Crystal Structure Studies on *p*-Substitutedbenzenesulphonamides 4-X-$C_6H_4SO_2NH_2$ (X = CH_3, NH_2 F, Cl or Br)

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Effect of ring substitution on the crystal structures of *p*-substitutedbenzenesulphonamides, *p*-$XC_6H_4SO_2NH_2$ (X = F, Cl, Br, CH_3 or NH_2) has been studied by determining the crystal structures of 4-chlorobenzenesulphonamide (4-$ClC_6H_4SO_2NH_2$) and 4-bromobenzenesulphonamide (4-$BrC_6H_4SO_2NH_2$) and analyzing the results along with the structures of 4-methylbenzenesulphonamide (4-$CH_3C_6H_4SO_2NH_2$), 4-fluorobenzene-sulphonamide (4-$FC_6H_4SO_2NH_2$) and 4-aminobenzenesulphonamide (4-$NH_2C_6H_4SO_2NH_2$). The crystal type, space group, formula units and lattice constants in Å of new structures are: (4-$ClC_6H_4SO_2NH_2$); monoclinic, $P2_1/n$, Z = 4, a = 6.6276(10), b = 16.219(3), c = 7.5716(10), β = 93.387(14)°; (4-$BrC_6H_4SO_2NH_2$): monoclinic, P $2_1/n$, Z = 4, a = 6.5660(10), b = 16.4630(10), c = 7.6900(10), β = 92.760(10)°. Orientation of the amine group with respect to the phenyl ring is given by the torsion angles C(2)-C(1)-S-N: 70.9° and C(6)-C(1)-S-N: −108.5°. Similarly, the orientation of S, O(1) and O(2) with respect to the ring are given by torsion angles. The comparison of bond lengths and bond angles of 4-fluoro-, 4-chloro-, 4-bromo-, 4-methyl- and 4-amino-benzenesulphonamides reveal that the S-N and C-S bond lengths decrease with the introduction of electron-withdrawing substituents such as F, Cl or Br, while these groups do not have significant effects on the S-O distances. The effect on ring C-C distances was not uniform. Substitution of F, Cl or Br decreases the O-S-N bond angle, but increases the O-S-N, N-S-C(1) and C(3)-C(4)-C(5) bond angles.

Key words: Crystal Structures; 4-Chloro- and 4-Bromo-benzenesulphonamide.

Introduction

Sulphonamides are of fundamental chemical interest as they show distinct physical, chemical and biological properties. Many sulphonamides and their N-chloro compounds exhibit pharmacological activity, which has further stimulated recent interest in their chemistry. Further, many sulphonamides and their N-chlorocompounds exhibit fungicidal and herbicidal activities, because of their oxidising action in aqueous, partial aqueous and non-aqueous media [1 – 9]. Therefore an understanding of formation, properties and structures of sulphonamides is central to future development in such areas as medicinal and redox chemistry. Thus we are interested in the spectroscopic and structural studies of them in their crystalline state [10 – 12].

In this paper we report the crystal structures of 4-chlorobenzenesulphonamide (4-$ClC_6H_4SO_2NH_2$) and 4-bromobenzenesulphonamide (4-$BrC_6H_4SO_2NH_2$) and consider the effect of ring substitution on the relevant bond lengths and bond angles by analysing the present data along with those of 4-methylbenzenesulphonamide (4-$CH_3C_6H_4SO_2NH_2$) [13], 4-fluoro-benzenesulphonamide (4-$FC_6H_4SO_2NH_2$) [14] and 4-aminobenzenesulphonamide (4-$NH_2C_6H_4SO_2NH_2$) [15].

Experimental

Preparation and Characterization of the Compounds

The 4-halobenzenesulphonamides were prepared by the chlorosulphonation of halobenzenes to 4-halobenzenesulphonylchlorides and subsequent conversion of the latter to 4-halobenzenesulphonamides [10, 16]:

Halobenzene (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

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of 4-chlorobenzenesulphonamide (4-$ClC_6H_4SO_2NH_2$) and 4-bromobenzenesulphonamide (4-$BrC_6H_4SO_2NH_2$). Diffractometer: Stoe-Stadi 4; Monochromator: Graphite (002); scan $2\theta/\omega$ = 1/1; Refinement method: Full-matrix least-squares on F^2.

