Crystal Structure Studies on Arylsulphonamides and *N*-Chloro-Arylsulphonamides

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The effect of ring substitution and *N*-chlorination on the molecular geometry of arylsulphonamides and *N*-chloro-arylsulphonamides have been studied by determining the crystal structures of 2-methyl-4-chloro-benzenesulphonamide (**2M4CBSA**) and the sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide (**NaNC2M4CBSA**). The results are analyzed along with the crystal structures of benzenesulphonamide, 4-methyl-benzenesulphonamide and 4-chloro-benzenesulphonamide. The crystal structure of **NaNC2M4CBSA** has also been compared and correlated with the crystal structures of the above compounds and those of the sodium salts of *N*-chloro-benzenesulphonamide, *N*-chloro-4-methyl-benzenesulphonamide, *N*-chloro-4-chloro-benzenesulphonamide and *N*-chloro-2,4-dichloro-benzenesulphonamide. The crystal system, space group, formula units and lattice constants in Å of the new structures are: **2M4CBSA**: triclinic, $P1$, $Z = 4$, $a = 7.9030(10)$, $b = 8.6890(10)$, $c = 13.272(2)$, $\alpha = 100.680(10)^\circ$, $\beta = 98.500(10)^\circ$, $\gamma = 90.050(10)^\circ$; **NaNC2M4CBSA**: monoclinic, $C2/c$, $Z = 4$, $a = 10.9690(10)$, $b = 6.7384(6)$, $c = 30.438(2)$, $\beta = 98.442(7)^\circ$. The structure of 2M4CBSA is quite complex with four molecules in its asymmetric unit. The S-N bond length slightly decreases with substitution of electron-withdrawing groups, while the effect is more pronounced with disubstitution. The structure of **NaNC2M4CBSA** confirms that there is no interaction between nitrogen and sodium, and Na^+ is attached to one of the sulphonyl oxygen atoms. The Na^+ coordination sphere involves oxygen atoms from water moleculess of crystallization and neighbouring molecules. The S-N distance of 1.586 Å for the compound is consistent with a S-N double bond. The molecules are held together by hydrogen bonds with distances varying from 2.12 to 2.85 Å.

Key words: Crystal Structure; 2-Methyl-4-chloro-/*N*-Chloro-2-methyl-4-chloro-benzenesulphonamide.

1. Introduction

The chemistry of sulphonamides is of interest as they show distinct physical, chemical and biological properties. Many arylsulphonamides and their *N*-halogen compounds exhibit pharmacological, fungicidal and herbicidal activities due to their oxidizing action in aqueous, partial aqueous and non-aqueous media [1 – 13]. Thus *N*-halogen arylsulphonamides are of interest in synthetic, mechanistic, analytical and biological chemistry. Their oxidizing power depends on the ease with which the halogen atom is released as positive ion in the reaction system, which in turn depends on the electron environment around the N-X bond. A sensitive measure for polarization of the X atom in the N-X bond is the infrared absorption, halogen nuclear quadrupole resonance or nitrogen NMR. Thus the effect of ring substitution on the infrared and ^{35}Cl NQR spectra and crystal structures of substituted *N*-chloro- and *N*-dichloro-benzenesulphonamides of the type: 4-X-C_6H_4-$SO_2NH_{2-i}Cl_i$ (where X = Cl or Br and $i = 0$, 1 or 2) are of interest. We have recently synthesized and measured the infrared, NMR and ^{35}Cl NQR spectra of this class of compounds and reported elsewhere [14 – 24]. The infrared absorptions of N-Cl, ^{35}Cl(N) NQR frequencies and NMR spectra of these compounds have also been correlated with each other. Attempts have also been made to correlate the relative strengths of *N*-chloro- and *N*-dichloro-arylsulphonamides by employing them as oxidimetric analytical reagents in solution through kinetic and other methods [1 – 13]. As part of our structural studies on this class of biologically significant compounds [25], we report in

this paper the crystal structures of 2-methyl-4-chloro-benzenesulphonamide, 2-CH_3-4-Cl-C_6H_3-SO_2NH_2 (**2M4CBSA**), and the sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide, 2-CH_3-4-Cl-C_6H_3-SO_2(Na)NCl · 1.5 H_2O (**NaNC2M4CBSA**). Effects of ring substitution and *N*-chlorination on the relevant bond lengths and bond angles are discussed by analyzing the present data along with the crystal structures [26 – 29] of benzenesulphonamide, 4-methyl-benzenesulphonamide, 4-chloro-benzenesulphonamide, and sodium salts of *N*-chloro-benzenesulphonamide, *N*-chloro-4-methyl-benzenesulphonamide, *N*-chloro-4-chloro-benzenesulphonamide and *N*-chloro-2,4-dichloro-benzenesulphonamide.

2. Materials and Methods

2.1. Preparation and Characterization of Compounds

2-Methyl-4-chloro-benzenesulphonamide was prepared by the chloro-sulphonation of 3-chlorotoluene and subsequent conversion of the resulting 2-methyl-4-chloro-benzenesulphonylchloride to the amide. The sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide was prepared by the *N*-chlorination of 2-methyl-4-chloro-benzenesulphonamide [16]. The commercial solids were purified by either recrystallization or zone refining. The liquids were purified by double distillation. All other reagents employed in the preparations and purification of the compounds were of analytical grade. 3-Chlorotoluene (10 g) was dissolved in chloroform (50 ml). 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 2-methyl-4-chloro-benzenesulphonylchloride was recrystallised from sulphonic solvent (choroform/ethanol/petroleum ether) and dried in vacuum over conc. H_2SO_4. The 2-methyl-4-chloro-benzenesulphonylchloride (15 g) was boiled for 10 min with concentrated ammonium hydroxide (100 ml; sp. gr. 0.90). It was cooled to room temperature and added to ice-cold water (100 ml). The resultant solid 2-methyl-4-chloro-benzenesulphonamide was filtered under suction, washed thoroughly with cold water, recrystallized to constant melting point from dilute ethanol and dried. The purity of the compound was checked by recording its IR and NMR spectra [15].

