

The O-Na Interaction and Octahedral Geometry around Sodium Moiety in Sodium Salt of N-bromo-4-methylbenzenesulphonamide

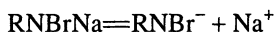
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The crystal structure of bromamine-T, an important brominating/oxidising agent, which crystallizes in the triclinic space group $P\bar{1}$, has been solved using DIFDIF programme and refined using SHELXL. Bond lengths, bond angles and packing are reported and discussed.

INTRODUCTION

The diverse nature of aromatic sulphonyl haloamines is due to their ability to act as sources of halonium cations, hypohalite species and N-anions which act as both bases and nucleophiles. As a result, these reagents react with a wide range of functional groups effecting an array of molecular transformations. Bromamine-T (BAT) or sodium salt of N-bromo-4-methylbenzenesulphonamide is extensively used as a brominating/oxidising agent in synthetic organic chemistry and reaction kinetics. Also, BAT is widely used in the analytical determination of various organic and inorganic substrates. The crystal and molecular structure studies of chloramine-T (CAT)¹, chloramine-B (CAB)², bromamine-B (BAB)³, dibromamine-B (DBB)³, dichloramine-T (DCT)³, dichloramine-B (DCB)³ and dibromamine-T (DBT)⁴ have already been reported. Recently, we have reported the photolysis of BAT⁵.

BAT is analogous to CAT in aqueous solution and behaves like a strong electrolyte dissociating as:



where R = H₃C—C₆H₄SO₂.

BAT undergoes a two-electron change in its oxidation reactions. The formal redox potential of the BAT/RNH₂ couple is found to be +1.60 V at 298 K.

In view of the importance of bromamine-T as an oxidising agent and in continuation of our work on organic haloamines, the present paper reports the crystal and molecular structure studies of bromamine-T (BAT).

EXPERIMENTAL

Bromamine-T was prepared⁶ by the partial debromination of dibromamine-T,

which in turn was prepared by the bromination of chloramine-T (Aldrich). Pale yellow crystals of BAT were obtained by recrystallization using methanol (available bromine content: found 24.50%; theoretical, 24.52%). Further, BAT was characterized by spectral studies.

(i) UV: $\lambda_{\max}(\text{H}_2\text{O}) = 224 \text{ nm}$

(ii) IR (nujol): $\nu(\text{OH}) = 3500$, $\nu_{\text{asym}}(\text{SO}_2) = 1235$, $\nu_{\text{sym}}(\text{SO}_2) = 1120$, $\nu(\text{S—N}) = 915$ and $\nu(\text{N—Br}) = 665 \text{ cm}^{-1}$.

(iii) ^1H spectrum (CDCl_3): δ (relative to TMS): 2.42 (singlet corresponding to $-\text{CH}_3$), 7.84 (doublet for *ortho* H), 7.42 (doublet for *meta* H), $J_{o,m}$ is 8.0 Hz.

(iv) ^{13}C spectrum (CDCl_3): ppm (relative to TMS): 145.39 (C-1), 140.5 (C-4), 131.75 (C-2,6), 129.40 (C-3,5) and 23.0 (methyl carbon).

(v) Electron impact mass spectrum: m/e : 326 (m^+), 171 ($\text{H}_3\text{C—C}_6\text{H}_4\text{SO}_2\text{NH}_2^+$), 155 ($\text{H}_3\text{C—C}_6\text{H}_4\text{SO}_2^+$) and 91 ($\text{H}_3\text{C—C}_6\text{H}_4^+$).

A pale yellow crystal of dimension $0.1 \times 0.1 \times 0.15 \text{ mm}$ was selected for X-ray data collection. All measurements were made on a Rigaku AFC 7S diffractometer with graphite monochromated $\text{Cu—K}\alpha$ radiation. The data were collected at a temperature of 293 K using the ω - 2θ scan technique. The structure was solved using DIRDIF⁷ programme and refined using SHELXL⁸. The function minimised throughout refinement was $\Sigma\omega(|F_0| - |F_c|)^2$ with $\omega = 1/\sigma^2(F_0)$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of all the three H_2O molecules were allowed to refine as isotropic atoms. The phenyl ring hydrogens were refined by use of a riding model on the bonded carbon and free thermal parameters. The methyl hydrogens are subject to very large thermal motion and were included in the structure factor calculation at fixed positions obtained from a difference map with free thermal parameters.