Description	**4-$ClC_6H_4SO_2NH_2$**	**4-$BrC_6H_4SO_2NH_2$**
Chemical formula	C_6 H_6 Cl N O_2 S	C_6 H_6 Br N O_2 S
Formula weight	191.63	236.09
Temperature, K	301(2)	293(2)
Wavelength, pm	71.069	71.093
Crystal system	monoclinic	monoclinic
Space group	P $2_1/n$	P $2_1/n$
a, Å	6.6276(10)	6.5660(10)
b, Å	16.219(3)	16.4630(10)
c, Å	7.5716(10)	7.6900(10)
β, deg.	93.387(14)	92.760(10)
Volume, Å^{33}	812.5(2)	830.29(17)
Z	4	4
D_{calcd}, g cm^{-3}	1.567	1.889
Abs. coeff., cm^{-1}	6.73	5.150
F(000)	392	464
Crystal size, mm^{33}	$0.52 \times 0.22 \times 0.19$	$0.58 \times 0.11 \times 0.11$
θ range, deg.	2.51 to 25.98	2.48 to 26.07
Index ranges	$-8 \le h \le 8$	$-8 \le h \le 3$
	$-1 \le k \le 18$	$-1 \le k \le 18$
	$-1 \le l \le 9$	$-1 \le l \le 9$
Reflections coll.	6369	1666
Independent refl.	1577	1390
[*R*(int)]	0.0284	0.0394
Absorption corr.	Empiric-psi-scans	Empiric-psi-scans
Max. and min. transm.	0.8827 and 0.7189	0.3011 and 0.2760
Data	1577	1390
Restraints/parameters	0 / 106	0 / 106
Goodness-of-fit on F^{22}	1.061	1.053
Final $R[I > 2\sigma(I)]$	$R1$ = 0.0323	$R1$ = 0.0303
	$wR2$ = 0.0858	$wR2$ = 0.0727
R indices (all data)	$R1$ = 0.0355	$R1$ = 0.0431
	$wR2$ = 0.0890	$wR2$ = 0.0806
Largest diff. peak and hole e$^-$Å^3	0.247 and −0.355	0.335 and −0.451

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 4-halobenzenesulphonylchlorides were then recrystallised from sulphonic solvent (Choroform, ethanol or petroleum ether) and dried in vacuum over conc. H_2SO_4. The recrystallised 4-halobenzenesulphonylchloride (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 4-halobenzenesulphonamide was filtered under suction and washed with cold water. It was recrystallised to constant melting point from dilute ethanol and dried at 105 °C.

All other reagents employed in the preparations and purification of compounds were of analytical grade. The purity of the compounds was checked by determining their melting points. The compounds were further characterised by recording their infrared and ^{35}Cl

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of 4-$ClC_6H_4SO_2NH_2$) and 4-$BrC_6H_4SO_2NH_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)
		4-$ClC_6H_4SO_2NH_2$		
C(1)	963(3)	3745(1)	2971(2)	40(1)
C(2)	−1050(3)	3664(1)	2418(3)	49(1)
C(3)	−2176(3)	4360(2)	2000(3)	58(1)
C(4)	−1283(4)	5120(1)	2166(3)	56(1)
C(5)	719(4)	5210(1)	2717(3)	63(1)
C(6)	1864(3)	4513(1)	3122(3)	54(1)
Cl(1)	−2751(1)	5990(1)	1694(1)	91(1)
S(1)	2363(1)	2839(1)	3458(1)	40(1)
O(1)	4316(2)	3077(1)	4187(2)	57(1)
O(2)	1114(2)	2321(1)	4465(2)	56(1)
N(1)	2714(3)	2359(1)	1664(2)	47(1)
		4-$BrC_6H_4SO_2NH_2$		
C(1)	6039(5)	11300(2)	3001(4)	39(1)
C(2)	6943(6)	10546(2)	3170(5)	50(1)
C(3)	5789(7)	9857(2)	2766(5)	59(1)
C(4)	3780(7)	9947(2)	2206(4)	50(1)
C(5)	2896(6)	10700(2)	2021(5)	52(1)
C(6)	4028(6)	11380(2)	2442(5)	49(1)
Br	2149(1)	9019(1)	1695(1)	75(1)
S	7447(1)	12194(1)	3480(1)	38(1)
O(1)	6165(4)	12703(2)	4469(3)	53(1)
O(2)	9410(4)	11966(2)	4191(3)	53(1)
N(1)	7797(5)	12669(2)	1705(4)	45(1)

Table 3. Bond lengths (Å) (standard deviation) of 4-$ClC_6H_4SO_2NH_2$) and 4-$BrC_6H_4SO_2NH_2$.

