

Hydrogen Bond Studies. XLIX.* The Crystal Structure of 2,5-Dibromobenzenesulphonic Acid Trihydrate, $\text{H}_7\text{O}_3^+\text{C}_6\text{H}_3\text{Br}_2\text{SO}_3^-$

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The crystal structure of 2,5-dibromobenzenesulphonic acid trihydrate has been determined from three-dimensional single-crystal X-ray diffraction data recorded using a Stoe-Philips two-circle Weissenberg diffractometer. The crystals are monoclinic, space group $P2_1/c$, with four formula units in a cell of dimensions: $a=7.040$, $b=7.656$, $c=22.157$ Å, $\beta=96.73^\circ$. The structure comprises oxonium ions tightly bonded to two water molecules to form H_7O_3^+ ions. The O-H...O distances within the ion are 2.458 and 2.484 Å. The H_7O_3^+ ions and 2,5-dibromobenzenesulphonate ions are hydrogen-bonded together to form layers. No hydrogen bonds exist between individual H_7O_3^+ ions.

Introduction

This work is part of a systematic study of the solid hydrates of strong acids currently in progress at this Institute. Other investigations in this series have demonstrated the presence of a dihydrated proton, H_5O_2^+ , in several hydrates of inorganic acids ($\text{HCl}\cdot 2\text{H}_2\text{O}$, $\text{HCl}\cdot 3\text{H}_2\text{O}$, Lundgren & Olovsson, 1967*a*, *b*; $\text{HClO}_4\cdot 2\text{H}_2\text{O}$, Olovsson, 1968; $\text{HBr}\cdot 2\text{H}_2\text{O}$, $\text{HBr}\cdot 3\text{H}_2\text{O}$, Lundgren, 1970; $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, Kjällman & Olovsson, 1970). Cases in which it has been possible to describe the bonding situation in terms of higher hydrates of the oxonium ion, e.g. H_7O_3^+ and H_9O_4^+ are so far rare in the solid state ($\text{HBr}\cdot 4\text{H}_2\text{O}$, Lundgren & Olovsson, 1968; $\text{HClO}_4\cdot 3\text{H}_2\text{O}$, Almlöf, 1972). It would thus appear that further studies of similar hydrates would be of interest. The structure determination of 2,5-dibromobenzenesulphonic acid trihydrate reported in the present paper is based on single-crystal X-ray diffraction data collected at room temperature.

Crystal data

2,5-Dibromobenzenesulphonic acid trihydrate,
 $\text{C}_6\text{H}_3\text{Br}_2\text{SO}_3\text{H}\cdot 3\text{H}_2\text{O}$
 F.W. 370.03. Monoclinic,
 $a=7.040$ (2),[†] $b=7.656$ (1), $c=22.157$ (2) Å,
 $\beta=96.73$ (2)°,
 $V=1186.0$ Å³ at 22°C.
 $Z=4$,
 $D_x=2.072$ g.cm⁻³.
 Space group $P2_1/c$.

Experimental

2,5-Dibromobenzenesulphonic acid was made from *p*-dibromobenzene and fuming sulphuric acid fol-

lowing a method described by de Crauw (1931) for synthesizing the corresponding chlorocompound.

The trihydrate was crystallized from an aqueous solution of the acid. The crystals form well-shaped rods. A crystal of dimensions $0.15\times 0.15\times 0.135$ mm was cut from a larger crystal and was mounted in a thin-walled glass capillary with four crystal faces parallel to the capillary axis. If the crystal is not protected in this way it will lose some of its water to the atmosphere within a few hours.

The intensity data were recorded at room temperature on a Stoe-Philips Automated X-ray 2-Circle Diffractometer using $\text{Cu } K\alpha$ radiation and an ω - 2θ scan technique. This is not to be confused with the more common ω - 2θ scan technique as used on a four-circle diffractometer. Different combinations of scan-time and filter selection were used to reduce all reflexions to an approximately common scale. Seven layers, $0\leq h\leq 6$, were recorded, giving a total of 2089 independent reflexions. This number corresponds to about 77% of the reflexions within the copper reflexion sphere. 522 reflexions with $I<2\sigma(I)$, where $\sigma(I)$ is based on counting statistics, were considered to be insignificantly different from the background and thus given zero weight in the refinements. The intensities of the 200 and $20\bar{2}$ reflexions were very large and thus considered to be less accurately measured. For this reason their values were used only when the structure was solved and were otherwise given zero weight.