Pure chlorine gas was bubbled through a clear aqueous solution of 2-methyl-4-chloro-benzenesulphonamide in 4 M NaOH at 70 °C for about 1 h. The precipitated sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide was filtered, washed, dried and recrystallized from water. Purity of the compound was checked by determining its melting point and by estimating iodometrically the amounts of active chlorine

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of 2-methyl-4-chloro-benzenesulphonamide, 2-CH_3-4-Cl-C_6H_3-SO_2NH_2 (**2M4CBSA**), and the sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide, 2-CH_3-4-Cl-C_6H_3-SO_2(Na)NCl · 1.5 H_2O (**NaNC2M4CBSA**). Diffractometer: Xcalibur (TM); monochromator: graphite (002); scan: $2\theta/\omega = 1/1$; refinement method: full-matrix least-squares on F^2.

Description	**2M4CBSA**	**NaNC2M4CBSA**
Chemical formula	$C_7H_8ClNO_2S$	$C_{14}H_{18}Cl_4N_2Na_2O_7S_2$
Formula mass, g mol^{-1}	205.65	578.20
Temperature, K	303(2)	303(2)
Wavelength, pm	71.073	71.073
Crystal system	triclinic	monoclinic
Space group	$P1$	$C2/c$
a, Å	7.9030(10)	10.9690(10)
b, Å	8.6890(10)	6.7384(6)
c, Å	13.272(2)	30.438(2)
α, deg.	100.680(10)	–
β, deg.	98.500(10)	98.442(7)
γ, deg.	90.050(10)	–
Volume, Å^3	885.4(2)	2225.4(3)
Z	4	4
Density (calcd.), g cm^{-3}	1.543	1.726
Absorption coeff., cm^{-1}	6.24	7.99
$F(000)$	424	1176
Crystal size, mm^3	0.32×0.16×0.02	0.50×0.35×0.25
θ Range, deg.	6.84 to 23.25	4.18 to 26.36
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 9$, $-14 \le l \le 14$	$-10 \le h \le 13$, $-8 \le k \le 8$, $-38 \le l \le 37$
Reflections collected	7337	6615
Independent reflections	4413	2260
R(int)	0.1050	0.0565
Completeness to 2θ	94.1%	99.5%
Absorption correction	none	analytical
Transmission, max. / min.	0.9876 / 0.8254	0.8003 / 0.7164
Data	4413	2260
Restraints/parameters	9/296	3/150
Goodness-of-fit on F^2	0.825	1.114
Final R $[I > 2\theta(I)]$	$R1$ = 0.0828, $wR2$ = 0.1811	$R1$ = 0.0615, $wR2$ = 0.1301
R Indices (all data)	$R1$ = 0.1980, $wR2$ = 0.2114	$R1$ = 0.0648, $wR2$ = 0.1316
Abs. structure parameter	0.1(2)	–
Largest diff. peak and hole, e Å^{-3}	0.946 and −0.402	0.347 and −0.462

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$) of **2M4CBSA** and **NaNC2M4CBSA**. $U(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
2M4CBSA									
C(1)	2810(20)	974(17)	2476(12)	38(4)	O(5)	5187(18)	9850(13)	6524(9)	77(4)
C(2)	1846(19)	783(17)	1492(12)	42(4)	O(6)	4738(15)	7717(15)	4956(8)	65(3)
C(3)	1450(20)	−690(18)	982(12)	38(4)	C(15)	3839(19)	7146(17)	6642(11)	39(4)
C(4)	1799(19)	−2038(17)	1348(11)	37(4)	C(16)	3320(20)	7570(19)	7660(13)	46(4)
C(5)	2750(20)	−1848(17)	2376(12)	43(4)	C(17)	3180(20)	6425(19)	8200(13)	42(4)
C(6)	3250(20)	−354(19)	2906(14)	55(5)	C(18)	3480(19)	4865(17)	7780(11)	34(4)
C(7)	1363(17)	2083(15)	874(10)	20(3)	C(19)	3850(20)	4446(18)	6821(12)	44(4)
Cl(1)	1225(7)	−3848(5)	676(4)	77(2)	C(20)	4120(20)	5590(20)	6277(14)	53(5)
S(1)	3527(5)	2766(5)	3238(3)	47(1)	C(21)	3090(15)	9224(13)	8209(9)	12(3)
N(1)	1957(16)	3698(14)	3611(11)	62(5)	Cl(3)	3270(7)	3457(5)	8542(4)	81(2)
O(1)	4224(17)	3706(12)	2620(10)	74(4)	S(3)	4151(5)	8549(5)	5886(4)	48(1)
O(2)	4580(14)	2536(13)	4164(8)	62(3)	N(3)	2386(16)	9240(16)	5504(11)	44(4)
O(3)	9520(15)	−2458(15)	4175(9)	70(3)	C(22)	−1150(20)	4335(17)	6676(11)	38(4)
O(4)	9182(16)	−4589(13)	2623(10)	74(4)	C(23)	−1550(20)	4524(19)	7703(12)	46(4)
C(8)	7744(19)	−1923(15)	2434(11)	32(4)	C(24)	−1750(20)	5961(19)	8206(13)	44(5)
C(9)	6813(19)	−2326(18)	1445(12)	39(4)	C(25)	−1600(20)	7278(19)	7797(13)	46(4)
C(10)	6440(20)	−1220(20)	925(14)	52(5)	C(26)	−1200(18)	7118(16)	6802(11)	35(4)
C(11)	6820(20)	346(18)	1287(12)	43(5)	C(27)	-920(20)	5680(20)	6258(14)	56(5)
C(12)	7701(19)	785(17)	2259(11)	36(4)	C(28)	−1790(18)	3216(15)	8285(10)	24(4)
C(13)	8200(20)	−370(17)	2830(12)	42(5)	Cl(4)	−1847(6)	9093(5)	8459(4)	71(2)
C(14)	6306(15)	−4033(14)	944(9)	13(3)	S(4)	−807(5)	2489(5)	5895(3)	44(1)
Cl(2)	6239(7)	1743(6)	572(5)	82(2)	N(4)	−2588(16)	1564(15)	5521(11)	63(4)
S(2)	8486(6)	−3271(5)	3254(3)	48(1)	O(7)	225(16)	1568(12)	6554(9)	71(4)
N(2)	6916(16)	−4002(16)	3614(12)	62(4)	O(8)	−247(15)	2755(13)	4967(8)	61(3)
NaNC2M4CBSA									
C(1)	−1744(4)	3254(6)	1182(1)	26(1)	O(1)	−2454(3)	1724(5)	1874(1)	38(1)
C(2)	−875(4)	3841(6)	911(1)	28(1)	O(2)	−584(3)	3728(5)	1996(1)	34(1)
C(3)	−1321(4)	4541(6)	489(1)	34(1)	O(3)	−5000	2783(7)	2500	38(1)
C(4)	−2565(5)	4622(7)	339(2)	39(1)	O(4)	−2110(3)	1855(5)	2923(1)	38(1)
C(5)	−3405(4)	4089(7)	602(2)	41(1)	S(1)	−1303(1)	2256(2)	1724(1)	26(1)
C(6)	−3003(4)	3406(7)	1028(2)	36(1)	Cl(1)	−1062(1)	−1399(2)	1355(1)	38(1)
C(7)	521(4)	3728(7)	1057(1)	33(1)	Cl(2)	−3067(2)	5351(2)	−207(1)	59(1)
N(1)	−370(3)	473(5)	1703(1)	30(1)	Na(1)	−3535(2)	65(3)	2376(1)	36(1)

