m	7.67	–
NO_2	7.81 t	7.77	8.34 d	8.37	–

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

Table 5. The observed and calculated ^{1}H chemical shifts (δ, ppm) of di-substituted benzenesulphonamides (*i*-X, *j*-$YC_6H_3SO_2NH_2$).

	δ (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-$(CH_3)_2$	–	–	–	–	7.16	7.12	7.56	7.17	7.63	7.47	2.25
2,4-$(CH_3)_2$	–	–	7.07	7.07	–	–	7.23	7.12	7.76	7.47	2.60 2.33
2,5-$(CH_3)_2$	–	–	7.15	7.12	7.15	7.12	–	–	7.72	7.42	2.55 2.29
2-CH_3, 4-Cl	–	–	7.15	7.22	–	–	7.23	7.27	7.87	7.57	2.48
2-CH_3, 5-Cl	–	–	7.28	7.22	7.39	7.27	–	–	7.87	7.57	2.59 2.34
3-CH_3, 4-Cl	7.47	7.52	–	–	–	–	7.26	7.27	7.77	7.57	2.37
2,4-Cl_2	–	–	7.36	7.37	–	–	7.49	7.37	7.99	7.67	–
3,4-Cl_2	7.28	7.37	–	–	–	–	7.62	7.37	7.77	7.67	–

modes are indicated in the tables. The infrared absorption frequencies of other reported arylsulphonamides were also measured under identical conditions and included in the tables for comparison.

The assignment of various bands in various compounds, in general, has been reported in detail elsewhere [13, 14]. 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.

N–H asymmetric and symmetric stretching vibrations absorb in the ranges, 3390 – 3323 cm^{-1} and 3279 – 3229 cm^{-1}, respectively. These conform with the values of about 3350 and 3250 cm^{-1} reported for p-toluenesulphonamide (PTS) [13]. Asymmetric and symmetric SO_2 stretching vibrations appear as strong absorptions in the ranges, 1344 – 1317 cm^{-1} and 1187 – 1147 cm^{-1}, respectively. The values reported for (PTS) [13] are about 1330 cm^{-1} and 1160 cm^{-1}, respectively. Sulphonamides exhibit S–N stretching vibrational absorptions in the range, 924 – 906 cm^{-1}, with the exception of 4-ethylbenzenesulphonamide which showed absorptions at 947.3 cm^{-1}. The other frequencies are assigned to various other vibrations of the ring (Tables 2 and 3). The discussions are similar to the other organic aromatic compounds in general.

Line diagrams are drawn to illustrate the effect of substitution in the benzene ring on the $\nu_{N-H(asym)}$,

Table 6. Shifts in the position of benzene protons (δ 7.27) caused by the substituents.

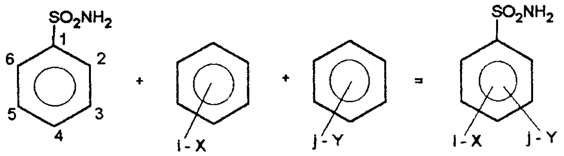
Substituent	ortho	meta	para
$-CH_3$, $-R$	-0.15	-0.10	-0.10
$-COOH$, $-COOR$	$+0.80$	$+0.15$	$+0.20$
$-CN$	$+0.30$	$+0.30$	$+0.30$
$-CONH_2$	$+0.50$	$+0.20$	$+0.20$
$-COR$	$+0.60$	$+0.30$	$+0.30$
$-SR$	$+0.10$	-0.10	-0.20
$-NH_2$, $-NHR$	-0.80	-0.15	-0.40
$-N(CH_3)_2$	-0.50	-0.20	-0.50
$-I$	$+0.30$	-0.20	-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
$-NO_2$	$+1.00$	$+0.30$	$+0.40$
$-SO_3H$, $-SO_2NH_2$	$+0.40$	$+0.10$	$+0.10$

$\nu_{N-H(sym)}$, $\nu_{S=O(asym)}$ and $\nu_{S=O(sym)}$ vibrations of both the mono- and di-substituted benzenesulphonamides. There is no systematic variation with the substitution. Thus the effect of substitution in the phenyl ring in terms of electron withdrawing and electron donating groups could not be generalised.

^1H and ^{13}C NMR Spectra

^1H chemical shift values of thirteen mono- and di-substituted benzenesulphonamides are listed in Tables 4 and 5. The ^1H chemical shifts of benzenesulphonamide, 4-methylbenzenesulphonamide and 4-chlorobenzenesulphonamide reported earlier [15] were also measured under identical conditions and included in Tables 4 and 5 for comparison.