The data were corrected for the Lorentz, polarization, absorption and secondary extinction effects. The linear absorption coefficient for $\text{Cu } K\alpha$ radiation is 113.1 cm⁻¹. The minimum and maximum values of the transmission factors were 0.1947 and 0.3674 respectively.

The cell dimensions were determined from quartz-calibrated oscillation photographs taken using a Weissenberg camera and $\text{Cu } K\alpha$ radiation [$\lambda(\text{Cu } K\alpha_1)=1.54051$, $\lambda(\text{Cu } K\alpha_2)=1.54433$ Å, $a_{\text{SiO}_2}=4.9131$ Å]. The cell parameters were fitted to the measured θ values by a least-squares procedure using the program *CELSIUS*.

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† Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

This and other programs mentioned in the following are described briefly by Liminga (1967) and Nahringsbauer (1967).

Space group and structure determination

The intensity data indicated the space group Pc or $P2/c$ (Nos. 7 or 13 respectively, *International Tables for X-ray Crystallography*, 1952).

The coordinates of the bromine atoms were determined from a three-dimensional Patterson synthesis and the positions of the other heavy atoms were derived from subsequent electron-density calculations. The positions of the atoms so determined were consistent with the centrosymmetric space group $P2/c$. All the atoms occupy the general fourfold positions of this space group.

The atomic coordinates were first refined in a series of electron-density calculations using the program *DRF*. The scale factor, atomic coordinates and individual isotropic thermal parameters were thereafter refined in a series of least-squares calculations. The refinement ceased to converge at a rather high R value, 0.197. The discrepancy index is defined as $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ (zero-weight data not included) The R value including zero-weight data is given in parenthesis.

A few cycles of refinement with anisotropic thermal parameters included lowered the R value drastically to 0.055 (0.084). The number of parameters in the anisotropic refinement was 136 compared with 61 in the isotropic refinement. The number of reflexions with non-zero weight was 1558. A difference Fourier synthesis calculated at this stage showed three well-resolved peaks corresponding to the hydrogen atoms bonded to the carbon ring. The hydrogen atoms of the water molecules could not be located in the electron density maps. The hydrogen atoms of the carbon ring were placed at 1.06 Å from the carbon atoms in the plane of the ring and with the angle C-C-H equal to 120°. An anisotropic least-squares refinement with these hydrogen atoms included with fixed parameters lowered R to 0.054. The hydrogen atoms were given a Debye-Waller factor of $B = 5.0 \text{ \AA}^2$.

Extinction correction was then applied according to the formula given by Zachariasen (1963). The constant in this formula was determined from the 21 strongest reflexions. The subsequent anisotropic refinement gave the final R value 0.048 (0.077). In the last cycle the shifts on the parameters were less than one tenth of the estimated standard deviations.

A series of refinements using the non-centrosymmetric space group Pc was also made. The trial parameters were those obtained in the isotropic refinement using $P2/c$ with the atoms moved somewhat away from their centrosymmetric positions. The isotropic refinement did not improve beyond $R = 0.188$. Further cycles of anisotropic refinement lowered the R value to 0.049. The number of parameters refined was 269.