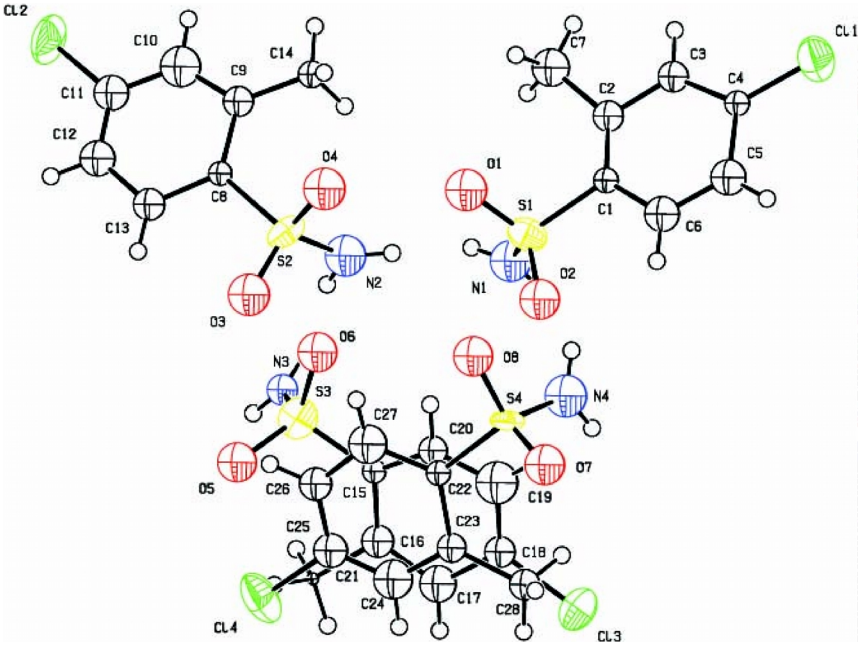

Fig. 1. Molecular geometry of 2-CH_3-4-Cl-C_6H_3-SO_2NH_2 (**2M4CBSA**) with the numbering of atoms.