RESULTS AND DISCUSSION

Crystal data and structure refinement details are given in Table-1. Table-2 gives the atomic coordinates and equivalent isotropic displacement parameters. Anisotropic displacement parameters for non-hydrogen atoms of BAT are given in Table-3. Table-4 shows some important bond lengths and bond angles.

X-ray crystallographic study of bromamine-T indicates that there is no interaction between nitrogen and sodium. Instead, the Na^+ ion interacts with one of the sulphonyl oxygens and a bromine from a neighbouring ion. The remainder of the octahedral Na^+ coordination sphere involves oxygens from water of crystallization. The structure of BAT is therefore closer to the formulation **B** than to its more common representation **A** as shown in Fig. 1. Fig. 2 represents the ORTEP diagram of the BAT molecule with thermal ellipsoids at 50% probability. A computer generated drawing of a centrosymmetric dimer is shown in Fig. 3. Figures 4 and 5 show the packing of the molecules down 'a' axis and down 'c' axis respectively.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT DETAILS

Empirical formula	C ₇ H ₇ BrNNaO ₂ S·3H ₂ O
Formula weight	326.10
Temperature	293(2) K
Wavelength	1.54184 Å
θ range for cell determination	3.17 to 35.27°
Crystal system	Triclinic
Space group	P $\bar{1}$
Cell dimensions	a = 7.5121(4) Å, b = 14.074(4) Å, c = 6.331(2) Å, α = 96.33(2)°, β = 105.92(2)° and γ = 84.24(2)°.
Volume	638.0(3) Å ³
Z	2
Density (calculated)	1.666 g cm ⁻³
Absorption coefficient (μ)	6.344 cm ⁻¹
F ₀₀₀	316
Crystal size	0.1 × 0.1 × 0.15 mm
θ range for data collection	3.17 to 70°
Index ranges	0 ≤ h ≤ 8, -15 ≤ k ≤ 16, -7 ≤ l ≤ 7
Reflections collected/Unique	1876/1594 [R (int) = 0.1380]
Absorption correction	Semiempirical absorption correction ⁹ based on ψ-scan
Refinement method	Full-matrix least-squares on F ²
Data/Restraints/Parameters	1594/0/166
Goodness-of-fit on F ²	1.021
Final R indices [I > 2σ(I)]	R ₁ = 0.08234 ωR ₂ = 0.1823
R indices (all data)	R ₁ = 0.09132 ωR ₂ = 0.2032
Extinction coefficient	0.009(2)
Largest diff. peak and hole	0.315 and -0.313e Å ⁻³
Maximum shift (Δ)/σ	0.034

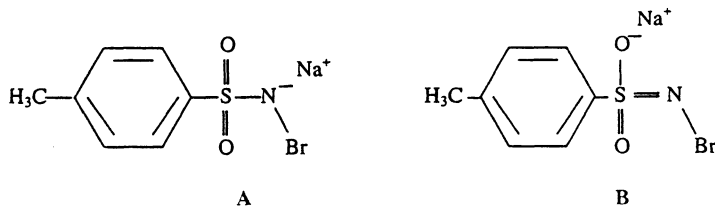


Fig. 1. Structures of Bromamine-T

TABLE-2
 ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT
 PARAMETERS ($\text{\AA}^2 \times 10^3$)

U(eq) is defined as one-third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U(eq)
C(1)	-2260(30)	1326(11)	3250(40)	107(6)
C(2)	-2500(30)	-285(10)	2690(30)	90(4)
C(3)	-3150(40)	482(15)	3940(30)	119(8)
C(4)	-3370(30)	1379(12)	3360(30)	95(5)
C(5)	-2941(15)	1576 (8)	1563(17)	57(3)
C(6)	-2390(30)	857(10)	250(30)	84(4)
C(7)	-2160(30)	-113(11)	890(30)	98(5)
S(8)	-3142 (4)	2770 (2)	860(5)	60(1)
O(9)	-3311(15)	2689 (7)	-1468(14)	76(3)
O(10)	-4694(14)	3259 (7)	1546(18)	79(3)
Na(11)	-6511 (6)	4560 (3)	2637 (7)	60(2)
O(12)	-8080(20)	4761(10)	-1070(20)	62(3)
O(13)	-5727(16)	4257 (8)	6320(20)	68(3)
O(14)	-8543(15)	5979 (7)	3336(14)	63(2)
N(15)	-1425(17)	3306 (7)	2363(19)	69(3)
Br(16)	808 (2)	2814 (1)	1762 (3)	79(1)