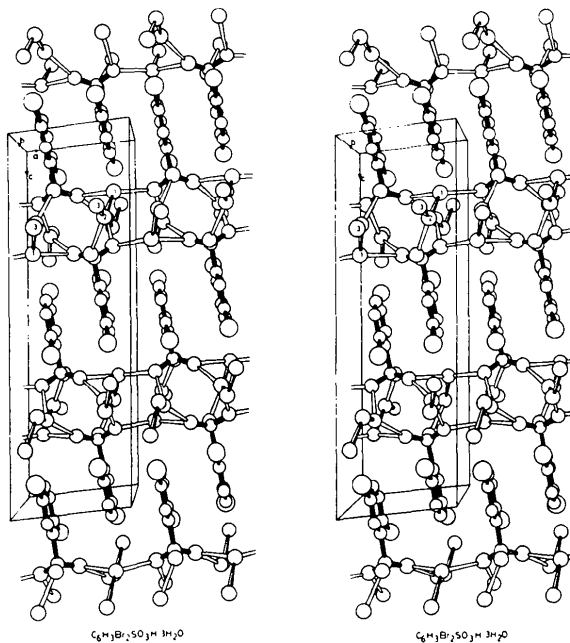


Fig. 1. Stereoscopic drawing of the crystal structure of $H_7O_3^+ C_6H_3Br_2SO_3^-$. The structure is viewed along the b axis. The oxygen atoms of the $H_7O_3^+$ ion are denoted by 1, 2 and 3. Covalent bonds are filled. Hydrogen bonds within $H_7O_3^+$ are half filled and other hydrogen bonds are open.

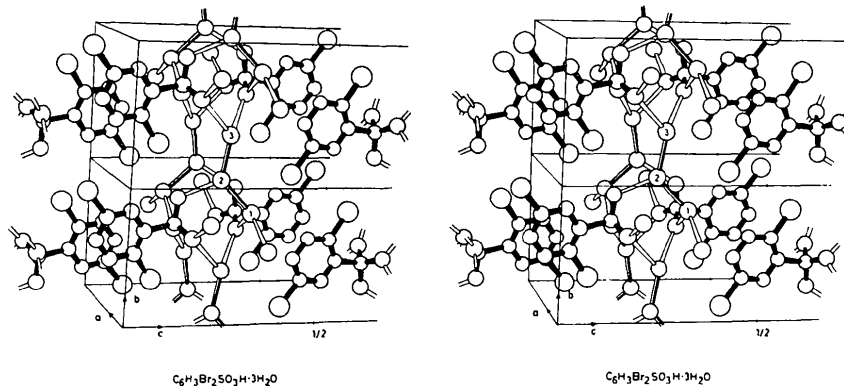


Fig. 2. Stereoscopic drawing showing in particular the bonding coordination of the $H_7O_3^+$ ion. For notation see Fig. 1.

Table 1. Atomic coordinates with estimated standard deviations ($\times 10^5$)

	x	y	z
Br(1)	30666 (15)	25579 (11)	9499 (4)
Br(2)	19836 (15)	5546 (10)	42012 (4)
S	33659 (30)	33523 (21)	65095 (7)
O(1)	34759 (91)	14523 (62)	65736 (22)
O(2)	51594 (87)	42041 (69)	67048 (24)
O(3)	17913 (84)	41173 (68)	67929 (23)
C(1)	28958 (104)	37250 (87)	57184 (29)
C(2)	27495 (112)	54064 (89)	54698 (31)
C(3)	23765 (114)	56330 (94)	48430 (33)
C(4)	21469 (125)	41715 (106)	44675 (34)
C(5)	22875 (122)	25416 (91)	47217 (31)
C(6)	26499 (114)	22725 (82)	53388 (32)
O(W1)	15751 (149)	21999 (81)	82082 (34)
O(W2)	22164 (106)	1170 (73)	24739 (27)
O(W3)	25257 (86)	32698 (70)	26714 (25)
H(3)	23100	69600	47200
H(4)	18700	45000	40400
H(6)	28700	10500	55000

The least-squares program used accepts a maximum of 140 parameters in a full-matrix refinement. The parameters were therefore divided into two equal blocks which were then refined in different cycles. Atoms related by a centre of symmetry in $P2/c$ were put in the same block. The convergence of the refinement was slow and the shifts on the parameters remained relatively large and erratic even when the R value had stopped falling. The standard deviations were three to four times larger than for $P2/c$ and the temperature factor coefficients of some of the carbon atoms were of non-positive definite form. The molecular dimensions calculated from the parameters obtained in these refinements were also most unlikely, e.g. the C-C distances were in the range 1.33 to 1.58 Å as compared to 1.37 to 1.40 Å for $P2/c$. A satisfactory refinement could therefore not be performed successfully using the space group Pc (cf. Parthasarathy, Sime & Speakman, 1969).