2M4CBSA				NaNC2M4CBSA	
Connection	Bond length	Connection	Bond length	Connection	Bond length
C(1)-C(2)	1.393(19)	O(5)-S(3)	1.450(12)	C(1)-C(6)	1.395(6)
C(1)-C(6)	1.400(20)	O(6)-S(3)	1.449(11)	C(1)-C(2)	1.404(6)
C(1)-S(1)	1.736(15)	C(15)-C(20)	1.377(19)	C(1)-S(1)	1.780(4)
C(2)-C(3)	1.346(19)	C(15)-C(16)	1.450(20)	C(2)-C(3)	1.391(6)
C(2)-C(7)	1.532(19)	C(15)-S(3)	1.755(15)	C(2)-C(7)	1.532(5)
C(3)-C(4)	1.362(18)	C(16)-C(17)	1.340(20)	C(3)-C(4)	1.375(6)
C(4)-C(5)	1.440(20)	C(16)-C(21)	1.511(19)	C(4)-C(5)	1.354(7)
C(4)-Cl(1)	1.683(16)	C(17)-C(18)	1.400(20)	C(4)-Cl(2)	1.741(5)
C(5)-C(6)	1.380(20)	C(18)-C(19)	1.333(18)	C(5)-C(6)	1.387(6)
S(1)-O(1)	1.422(12)	C(18)-Cl(3)	1.748(16)	N(1)-S(1)	1.586(3)
S(1)-O(2)	1.426(10)	C(19)-C(20)	1.370(20)	N(1)-Cl(1)	1.748(3)
S(1)-N(1)	1.574(11)	S(3)-N(3)	1.570(10)	O(1)-S(1)	1.451(3)
O(3)-S(2)	1.430(11)	C(22)-C(27)	1.410(20)	O(1)-Na(1)	2.350(3)
O(4)-S(2)	1.448(11)	C(22)-C(23)	1.430(20)	O(2)-S(1)	1.450(3)
C(8)-C(13)	1.381(19)	C(22)-S(4)	1.786(15)	O(2)-Na(1)$^{\#1}$	2.436(3)
C(8)-C(9)	1.390(19)	C(23)-C(24)	1.320(20)	O(2)-Na(1)$^{\#2}$	2.537(3)
C(8)-S(2)	1.784(14)	C(23)-C(28)	1.510(20)	O(3)-Na(1)$^{\#3}$	2.501(4)
C(9)-C(10)	1.300(20)	C(24)-C(25)	1.370(20)	O(3)-Na(1)	2.501(4)
C(9)-C(14)	1.535(19)	C(25)-C(26)	1.387(19)	O(4)-Na(1)	2.429(4)
C(10)-C(11)	1.370(20)	C(25)-Cl(4)	1.683(17)	O(4)-Na(1)$^{\#1}$	2.490(4)
C(11)-C(12)	1.359(19)	C(26)-C(27)	1.360(20)	S(1)-Na(1)$^{\#1}$	3.356(2)
C(11)-Cl(2)	1.699(16)	S(4)-O(8)	1.426(10)	Na(1)-O(2)$^{\#4}$	2.436(3)
C(12)-C(13)	1.389(19)	S(4)-O(7)	1.457(11)	Na(1)-O(4)$^{\#4}$	2.490(4)
S(2)-N(2)	1.567(12)	S(4)-N(4)	1.586(12)	Na(1)-O(2)$^{\#5}$	2.537(3)
				Na(1)-S(1)$^{\#4}$	3.356(2)
				Na(1)-Na(1)$^{\#3}$	3.406(3)
				Na(1)-Na(1)$^{\#1}$	4.071(2)
				Na(1)-Na(1)$^{\#4}$	4.071(2)

Table 3. Bond lengths (Å) (standard deviation) of **2M4CBSA** and **NaNC2M4CBSA**.

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ $-x-1/2, y+1/2, -z+1/2$;
$^{\#2}$ $x+1/2, y+1/2, z$;
$^{\#3}$ $-x-1, y, -z+1/2$;
$^{\#4}$ $-x-1/2, y-1/2, -z+1/2$;
$^{\#5}$ $x-1/2, y-1/2, z$.

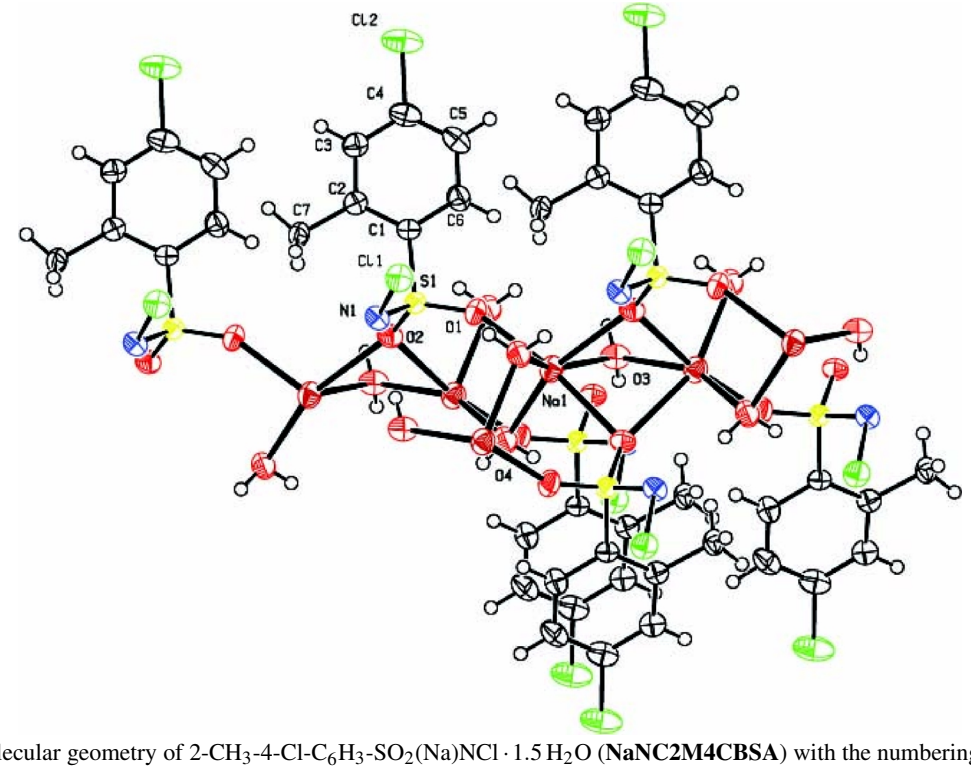

Fig. 2. Molecular geometry of 2-CH_3-4-Cl-C_6H_3-SO_2(Na)NCl · 1.5 H_2O (**NaNC2M4CBSA**) with the numbering of atoms.

Table 4. Bond angles (degree) (standard deviation) of **2M4CBSA** and **NaNC2M4CBSA**.