TABLE-3
 ANISOTROPIC DISPLACEMENT PARAMETERS ($\text{\AA}^2 \times 10^3$) FOR NON-HYDROGEN
 ATOMS OF BAT

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	177(18)	42(9)	115(13)	31(9)	42(12)	30(8)
C(2)	136(13)	40(7)	103(11)	20(7)	31(9)	33(7)
C(3)	200(20)	93(13)	88(11)	75(14)	66(12)	-1(10)
C(4)	173(16)	55(8)	78(9)	31(9)	59(9)	8(7)
C(5)	72(6)	37(6)	64(6)	29(4)	16(4)	5(4)
C(6)	144(13)	36(6)	83(9)	-2(7)	54(8)	2(6)
C(7)	154(16)	39(7)	116(13)	7(8)	60(11)	20(8)
S(8)	80(2)	35(2)	72(2)	17(1)	25(1)	0(1)
O(9)	118(7)	54(5)	61(5)	33(4)	21(4)	16(4)
O(10)	81(6)	51(5)	105(7)	10(4)	30(4)	-4(5)
Na(11)	73(3)	46(3)	65(3)	26(2)	17(2)	3(2)
O(12)	68(7)	56(6)	64(6)	20(5)	14(5)	3(4)
O(13)	81(5)	49(5)	84(7)	23(4)	28(5)	13(5)
O(14)	75(6)	53(5)	65(5)	25(4)	21(4)	4(4)
N(15)	99(7)	40(5)	76(6)	36(5)	27(5)	-1(4)
Br(16)	85(2)	57(2)	102(2)	21(1)	27(1)	12(1)

TABLE-4
BOND LENGTHS (Å) AND BOND ANGLES (°) OF BAT

C(1)–C(2)	1.526(7)	C(7)–C(2)–C(3)	118.1(7)
C(2)–C(7)	1.290(2)	C(7)–C(2)–C(1)	117.4(8)
C(2)–C(3)	1.400(3)	C(3)–C(2)–C(1)	124.5(8)
C(3)–C(4)	1.340(2)	C(4)–C(3)–C(2)	122.1(8)
		C(5)–C(4)–C(3)	120.7(8)
C(4)–C(5)	1.328(7)	C(4)–C(5)–C(6)	119.4(8)
C(5)–C(6)	1.341(8)	C(4)–C(5)–S(8)	120.5(5)
C(5)–S(8)	1.767(9)	C(6)–C(5)–S(8)	120.1(5)
C(6)–C(7)	1.450(2)	C(5)–C(6)–C(7)	119.7(7)
S(8)–O(9)	1.437(9)	C(2)–C(7)–C(6)	120.0(8)
S(8)–O(10)	1.440(9)	O(9)–S(8)–O(10)	115.9(3)
S(8)–N(15)	1.582(8)	O(9)–S(8)–N(15)	115.7(3)
O(10)–Na(11)	2.330(8)	O(10)–S(8)–N(15)	103.4(4)
		O(9)–S(8)–C(5)	104.9(4)
Na(11)–O(12)	2.353(8)	O(10)–S(8)–C(5)	107.4(3)
Na(11)–O(13)	2.322(8)	N(15)–S(8)–C(5)	109.1(6)
Na(11)–O(14)	2.466(7)	S(8)–O(10)–Na(11)	156.9(4)
Na(11)–Br(16)	3.237(4)	O(13)–Na(11)–O(10)	95.5(3)
Na(15)–Br(16)	1.870(6)	O(13)–Na(11)–O(12)	164.9(3)
		O(10)–Na(11)–O(12)	90.4(3)
		O(13)–Na(11)–O(14)	91.2(3)
		O(10)–Na(11)–O(14)	173.3(3)
		O(12)–Na(11)–O(14)	83.0(3)
		S(8)–N(15)–Br(16)	112.2(3)