Table 2. Anisotropic thermal parameters with estimated standard deviations ($\times 10^4$)

The form of the temperature factor is $\exp [-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. The r.m.s. components (R_i) of thermal displacement of the atoms along the ellipsoid axes are also listed ($\times 10^3$ Å).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Br(1)	431 (3)	91 (1)	25 (1)	4 (2)	18 (1)	6 (1)	162 (1)	246 (1)	327 (1)
Br(2)	443 (3)	141 (1)	18 (1)	-15 (2)	14 (1)	-12 (1)	182 (2)	231 (2)	331 (1)
S	296 (5)	87 (3)	13 (1)	-1 (4)	12 (1)	-1 (1)	161 (3)	177 (3)	271 (3)
O(1)	455 (19)	83 (8)	16 (1)	26 (15)	17 (5)	9 (4)	145 (12)	205 (10)	337 (7)
O(2)	340 (17)	136 (9)	20 (1)	2 (14)	3 (5)	-2 (4)	199 (8)	224 (8)	295 (8)
O(3)	335 (17)	148 (10)	19 (1)	-9 (14)	26 (5)	-9 (4)	188 (13)	223 (12)	293 (9)
C(1)	203 (18)	112 (11)	15 (1)	-13 (16)	8 (6)	-2 (4)	181 (12)	193 (12)	226 (11)
C(2)	253 (20)	102 (12)	18 (2)	-4 (17)	11 (6)	1 (5)	175 (11)	206 (11)	251 (11)
C(3)	255 (21)	118 (12)	19 (2)	2 (19)	11 (6)	14 (5)	166 (18)	229 (16)	257 (13)
C(4)	288 (23)	169 (15)	16 (1)	-1 (21)	16 (6)	8 (6)	187 (16)	232 (14)	270 (12)
C(5)	309 (23)	117 (12)	14 (1)	6 (20)	19 (6)	-2 (5)	177 (18)	189 (16)	281 (11)
C(6)	254 (21)	82 (11)	19 (2)	-12 (16)	20 (6)	5 (5)	149 (14)	211 (15)	262 (13)
O(W1)	326 (17)	150 (10)	22 (1)	8 (15)	22 (5)	5 (4)	208 (11)	225 (12)	287 (9)
O(W2)	877 (39)	134 (11)	37 (2)	-9 (24)	110 (11)	-1 (6)	197 (9)	228 (17)	493 (15)
O(W3)	513 (23)	128 (10)	25 (1)	-60 (18)	-8 (6)	2 (4)	186 (9)	241 (9)	370 (11)

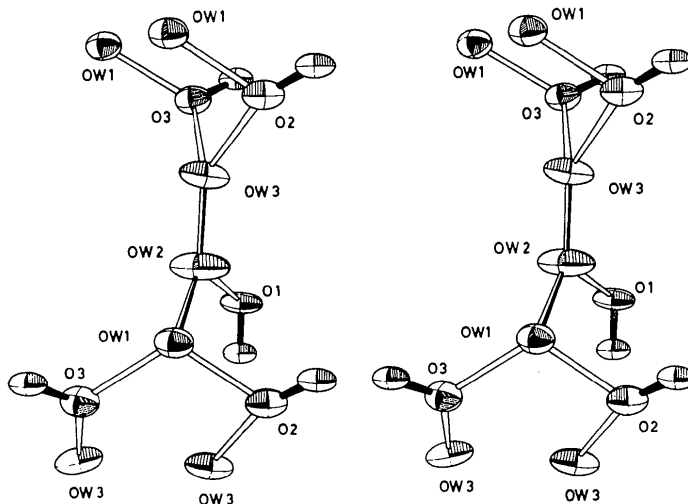


Fig. 3. The hydrogen-bond system around the $H_7O_3^+$ ion viewed along the c axis. The ellipsoids are scaled to enclose 50% probability. For notation see Fig. 1.

Table 3. Observed and calculated structure factors.

The columns are in order l , $10|F_o|$, $10|F_c|$. Reflexions marked with an asterisk were given zero weight in the refinement.

Table with multiple columns containing numerical data for structure factors. The table is organized into several vertical sections, each starting with a column of indices (e.g., 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 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The least-squares refinements were performed using the full-matrix program *LALS*, where the quantity $\sum w(|F_o| - |F_c|)^2$ is minimized. The weights were calculated according to the expression $w = 1/(a + |F_o| + c|F_c|^2)$. The final values used for the parameters a and c were 200.0 and 0.012 respectively. A weight analysis showed that these values were satisfactory. The atomic scattering factors used were those for neutral Br, S, O and C given in the *International Tables for X-ray Crystallography* (1962, p. 202). The spherical scattering factor used for the hydrogen atoms was that proposed by Stewart, Davidson & Simpson (1965). All calculations were carried out on the CDC 3600 computer in Uppsala.