Connection	Bond angle	Connection	Bond angle
2M4CBSA			
C(2)-C(1)-S(1)	124.7(12)	C(20)-C(15)-S(3)	119.7(12)
C(6)-C(1)-S(1)	116.1(13)	C(16)-C(15)-S(3)	122.1(11)
O(1)-S(1)-O(2)	117.2(8)	O(6)-S(3)-O(5)	119.0(8)
O(1)-S(1)-N(1)	104.7(8)	O(6)-S(3)-N(3)	105.5(7)
O(2)-S(1)-N(1)	105.2(7)	O(5)-S(3)-N(3)	106.4(8)
O(1)-S(1)-C(1)	109.5(7)	O(6)-S(3)-C(15)	106.6(8)
O(2)-S(1)-C(1)	110.3(8)	O(5)-S(3)-C(15)	109.2(7)
N(1)-S(1)-C(1)	109.5(8)	N(3)-S(3)-C(15)	109.8(8)
C(13)-C(8)-S(2)	115.5(11)	C(27)-C(22)-S(4)	117.0(12)
C(9)-C(8)-S(2)	125.3(11)	C(23)-C(22)-S(4)	124.2(11)
O(3)-S(2)-O(4)	119.2(8)	O(8)-S(4)-O(7)	119.7(7)
O(3)-S(2)-N(2)	106.3(8)	O(8)-S(4)-N(4)	105.0(8)
O(4)-S(2)-N(2)	103.9(8)	O(7)-S(4)-N(4)	106.1(7)
O(3)-S(2)-C(8)	109.9(8)	O(8)-S(4)-C(22)	108.8(7)
O(4)-S(2)-C(8)	107.7(7)	O(7)-S(4)-C(22)	107.8(7)
N(2)-S(2)-C(8)	109.3(7)	N(4)-S(4)-C(22)	109.0(7)
NaNC2M4CBSA			
C(6)-C(1)-S(1)	117.3(3)	O(4)-Na(1)-O(4)$^{\#4}$	119.5(1)
C(2)-C(1)-S(1)	122.3(3)	O(1)-Na(1)-O(3)	98.4(1)
S(1)-N(1)-Cl(1)	110.2(2)	O(4)-Na(1)-O(3)	84.1(1)
S(1)-O(1)-Na(1)	150.4(2)	O(2)$^{\#4}$-Na(1)-O(3)	79.4(1)
S(1)-O(2)-Na(1)$^{\#1}$	117.2(2)	O(4)$^{\#4}$-Na(1)-O(3)	156.2(1)
S(1)-O(2)-Na(1)$^{\#2}$	151.0(2)	O(1)-Na(1)-O(2)$^{\#5}$	111.7(1)
Na(1)#3-O(3)-Na(1)	85.9(2)	O(4)-Na(1)-O(2)$^{\#5}$	157.9(1)
Na(1)-O(4)-Na(1)$^{\#1}$	111.7(1)	O(3)-Na(1)-O(2)#5	77.5(1)
O(2)-S(1)-O(1)	114.5(2)	O(1)-Na(1)-S(1)$^{\#4}$	153.1(1)
O(2)-S(1)-N(1)	103.9(2)	O(4)-Na(1)-S(1)$^{\#4}$	80.0(1)
O(1)-S(1)-N(1)	114.9(2)	O(2)#4-Na(1)-S(1)$^{\#4}$	22.6(1)
O(2)-S(1)-C(1)	108.8(2)	O(4)#4-Na(1)-S(1)$^{\#4}$	82.0(1)
O(1)-S(1)-C(1)	104.8(2)	O(3)-Na(1)-S(1)$^{\#4}$	100.3(1)
N(1)-S(1)-C(1)	109.9(2)	O(1)-Na(1)-Na(1)$^{\#3}$	136.6(1)
O(2)-S(1)-Na(1)$^{\#1}$	40.2(1)	O(4)-Na(1)-Na(1)$^{\#3}$	112.5(1)
O(1)-S(1)-Na(1)$^{\#1}$	74.2(1)	O(3)-Na(1)-Na(1)$^{\#3}$	47.1(1)
N(1)-S(1)-Na(1)$^{\#1}$	124.8(1)	O(1)-Na(1)-Na(1)$^{\#1}$	53.5(1)
C(1)-S(1)-Na(1)$^{\#1}$	120.2(1)	O(4)-Na(1)-Na(1)$^{\#1}$	34.6(1)
O(1)-Na(1)-O(4)	82.8(1)	O(3)-Na(1)-Na(1)$^{\#1}$	73.7(1)
O(1)-Na(1)-O(2)$^{\#4}$	169.1(1)	O(1)-Na(1)-Na(1)$^{\#4}$	101.1(1)
O(4)-Na(1)-O(2)$^{\#4}$	86.4(1)	O(4)-Na(1)-Na(1)$^{\#4}$	89.9(1)
O(1)-Na(1)-O(4)$^{\#4}$	88.7(1)	O(3)-Na(1)-Na(1)$^{\#4}$	158.7(1)

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ $-x-1/2, y+1/2, -z+1/2$; $^{\#2}$ $x+1/2, y+1/2, z$;
$^{\#3}$ $-x-1, y, -z+1/2$; $^{\#4}$ $-x-1/2, y-1/2, -z+1/2$;
$^{\#5}$ $x-1/2, y-1/2, z$.

present in it. The compound was further characterized by recording its infrared and NMR spectra [16].

2.2. X-Ray Diffraction Studies

Small single crystals of 2-methyl-4-chloro-benzenesulphonamide and the sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide were used for structure determination at room temperature. The collected intensity data were corrected for Lorentz polarization and absorption. The positional parameters were determined by direct methods and least-squares refinement (SHELXL-97) [30 – 36]. For locating the hydrogen atom positions, the C-H distances were fixed to 0.93 Å for the ring hydrogen atoms, while the side chain C-H distances were fixed to 0.96 Å for the CH_3 group.

Table 5. Hydrogen bond distances in 2-CH_3-4-Cl-C_6H_3-SO_2(Na)NCl · 1.5 H_2O (**NaNC2M4CBSA**).

D-H...A	*d*(D-H)	*d*(H...A)	*d*(D...A)	∠(DHA)
O(3)-H(3O)...N(1)$^{\#1}$	0.851(10)	2.156(11)	3.006(4)	178(5)
O(3)-H(3O)...Cl(1)$^{\#1}$	0.851(10)	2.850(30)	3.552(1)	141(4)
O(4)-H(41O)...N(1)$^{\#2}$	0.846(10)	2.115(18)	2.941(5)	165(5)
O(4)-H(42O)...Cl(1)$^{\#1}$	0.849(10)	2.552(13)	3.396(3)	172(5)

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ $-x-1/2, y+1/2, -z+1/2$; $^{\#2}$ $-x, y, -z+1/2$.