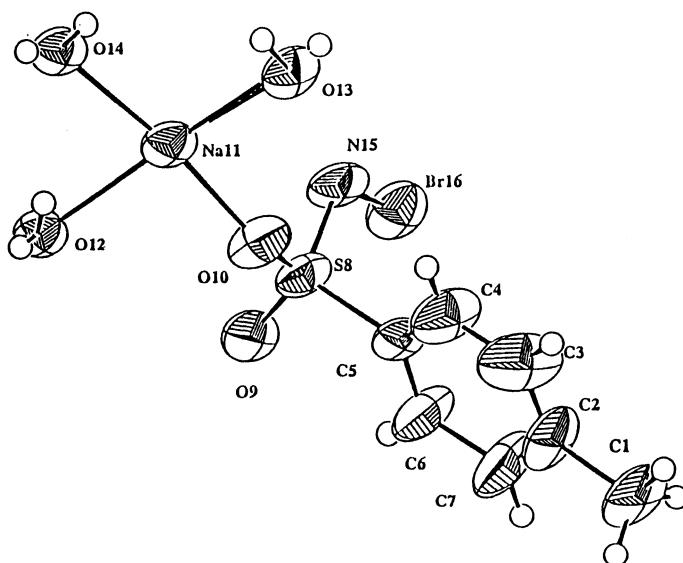


Fig. 2. ORTEP of the molecule at 50% probability

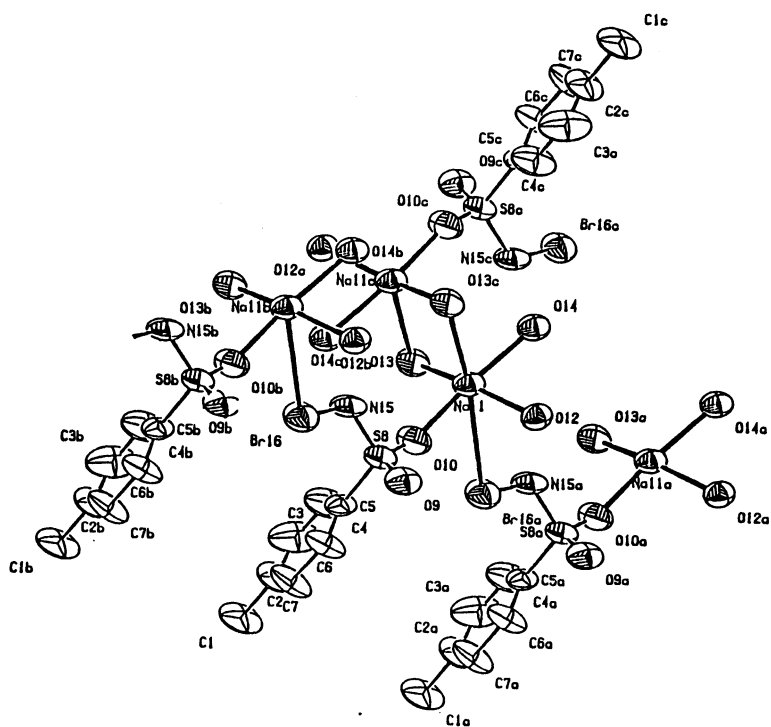


Fig. 3. Computer-generated drawing of a centrosymmetric dimer. Hydrogen atoms are not shown for clarity. Octahedral geometry around Na(11) is fairly seen.

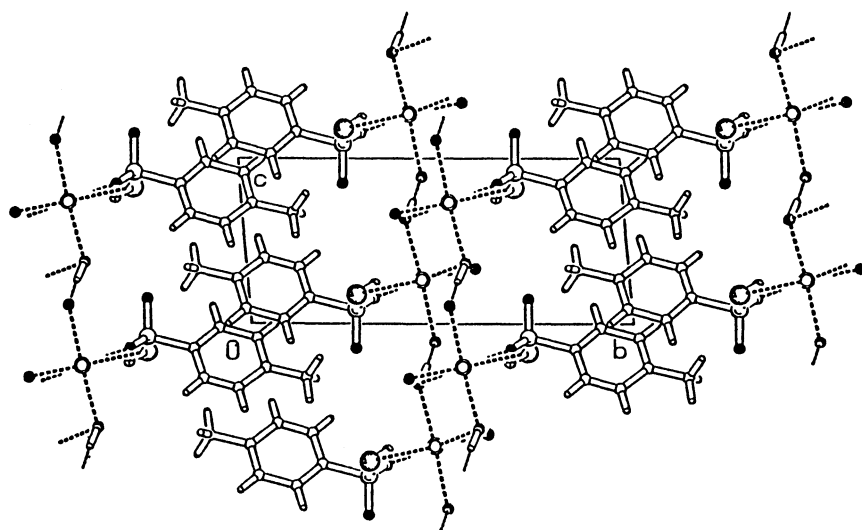


Fig. 4. Packing of the molecules down a-axis.