The atomic parameters from the final refinement in $P2/c$ are listed in Tables 1 and 2. The root-mean-square

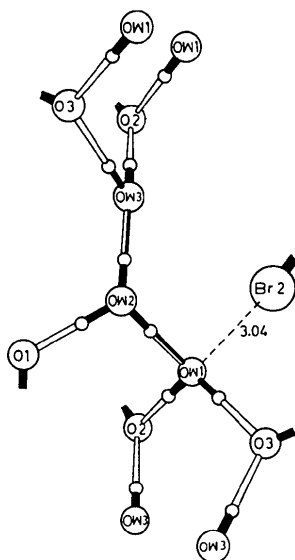


Fig. 4. The assignment of the hydrogen atoms to the bonds. The hydrogen atoms are indicated schematically on the lines connecting the heavy atoms and at 1.0 Å from the hydrogen donor.

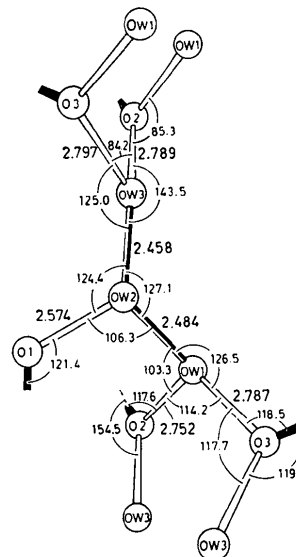


Fig. 5. Distances and angles involving hydrogen bonds. The orientation is approximately the same as in Fig. 2. For the notation of the bonds see Fig. 1. Standard deviations of the angles are 0.3–0.4°.

components of thermal displacement along the principal axes of vibration are given in Table 2. Observed and calculated structure factors are listed in Table 3.

Description of the structure

The structure is illustrated in Figs. 1, 2 and 3. Bond distances and angles are shown in Figs. 4, 5, 6 and 7. The bond distances are also listed in Table 4. The interatomic distances and angles have been calculated with the program *ORFFE*. Standard deviations have been estimated from the errors in the atomic coordinates obtained in the form of a variance-covariance matrix from the final cycle of refinement. The effect of uncertainties in the cell dimensions has also been taken into account. All illustrations in this paper have been prepared using the plotting program *ORTEP*.

Table 4. *Interatomic distances with estimated standard deviations*

Distances corrected for thermal riding motion are given within brackets.

Covalent bonds

C(1)–C(2)	1.399 (10) Å	C(2)–Br(1)	1.885 [1.901] (7) Å
C(2)–C(3)	1.394 (10)	C(5)–Br(2)	1.906 [1.920] (7)
C(3)–C(4)	1.392 (11)	C(1)–S	1.768 (7)
C(4)–C(5)	1.368 (11)	S—O(1)	1.463 [1.479] (5)
C(5)–C(6)	1.377 (10)	S—O(2)	1.442 [1.454] (6)
C(6)–C(1)	1.393 (10)	S—O(3)	1.459 [1.472] (6)
C(3)–H(3)	1.05		
C(4)–H(4)	0.98		
C(6)–H(6)	1.01		

Hydrogen bonds

O(W1)···O(2)	2.752 (9) Å	O(W3)···O(2)	2.789 (9)
O(W1)···O(3)	2.787 (9)	O(W3)···O(3)	2.797 (8)
O(W2)···O(1)	2.574 (8)		
O(W2)···O(W1)	2.484 (9)		
O(W2)···O(W3)	2.458 (9)		

The only hydrogen atoms located experimentally in this investigation were those bonded to the carbon ring. The hydrogen bonds have therefore been derived from interatomic distances and angles involving heavy atoms only.