3. Results and Discussion

The crystallographic data for the compound 2-methyl-4-chloro-benzenesulphonamide and the sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide 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. The hydrogen bond distances in **NaNC2M4CBSA** are shown in Table 5. The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations of these compounds, **2M4CBSA** and **NaNC2M4CBSA**, have been deposited at the Cambridge Crystallographic Data Centre [CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)]. The CCDC numbers are 614956, and 614964, respectively, for 2-methyl-4-chloro-benzenesulphonamide (**2M4CBSA**) and the sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide (**NaNC2M4CBSA**). Figures 1 and 2 show, respectively, the molecules of **2M4CBSA** and **NaNC2M4CBSA** as they appear in suitable projections with the numbering of the atoms used. The projection of the hydrogen bonds in **NaNC2M4CBSA** are shown in Figure 3.

*3.1. Structure of 2-Methyl-4-chloro-benzenesulphonamide (**2M4CBSA**)*

The structure of **2M4CBSA** is quite complex. It has four molecules in its asymmetric unit. The orientation of the amine group with respect to the phenyl ring in

Table 6. Comparison of bond lengths (Å) and angles (degree) of benzenesulphonamide, C_6H_5-SO_2NH_2, 4-substituted benzenesulphonamides, 4-X-C_6H_4-SO_2NH_2, and 2-methyl-4-chloro-benzenesulphonamide, 2-CH_3-4-Cl-C_6H_3-SO_2NH_2.

	i-X-C_6H_4-SO_2NH_2, where *i*-X =					
Connection	H [29a]	4-CH_3 [26]	4-F [27]	4-Cl [25]	4-Br [25]	2-CH_3-4-Cl-C_6H_3-SO_2NH_2
S(1)-N(1)	1.605	1.610	1.601	1.595	1.599	1.574
S(1)-O(1)	1.410	1.433	1.437	1.430	1.432	1.440
S(1)-O(2)	1.415	1.428	1.431	1.430	1.426	1.437
C(1)-S(1)	1.739	1.788	1.763	1.767	1.768	1.765
N(1)-S(1)-O(1)	106.7	108.8	106.5	106.7	107.0	105.9
N(1)-S(1)-O(2)	107.1	105.2	106.5	106.6	106.2	104.9
N(1)-S(1)-C(1)	108.9	107.7	109.5	109.2	108.9	109.4
O(1)-S(1)-O(2)	119.1	118.9	119.0	119.5	119.6	118.8
O(1)-S(1)-C(1)	109.7	108.7	107.7	107.9	108.3	109.1
O(2)-S(1)-C(1)	105.1	107.1	107.4	106.7	106.5	108.4
S(1)-C(1)-C(2)	121.1	120.8	119.5	120.9	120.7	124.1
S(1)-C(1)-C(6)	117.9	117.8	119.2	118.1	118.1	117.1

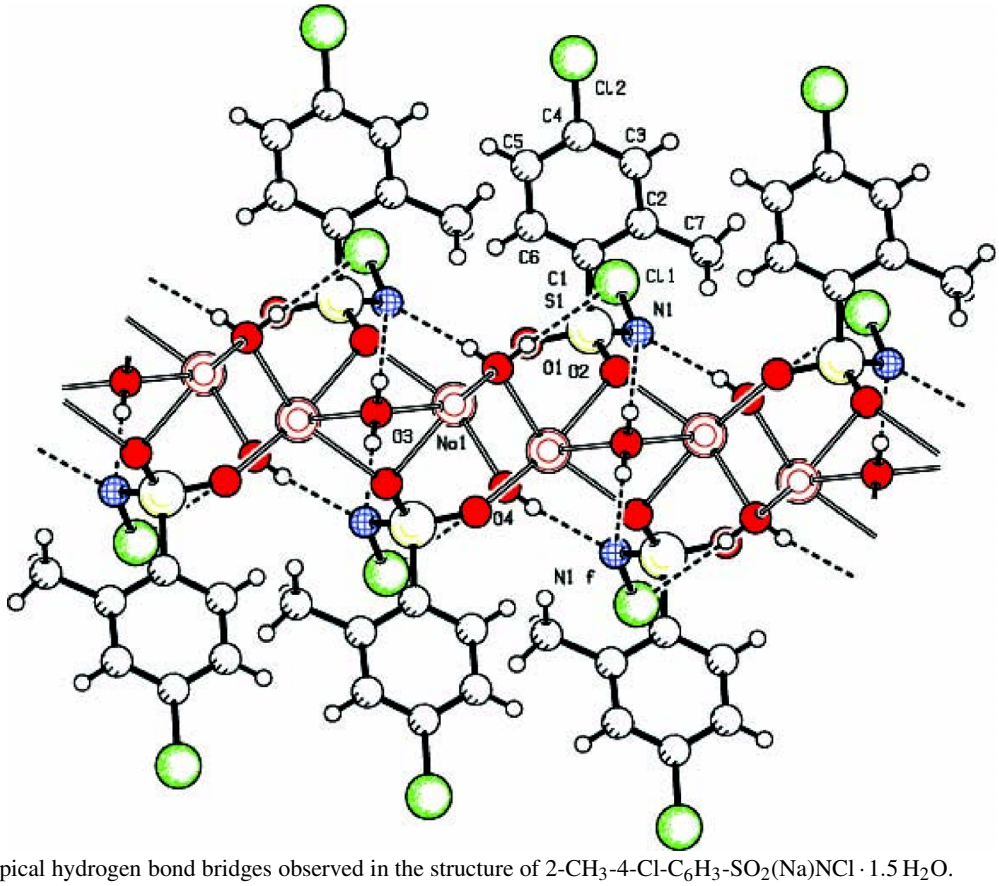

Fig. 3. Typical hydrogen bond bridges observed in the structure of 2-CH_3-4-Cl-C_6H_3-SO_2(Na)NCl · 1.5 H_2O.

the four molecules is given by the torsion angles C(2)-C(1)-S-N, 69.0, −68.7, −69.1, 72.5°, and C(6)-C(1)-S-N, −110.7, 113.3, 112.2, −110.8°, respectively.