	Connection	Bond length (Å)
	4-$ClC_6H_4SO_2NH_2$	**4-$BrC_6H_4SO_2NH_2$**
S(1)-N(1)	1.595(18)	1.599(3)
S(1)-O(1)	1.430(14)	1.432(2)
S(1)-O(2)	1.430(14)	1.426(3)
C(1)-S(1)	1.767(18)	1.768(3)
C(1)-C(2)	1.382(3)	1.379(5)
C(1)-C(6)	1.381(3)	1.375(5)
C(2)-C(3)	1.387(3)	1.391(5)
C(3)-C(4)	1.375(4)	1.376(6)
C(4)-C(5)	1.371(3)	1.373(5)
C(4)-X(1)	1.738(2)	1.896(4)
C(5)-C(6)	1.378(3)	1.373(5)

Table 4. Bond angles (degree) (standard deviation) of 4-$ClC_6H_4SO_2NH_2$) and 4-$BrC_6H_4SO_2NH_2$.

	Connection	Bond angle (degree)
	4-$ClC_6H_4SO_2NH_2$	**4-$BrC_6H_4SO_2NH_2$**
O(1)-S(1)-N(1)	106.7(10)	107.0(17)
O(2)-S(1)-N(1)	106.6(10)	106.2(17)
O(1)-S(1)-O(2)	119.5(9)	119.6(16)
C(2)-C(1)-S(1)	118.1(14)	118.1(2)
N(1)-S(1)-C(1)	109.2(9)	108.9(16)
O(1)-S(1)-C(1)	107.9(9)	108.3(16)
O(2)-S(1)-C(1)	106.7(8)	106.5(15)
C(6)-C(1)-S(1)	120.9(15)	120.7(3)
C(2)-C(1)-C(6)	121.1(18)	121.2(3)
C(3)-C(2)-C(1)	119.5(19)	119.0(4)
C(4)-C(3)-C(2)	119.4(2)	119.0(3)
C(3)-C(4)-C(5)	121.8(19)	121.6(3)
C(3)-C(4)-X(1)	118.6(19)	118.3(3)
C(5)-C(4)-X(1)	119.6(18)	120.0(3)
C(4)-C(5)-C(6)	119.1(2)	119.3(4)
C(1)-C(6)-C(5)	119.2(2)	119.8(3)

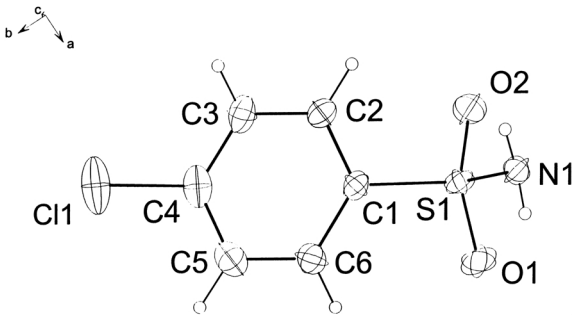


Fig. 1. Molecular geometry of 4-chlorobenzenesulphonamide (4-$ClC_6H_4So_2NH_2$) with numbering of atoms.

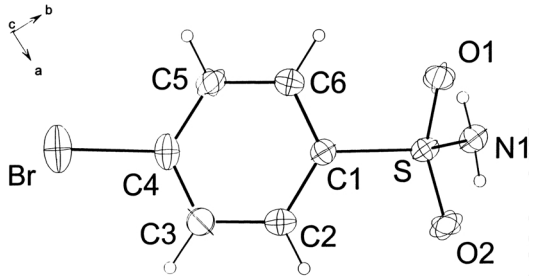


Fig. 2. Molecular geometry of 4-chlorobenzenesulphonamide (4-$BrC_6H_4So_2NH_2$) with numbering of atoms.

NQR spectra and comparing the frequencies with the literature values.

Crystal Structure Studies

The compounds, 4-chlorobenzenesulphonamide and 4-bromobenzenesulphonamide were recrystallised several times to get good crystals. Small simple crystals were selected for structure determinations, carried out at room temperature. The collected intensity data were corrected for Lorentz polarisation and absorption. The positional parameters were determined by direct methods and least squares refinement (SHELXL-97) [17 – 23]. For locating the hydrogen atom positions, the C-H distances were fixed to 0.93 Å for the ring hydrogen atoms. Further experimental conditions for structure determinations and refinements are given in Table 1.