The structure is made up both of oxonium ions tightly bonded to two water molecules and of 2,5-dibromobenzenesulphonate ions. The oxonium ions, water molecules and sulphonate groups are hydrogen bonded together to form layers parallel to the *ab* plane. The carbon rings point outwards from these layers alternately in the positive and negative *c* direction (see Fig. 1). The angle between the plane of the carbon ring and the *bc* plane is 11.0°. The shortest contact between different hydrogen bonded layers occurs between Br(2) and O(W1), where the distance is 3.04 Å. This short contact is not thought to represent a hydrogen bond (see below). The distance between the planes of the parallel carbon rings is 3.55 Å. In Fig. 2 the hydrogen bonded layers are viewed in a direction perpendicular to the *bc* plane.

Hydrogen bonds. H_3O^+

There are seven hydrogen atoms available for hydrogen bonding in the asymmetric unit. The interatomic distances and angles indicate seven possible $\text{O}\cdots\text{O}$ hydrogen bonds. The short bonds $\text{O}(W1)\cdots\text{O}(W2)$, 2.484 Å and $\text{O}(W2)\cdots\text{O}(W3)$, 2.458 Å indicate that the proton of the acid has been transferred to the water molecules, since a hydrogen bond between water molecules normally is about 2.76 Å. The equality of the S–O bonds in the sulphonate group also supports this conclusion.

The hydrogen bond distances around O(W2) indicate that the extra proton is bonded to this water molecule to form an H_3O^+ ion. On this assumption, the assignment of hydrogen to the other bonds is as follows. $\text{H}_3\text{O}(W2)^+$ acts as the hydrogen donor in three short bonds, one to a sulphonate oxygen, 2.574 Å, and two to the other water molecules, 2.458 and 2.484 Å. The next nearest neighbour of O(W2) is another O(W2) atom at a distance of 3.14 Å. The bonding coordination around O(W2) is relatively flat; O(W2) is situated only 0.21 Å from the plane defined by O(1), O(W1) and O(W3).

Apart from O(W2), the nearest neighbours of O(W1) within possible hydrogen bond distance are two sulphonate oxygen atoms, O(2) and O(3), and a bromine atom, Br(2), at distances 2.752, 2.787 and 3.045 Å. Other distances around O(W1) are greater than 3.40 Å. The angles around O(W1) involving Br(2) and O(W2), O(2), O(3) (88 to 112°) are favourable for the formation of a hydrogen bond $\text{O}-\text{H}\cdots\text{Br}$. However, because of the greater electronegativity of the sulphonate oxygen atoms, the hydrogen atoms of O(W1) are assigned to two hydrogen bonds of the $\text{O}-\text{H}\cdots\text{O}$ type rather than one $\text{O}-\text{H}\cdots\text{O}$ bond and one $\text{O}-\text{H}\cdots\text{Br}$ bond. The bonding coordination around O(W1) is pyramidal.

The third water molecule, O(W3), has two sulphonate

oxygen atoms, O(2) and O(3), as possible hydrogen bond acceptors at distances 2.797 and 2.789 Å, respectively. Other atoms are more than 3.56 Å away.

$\text{H}_3\text{O}(W2)^+$, $\text{H}_2\text{O}(W1)$ and $\text{H}_2\text{O}(W3)$ are thus tightly bonded together to form an aggregate $[\text{H}_2\text{O}\cdots\text{H}_3\text{O}\cdots\text{OH}_2]^+$. There are no hydrogen bonds between individual aggregates which can thus best be described as H_7O_3^+ ions. The bonding coordination of the ion is shown in Figs. 2 and 3. The assignment of the hydrogen atoms to the bonds is shown in Fig. 4, where the short $\text{O}(W1)\cdots\text{Br}$ contact is also shown. In Fig. 3 it can be seen that the thermal ellipsoid of O(W2) is strongly elongated in a direction perpendicular to the bonds around O(W2). The angles between the longest principal axis of the ellipsoid and the bonds are in the range 83 to 87°. The thermal ellipsoids of O(W3) and O(1) show the same tendency but to a smaller extent. It is, however, not possible to distinguish from the present data whether these elongated ellipsoids, especially that of O(W2), indicate highly anisotropic thermal motion, static disorder or systematic errors in the data.

The 2,5-dibromobenzenesulphonate ion

Bond distances and angles in the 2,5-dibromobenzenesulphonate ion are shown in Figs. 6 and 7.