To consider the effect of ring substitution on the structural data, the selected bond lengths and bond angles of 2-methyl-4-chloro-benzenesulphonamide have been compared with those of benzenesulphonamide, 4-methyl-benzenesulphonamide and 4-chloro-benzenesulphonamide (Table 6). The data revealed that the S-N bond length slightly decreased with the introduction of electron-withdrawing substituents, while the effect is more pronounced with disubstitution in the title compound. The C-S and S-O bond lengths increased with substitution irrespective of the nature of the substituent. The effect of substitution on the bond angles was non-uniform.

Table 7. Comparison of bond lengths (Å) and angles (degree) of the sodium salt of *N*-chloro-2-methyl-4-chloro-benzenesulphonamide with those of 2-methyl-4-chloro-benzenesulphonamide and sodium salts of *N*-chloro-benzenesulphonamide, *N*-chloro-4-substituted benzenesulphonamides, 4-X-C_6H_4-SO_2(Na)NCl · 1.5 H_2O and *N*-chloro-2,4-dichloro-benzenesulphonamide, 2,4-Cl_2-C_6H_3-SO_2(Na)NCl · 1.5 H_2O.

	2-CH_3-4-	2-CH_3-4-Cl-C_6H_4-	*i*-X-C_6H_4-SO_2(Na)NCl · 1.5 H_2O			2,4-Cl_2-C_6H_3-
Connection	C_6H_3-SO_2NH_2	SO_2(Na)NCl · 1.5 H_2O	*i*-X = H	*i*-X = 4-CH_3	*i*-X = 4-Cl	SO_2(Na)NCl · 1.5 H_2O
C(1)-S(1)	1.765	1.780	1.756	1.767	1.775	1.785
S(1)-O(1)	1.440	1.451	1.456	1.455	1.455	1.450
S(1)-O(2)	1.437	1.450	1.428	1.439	1.445	1.447
S(1)-N(1)	1.574	1.586	1.580	1.590	1.592	1.576
N(1)-Cl(1)	–	1.748	1.759	1.750	1.750	1.748
Na(1)-O(2)	–	2.350	2.353	2.365	2.303	2.341
C(2)-C(1)-S(1)	124.1	122.3	120.4	–	120.5	123.7
C(6)-C(1)-S(1)	117.1	117.3	119.3	–	119.1	117.8
O(1)-S(1)-O(2)	118.8	114.5	115.6	116.1	115.5	115.2
O(1)-S(1)-N(1)	105.9	114.9	115.0	–	115.5	115.0
O(2)-S(1)-N(1)	104.9	103.9	103.3	103.6	103.9	104.6
O(1)-S(1)-C(1)	109.1	104.8	106.2	105.8	107.5	108.3
O(2)-S(1)-C(1)	108.4	108.8	108.3	103.3	105.9	103.9
N(1)-S(1)-C(1)	109.4	109.9	108.1	109.6	108.5	109.7
S(1)-N(1)-Cl(1)	–	110.2	109.7	110.9	110.0	110.6
S(1)-O(1)-Na(1)	–	150.4	145.7	157.0	147.5	152.1

*3.2. Structure of the Sodium Salt of N-Chloro-2-methyl-4-chloro-benzenesulphonamide (**NaNC2M4CBSA**)*

The crystal structure of the title compound is similar to those obtained for the sodium salts of *N*-chloro-4-chloro-benzenesulphonamide and *N*-chloro-4-methyl-benzenesulphonamide and *N*-chloro-2,4-dichloro-benzenesulphonamide [28, 29]. In particular, the structure of the compound is complex like those of other *N*-chloro-arylsulphonamides. Further, the structure confirms that there is no interaction between the nitrogen and sodium atoms in the molecule, and Na^+ is attached to one of the sulphonyl oxygen atoms. Na^+ coordination sphere involves oxygen atoms from water molecules of crystallization and neighbouring molecules. The S-N distance of 1.586 Å in **NaNC2M4CBSA** is in agreement with those of similar compounds [28, 29] and consistent with a S-N double bond. Na^+ ion coordination in the structure is also similar giving rise to several hydrogen bonds between water hydrogen, oxygen and nitrogen or chlorine atoms. The molecules are held together by hydrogen bonds between coordinated water molecules and other atoms as shown in Figs. 2 and 3. The hydrogen bond distances vary in the range 2.12 to 2.85 Å (Table 5).

The orientation of Cl attached to the amine nitrogen atom with respect to the phenyl ring is given by the torsion angle Cl(1)-N(1)-S(1)-C(1), −60.0°, and the orientations of the amine nitrogen atom and sulphonyl oxygen atoms are given by the torsional angles C(6)-C(1)-S(1)-N(1), 126.7°; C(2)-C(1)-S(1)-N(1), −52.2°; C(6)-C(1)-S(1)-O(2), −120.1°; C(2)-C(1)-S(1)-O(2), 61.0°; C(6)-C(1)-S(1)-O(1), 2.7°; C(2)-C(1)-S(1)-O(1), −176.2°. The orientation of Na with respect to the phenyl ring is given by the torsion angle Na(1)-O(1)-S(1)-C(1), 166.7°. The orientation between the Cl attached to the amine nitrogen atom and sulphonyl oxygen atoms are given by the torsional angles Cl(1)-N(1)-S(1)-O(2), −176.3° and Cl(1)-N(1)-S(1)-O(1), 57.9°.