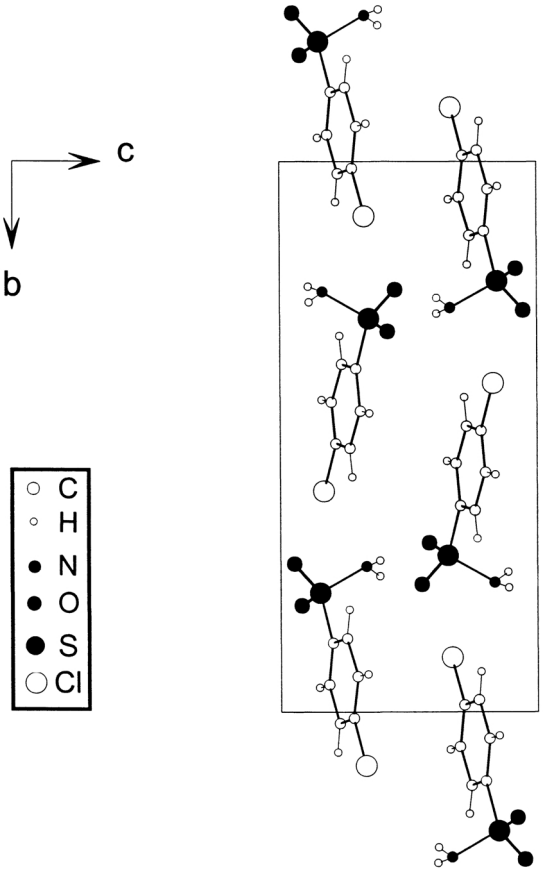


Fig. 3. Projection of the unit cell of 4-chlorobenzenesulphonamide (4-$ClC_6H_4So_2NH_2$).

Results and Discussion

The crystallographic data for the compounds, 4-chlorobenzenesulphonamide and 4-bromobenzenesulphonamide are given in Table 1. The atomic coordinates and the mean displacement parameters are given in Table 2, while Tables 3 and 4 give the intermolecular bond distances and bond angles, respectively.

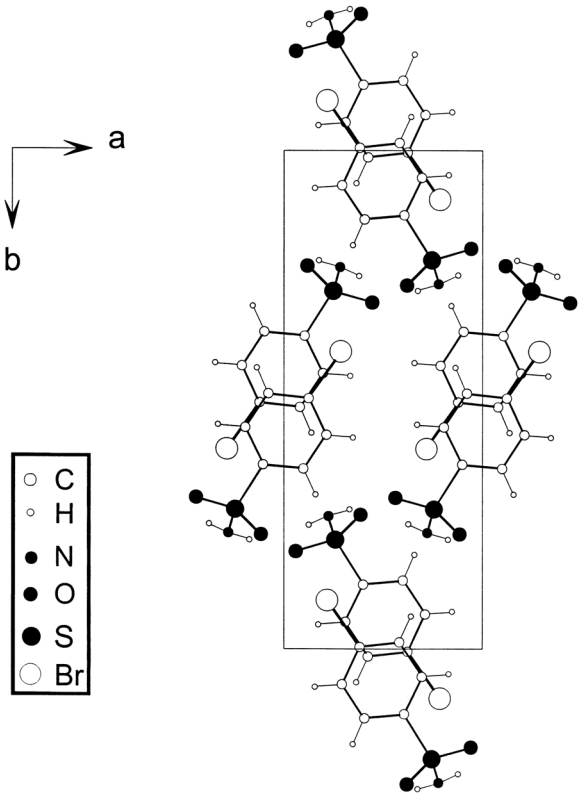


Fig. 4. Projection of the unit cell of 4-chlorobenzenesulphonamide (4-$BrC_6H_4So_2NH_2$).

The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations have been deposited at the Cambridge Crystallographic Data Centre. The CCDC numbers are 200388 and 200389, respectively, for 4-chlorobenzenesulphonamide and 4-bromobenzenesulphonamide. Figures 1 and 2 show the molecules of the title compounds as they appear in suitable projections with the numbering of the atoms used. The projections of unit cells of some compounds are shown in Figs. 3 and 4.

Orientation of the amine group with respect to the phenyl ring is given by the torsion angles C(2)-C(1)-S-N: 70.9° and C(6)-C(1)-S-N: −108.5°.