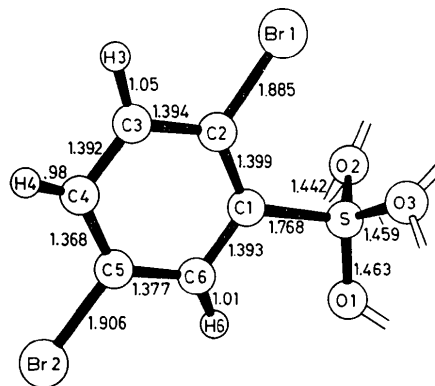


Fig. 6. Distances in the 2,5-dibromobenzenesulphonate ion.

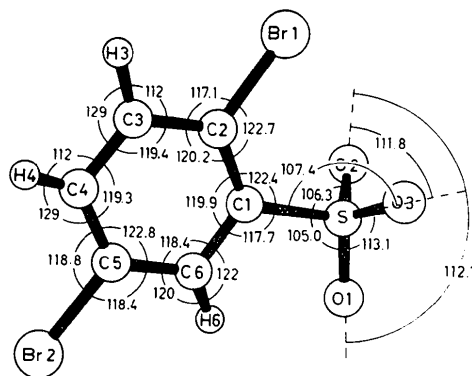


Fig. 7. Angles in the 2,5-dibromobenzenesulphonate ion. Standard deviations of the angles are 0.3–0.7°.

The C–H distances are calculated using the positions of the hydrogen atoms as obtained from the difference synthesis.

The benzene ring is a slightly distorted regular hexagon and the average C–C distance is 1.387 Å. The least-squares plane defined by the six carbon atoms was calculated using a method described by Blow (1960). The carbon ring is not significantly different from planar. The deviations of the atoms from the plane are shown in Fig. 8. The S–O distances 1.463, 1.442 and 1.459 Å are normal for an aromatic sulphonate group. The orientation of the sulphonate group with respect to the carbon ring is such that atom O(1) lies nearly in the plane of the ring. The angle between the least-squares plane and the plane defined by C(1), S and O(1) is only 2.3°. The average O–S–O and C–S–O angles in the group are 112.5° and 106.2° respectively. These angles are similar to those found in related structures, e.g. 112.4° and 106.4° in ammonium

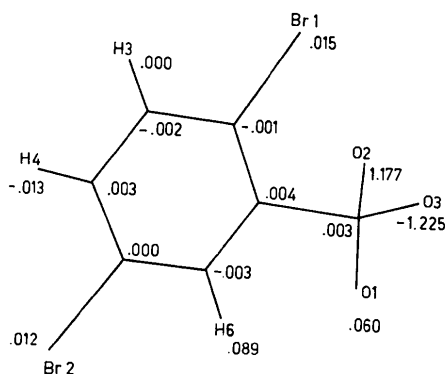


Fig. 8. Deviations of the atoms from the least-squares plane defined by the six carbon atoms of the 2,5-dibromobenzenesulphonate ion (Å).

acid *o*-carboxybenzenesulphonate (Okaya, 1967) and 112.9° and 106.7° in 2-aminoethylsulphonic acid (Okaya, 1966).

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Hydrogen Bond Studies. L. The Crystal Structure of Perchloric Acid Trihydrate

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The crystal structure of $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$ has been determined from three-dimensional single-crystal X-ray diffraction data recorded at -188°C . The crystals are orthorhombic, space group *Pbca*, with eight formula units in a cell of dimensions: $a=8.252$, $b=13.105$, $c=10.218$ Å. Two water molecules are bonded to an H_3O^+ ion by short hydrogen bonds (2.49 and 2.54 Å) to form H_7O_3^+ ions. Longer hydrogen bonds (2.74–2.89 Å) connect these with the ClO_4^- ions and with one another to form a three-dimensional network. The shape of the ClO_4^- ion is almost perfectly tetrahedral with a mean uncorrected Cl–O distance of 1.437 Å.

Introduction

This work is part of a current series of investigations at this Institute directed towards the study of the hydro-

tion of the proton in the solid state. Earlier papers in this series reported the crystal structures of $\text{HCl} \cdot n\text{H}_2\text{O}$, $n=2,3$ (Lundgren & Olovsson, 1967*a,b*), $\text{HBr} \cdot n\text{H}_2\text{O}$, $n=1,2,3,4$ (Lundgren, 1970; Lundgren & Olovsson,