4. Comparisons and Conclusions

The effect of *N*-chlorination and substitution of the phenyl ring on the structural data have been considered by comparing the bond lengths and bond angles of **NaNC2M4CBSA** with those of **2M4CBSA** and the sodium salts of *N*-chloro-benzenesulphonamide [29d], *N*-chloro-4-methyl-benzenesulphonamide [28], *N*-chloro-4-chloro-benzenesulphonamide [29b], and *N*-chloro-2,4-dichloro-benzenesulphonamide [29c] (Table 7).

Comparison of the bond lengths revealed that *N*-chlorination of **2M4CBSA** increased the C-S, S-O and S-N bond lengths marginally. Introduction of a substituent into the ring generally increased C-S and S-N bond lengths marginally, while one of the

S-O bond lengths decreased marginally and the other increased. The N-Cl bond length decreased marginally. Substitution of an electron-donating group increased the Na-O bond length, while the electron-withdrawing groups decreased it.

Comparison of the bond angles showed that *N*-chlorination of **2M4CBSA** decreased the bond angle C(2)-C(1)-S(1), while C(6)-C(1)-S(1) remained more or less the same. *N*-Chlorination also decreased the O(1)-S(1)-O(2) bond angle and increased O(1)-S(1)-N(1) substantially, while decreasing marginally the other bond angle O(2)-S(1)-N(1). O(1)-S(1)-C(1) is also decreased by *N*-chlorination, while the other two bond angles, O(2)-S(1)-C(1) and N(1)-S(1)-C(1), are little affected. Ring substitution also showed mixed effects.

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[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 R. V. Rao, J. Chem. Soc. Perkin Trans. **2**, 355 (1988).
[5] B. T. Gowda and J. I. Bhat, Tetrahedron **43**, 2119 (1987).
[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 P. J. M. Rao, Bull. Chem. Soc. Jpn. **62**, 3303 (1989).
[9] B. T. Gowda, J. D. D'Souza, and K. R. Bhat, J. Indian Chem. Soc. **78**, 412 (2002).
[10] B. T. Gowda and M. Shetty, J. Phys. Org. Chem. **17**, 848 (2004).
[11] M. Shetty and B. T. Gowda, Z. Naturforsch. **59b**, 63 (2004).
[12] B. T. Gowda, N. Damodara, and K. Jyothi, Int. J. Chem. Kinet. **37**, 572 (2005).
[13] K. M. Usha and B. T. Gowda, J. Chem. Sci. **118**, 351 (2006).
[14] B. T. Gowda, J. D. D'Souza, and H. Fuess, Z. Naturforsch. **58a**, 220 (2003).
[15] B. T. Gowda, K. Jyothi, and J. D. D'Souza, Z. Naturforsch. **57a**, 967 (2002).
[16] B. T. Gowda, J. D. D'Souza, and B. H. A. Kumar, Z. Naturforsch. **58a**, 51 (2003).
[17] B. T. Gowda and K. M. Usha, Z. Naturforsch. **58a**, 351 (2003).
[18] B. T. Gowda, K. Jyothi, and N. Damodara, Z. Naturforsch. **58a**, 563 (2003).
[19] K. Jyothi and B. T. Gowda, Z. Naturforsch. **59a**, 64 (2004).
[20] B. T. Gowda, K. L. Jayalakshmi, and M. Shetty, Z. Naturforsch. **59a**, 239 (2004).
[21] K. L. Jayalakshmi and B. T. Gowda, Z. Naturforsch. **59a**, 491 (2004).
[22] B. T. Gowda, M. Shetty, and K. L. Jayalakshmi, Z. Naturforsch. **60a**, 106 (2005).
[23] M. Shetty and B. T. Gowda, Z. Naturforsch. **60a**, 113 (2005).
[24] S. M. Basappa and B. T. Gowda, Z. Naturforsch. **61a**, 600 (2005).
[25] B. T. Gowda, K. Jyothi, J. Kožíšek, and H. Fuess, Z. Naturforsch. **58a**, 656 (2003).
[26] S. V. Kumar, S. E. Senadhi, and M. Leela, Z. Kristallogr. **202**, 1 (1992).
[27] P. G. Jones and A. Weinkauf, Z. Kristallogr. **208**, 128 (1997).
[28] M. M. Olmstead and P. P. Power, Inorg. Chem. **25**, 4057 (1986).
[29] a) B. T. Gowda, R. Nayak, J. Kozisek, M. Tokarcik, and H. Fuess, Acta Cryst. E **63**, o2967 (2007). b) B. T. Gowda, K. Jyothi, J. Kozisek, M. Tokarcik, and H. Fuess, Acta Cryst. E **63**, m1644 (2007). c) B. T. Gowda, M. B. Savitha, J. Kozisek, M. Tokarcik, and H. Fuess, Acta Cryst. E **63**, m1646 (2007). d) B. T. Gowda et al., unpublished results (sodium *N*-chlorobenzenesulphonamide).
[30] Oxford Diffraction, 'CrysAlis CCD', Oxford Diffraction Ltd., Abingdon, Oxfordshire, England 2002.
[31] Oxford Diffraction (2002), 'CrysAlis RED-CCD', Oxford Diffraction Ltd., Abingdon, Oxfordshire, England 2002.
[32] M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany 1997.
[33] M. Sheldrick, SHELXL-97, Program for Crystal Structure Determination, University of Göttingen, Germany 1997.
[34] L. Spek, PLUTON-2003, Program for the Display and Analysis of Crystal and Molecular Structures, University of Utrecht, The Netherlands 2003.
[35] C. T. North, D. C. Philips, and F. S. Mathews, Acta Cryst. **24A**, 351 (1968).
[36] D. Flack, Acta Cryst. **39A**, 876 (1983).