The chemical shift is highly 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 have been discussed. Thus the chemical shifts of aromatic protons in all the arylsulphonamides have been calculated by adding substituent contributions (Table 6) to the shift of benzene (7.27 ppm), as per the principle of substituent addition.



Scheme 1.

The incremental shifts of aromatic protons (ppm from that of benzene proton value of 7.27) for different substituents are shown in Table 6 and used in the calculations. The values of shifts in aromatic protons due to $-SO_2NH_2$ were calculated comparing the values of benzenesulphonamide with that of the benzene proton value of 7.27 ppm. The values are $H_o(2,6) = +0.4$ and $H_m(3,4,5) = +0.1$.

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

Table 7. The observed and calculated ^{13}C chemical shifts (δ, ppm) of *p*-substituted benzenesulphonamides ($4-XC_6H_4SO_2NH_2$).

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	143.8	–	126.3	–	129.7	–	132.5	–	–
CH_3	140.8	140.9	126.1	125.5	129.5	129.6	142.6	141.1	21.5
C_2H_5	140.9	141.2	126.4	125.6	128.7	128.4	148.9	147.4	28.7 15.2
F	139.7	139.3	128.8	126.5	115.9	114.6	166.1	166.9	–
Cl	142.0	141.8	127.6	126.6	128.9	129.1	137.8	138.2	–
Br	139.6	142.3	128.4	127.8	132.2	132.3	127.3	126.4	–
I	133.1	136.5	128.2	128.2	137.8	138.8	98.8	99.6	–
NO_2	131.3	149.8	126.3	126.5	121.1	123.6	146.8	151.4	–

Table 8. The observed and calculated ^{13}C chemical shifts (δ, ppm) of di-substituted benzenesulphonamides, (*i*-X, *j*-$YC_6H_3SO_2NH_2$).

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-$(CH_3)_2$	141.1	143.9	137.3	135.6	140.9	138.9	129.9	132.4	126.9	125.9	123.5	122.6	19.6
2,4-$(CH_3)_2$	142.1	141.6	139.3	134.8	136.2	130.3	140.3	141.0	127.2	126.7	126.4	125.4	21.1 20.0
2,5-$(CH_3)_2$	141.6	144.4	132.6	132.0	132.3	129.5	133.1	134.4	135.5	135.3	127.8	126.2	20.8 19.8
2-CH_3, 4-Cl	140.2	142.5	137.1	135.9	131.5	129.8	138.3	138.1	128.9	126.2	125.5	126.5	20.5 19.7
2-CH_3, 5-Cl	143.5	145.5	135.0	132.9	129.5	130.6	131.2	131.9	133.8	132.4	127.4	125.6	20.7 19.5
3-CH_3, 4-Cl	142.8	141.7	126.2	127.3	137.1	138.4	139.5	138.9	129.3	129.0	124.5	123.7	19.8
2,4-Cl_2	139.3	142.0	132.1	133.0	130.6	129.3	138.1	139.2	127.1	127.1	126.0	127.6	–
3,4-Cl_2	143.9	142.8	125.7	126.8	132.5	135.5	135.7	138.4	128.1	130.1	131.1	130.4	–

Table 9. Incremental shifts of aromatic carbon atoms of monosubstituted 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	–

^{13}C chemical shifts are tabulated in Tables 7 and 8. The values of benzenesulphonamide, 4-methylbenzenesulphonamide and 4-chlorobenzenesulphonamide reported earlier [15] are also measured under identical conditions and included in the tables for comparison purpose (Tables 7 and 8).

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 ^{13}C in all the arylsulphonamides 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 incremental shifts of the aromatic ^{13}C (ppm from that of benzene carbon-13 value of 128.5) for different substituents [13, 16] are given in Table 9 and are used in the calculations. The values of shifts in aromatic carbons due to $-SO_2NH_2$ were calculated, comparing the values of benzenesulphonamide with that of benzene carbon-13 of 128.5 ppm. The values are ^{13}C-1 = +15.3, ^{13}C-4 = +3.3, ^{13}C-3 or 5 = +0.4 and ^{13}C-2 or 6 = –2.9.

The calculated chemical shifts for different aromatic carbons compared with the experimental values are included in Tables 7 and 8. The agreement between the calculated and experimental chemical shifts is reasonably good. Generally, electron-withdrawing groups show high-chemical shifts compared to electron-donating groups.

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