The bond lengths and bond angles of 4-chloro- and 4-bromo-benzenesulphonamides have been compared with those of 4-methyl-, 4-fluoro-, and 4-aminobenzenesulphonamides, to consider the effect of ring substitution on the structural data (Tables 5 and 6). The data revealed that the S-N and C-S bond lengths decreased with the introduction of electron-withdrawing substituents such as F, Cl or Br, while these groups did not have significant effect on the S-O distances. The effect on ring C-C distances was not uniform. Substitution of F, Cl or Br decreased the O-S-N bond angle, but increased the O-S-N, N-S-C(1) and C(3)-C(4)-C(5) bond angles.

Table 5. Bond lengths (Å) (standard deviation).

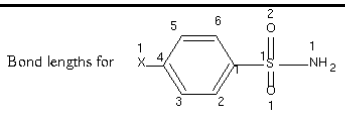
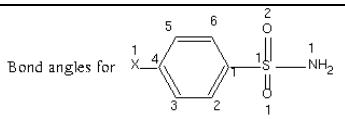
Connections	CH_3 [13]	NH_2 [15]	F [14]	Cl	Br
Bond lengths for  X =					
S(1)-N(1)	1.610(6)	1.610	1.601(2)	1.595(18)	1.599(3)
S(1)-O(1)	1.433(5)	1.470	1.437(14)	1.430(14)	1.432(2)
S(1)-O(2)	1.428(5)	1.410	1.431(14)	1.430(14)	1.426(3)
C(1)-S(1)	1.788(8)	1.740	1.763(2)	1.767(18)	1.768(3)
C(4)-X(1)	1.540(5)	1.400	1.359(2)	1.738(2)	1.896(4)
C(1)-C(2)	1.396(5)	1.410	1.394(2)	1.382(3)	1.379(5)
C(1)-C(6)	1.381(5)	1.400	1.384(3)	1.381(3)	1.375(5)
C(2)-C(3)	1.363(5)	1.390	1.390(3)	1.387(3)	1.391(5)
C(3)-C(4)	1.391(5)	1.440	1.377(3)	1.375(4)	1.376(6)
C(4)-C(5)	1.378(5)	1.390	1.372(3)	1.371(3)	1.373(5)
C(5)-C(6)	1.334(5)	1.380	1.379(3)	1.378(3)	1.373(5)

Table 6. Bond angles (degree) (standard deviation).

Connections	CH_3 [13]	NH_2 [15]	F [14]	Cl	Br
Bond angles for  X =					
O(1)-S(1)-N(1)	108.8(3)	107.9	106.5(9)	106.7(10)	107.0(17)
O(2)-S(1)-N(1)	105.2(4)	105.7	106.5(9)	106.6(10)	106.2(17)
N(1)-S(1)-C(1)	107.7(3)	–	109.5(9)	109.2(9)	108.9(16)
O(1)-S(1)-O(2)	118.9(4)	119.0	119.0(9)	119.5(9)	119.6(16)
O(1)-S(1)-C(1)	108.7(3)	107.8	107.7(8)	107.9(9)	108.3(16)
O(2)-S(1)-C(1)	107.1(3)	107.5	107.4(8)	106.7(8)	106.5(15)
C(2)-C(1)-S(1)	120.8(3)	120.0	119.5(13)	120.9(15)	120.7(3)
C(6)-C(1)-S(1)	117.8(3)	119.8	119.2(14)	118.1(14)	118.1(2)
C(2)-C(1)-C(6)	121.4(3)	121.4	123.8(2)	121.8(19)	121.6(3)
C(1)-C(6)-C(5)	118.3(3)	121.4	119.5(2)	119.5(19)	119.8(3)
C(3)-C(2)-C(1)	118.1(3)	119.7	119.4(2)	119.2(2)	119.0(4)
C(4)-C(3)-C(2)	122.5(3)	119.5	118.0(2)	119.4(2)	119.3(4)
C(3)-C(4)-C(5)	117.8(3)	120.1	121.3(2)	121.1(18)	121.3(3)
C(3)-C(4)-X(1)	122.3(2)	119.8	118.2(2)	119.6(18)	120.0(3)
C(5)-C(4)-X(1)	119.7(3)	118.6	118.2(2)	118.6(19)	118.3(3)
C(4)-C(5)-C(6)	121.6(3)	117.8	118.0(2)	119.1(2)	119.0(3)

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