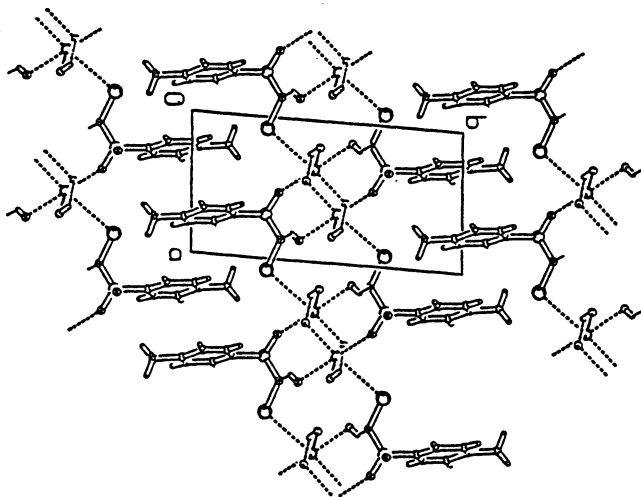


Fig. 5. Packing of the molecules down c-axis.

The crystal structure shows the dominant motif which can be described as an aquo-bridged sodium dimer ($\text{Na}(11)\text{--O}(12), \text{Na}(11)\text{--O}(13) = 2.353(8), 2.322(8)$ Å). In addition to the bridging of water molecules, the halves of the dimer are held together by a hydrogen bond between a coordinated molecule and the amido nitrogen. The sixth coordination site on each sodium is occupied by the bromine of a neighbouring dimer, obtained by a unit translation ($\text{Na}(11b)\text{--Br}(16) = 3.237(5)$ Å).

A different dimer, related by inversion, provides additional hydrogen bonds to $\text{N}(15), \text{O}(9), \text{O}(12)$ and $\text{O}(14)$. Thus each hydrogen belonging to a water molecule is involved in some type of hydrogen bonding, while each water oxygen, as well as the nitrogen atom, has two hydrogen-bonded contacts. In addition, $\text{O}(9)$, a sulphonyl oxygen, has two hydrogen bonds, but $\text{O}(10)$ has none, as it is involved in coordination to the sodium. The “*N-Sodio*” interaction is clearly a misnomer, at least in the solid state. The closest $\text{N}(15) \dots \text{Na}(11)$ distance is $4.0845(4)$ Å and it involves the nitrogen bonded to the coordinated bromine. Furthermore, the octahedral set of five oxygens and one bromine surrounding each sodium precludes the close approach of a nitrogen atom.

The $\text{N}(15)\text{--Br}(16)$ distance of $1.870(6)$ Å is comparable with that found in DBT, DBB and BAB structures. The $\text{S}(8)\text{--O}(9)$ and $\text{S}(8)\text{--O}(10)$ distances are $1.437(9)$ and $1.440(9)$ Å respectively, which are well within the range of those reported for similar molecules. The slightly longer $\text{S}(8)\text{--O}(10)$ bond length is presumably due to hydrogen bonding to $\text{O}(10)$, but not to $\text{O}(9)$. The octahedral geometry around sodium is fairly regular. The five $\text{Na}(11)\text{--O}$ bonds range from $2.330(8)$ to $2.466(7)$ Å.

As per our knowledge, the structure of RSO_2NBr^- grouping is reported here for the *second time* (first time in BAB). Support of formulation **B** for the structure

of its sodium salt comes from three major structural features: (i) the only interaction between sodium and the SO₂N moiety involves a Na—O rather than Na—N contact. (ii) The S—N distance 1.582(8) Å is consistent with a double bond rather than a single bond. (iii) Aggregation is a result of the tendency of the Na⁺ ion to achieve six coordination which it does through coordination to one sulphonyl oxygen only; two bridging and two terminal waters and a bromine from another BAT molecule comprise the rest of the coordination sphere. This in turn gives rise to several hydrogen bonding contacts between water hydrogens, oxygen and nitrogen atoms. Clearly, then the aggregation seems to have no significant effect on the structure of the [MeC₆H₄SO₂NBr]⁻ ion. *The molecules are stacked in layers with parts of phenyl rings separated by water and sodium groups. Stacking of molecules one above the other along c-axis can be seen. Octahedral geometry of sodium moiety can be observed in both a and c axes. Also, from the packing diagrams, we can observe that BAT has infinite lattice. Hence, it generates multiple number of molecules.*

Finally, we can conclude that the best description of bromamine-T is that its structure is close to that depicted in **B** rather than its more common representation of **A** as shown in Fig. 1.

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