

Hydrogen Bond Studies. XCVII.* The Crystal Structure of Trifluoromethanesulphonic Acid Dihydrate, $\text{H}_5\text{O}_2^+\text{CF}_3\text{SO}_3^-$, at 225 and 85 K

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The crystal structure of trifluoromethanesulphonic acid dihydrate has been determined from three-dimensional single-crystal X-ray diffractometer data at 225 and 85 K. The crystals are monoclinic, space group $P2_1/c$, with four formula units in a unit cell of dimensions $a=10.1192$ (5), $b=8.8700$ (3), $c=7.7545$ (3) Å, $\beta=97.556$ (6)° at 225 K and $a=9.9431$ (6), $b=8.8680$ (5), $c=7.6159$ (3) Å, $\beta=97.083$ (5)° at 85 K. The structure consists of H_5O_2^+ ions and trifluoromethanesulphonate ions hydrogen-bonded together to form double layers which are held together by van der Waals forces. Two water molecules are bonded together by a short hydrogen bond [2.409 (2) Å at 85 K] to form H_5O_2^+ ions which are of the asymmetric type with a *gauche* conformation. The CF_3SO_3^- ion has a staggered conformation with approximate C_{3v} symmetry. The S-O bond distances are 1.441 (1), 1.456 (1), and 1.434 (1) Å at 85 K. The structures at 225 and 85 K are nearly identical; differences in the corresponding structural parameters are only those expected from changes of temperature.

Introduction

In solid hydrates of strong acids the proton has been found to be hydrated to form a series of complexes which have been characterized as H_3O^+ , H_5O_2^+ , H_7O_3^+ and H_9O_4^+ depending upon the degree of hydration. Crystallographic studies of the hydrated proton in solids have been reviewed recently by Lundgren (1974*a*) and Lundgren & Olovsson (1975).

The present study is part of a systematic investigation of the solid hydrates of trifluoromethanesulphonic acid. The phase diagram of the $\text{CF}_3\text{SO}_3\text{H}-\text{H}_2\text{O}$ system as shown in Fig. 1 indicates the following solid phases: $\text{CF}_3\text{SO}_3\text{H} \cdot n\text{H}_2\text{O}$ where $n=\frac{1}{2}, 1, 2, 4$ and 5. The structure of the monohydrate of trifluoromethanesulphonic acid has been reported previously (Spencer & Lundgren, 1973; Lundgren, Tellgren & Olovsson, 1975). This paper presents the structure determination of the dihydrate of trifluoromethanesulphonic acid at 225 and 85 K from single-crystal X-ray diffractometer data.

Experimental

The melting points of a large number of samples with different composition in the system $\text{CF}_3\text{SO}_3\text{H}-\text{H}_2\text{O}$ were determined. The resulting phase diagram is shown in Fig. 1.

Crystals for the X-ray work were grown by cooling aqueous solutions of commercial trifluoromethanesulphonic acid (molar ratio 2:1) sealed in glass capillaries (m.p. -6°C). The intensities and unit-cell dimensions were measured with a Stoe-Philips semi-automatic two-circle diffractometer (Cu $K\alpha$, Ni-

filtered, moving-crystal moving-detector scan technique) modified for low-temperature studies. Measurements were obtained at both 85 and 225 K from two cylindrical crystals mounted about the a and b axes, respectively. The first crystal had a diameter of 0.19 mm and a length of 0.50 mm (hereafter called crystal *A*). The corresponding dimensions for the second crystal were 0.25 and 0.28 mm, respectively (hereafter called crystal *B*). Cell parameters (Table 1) were obtained from a least-squares refinement using the 2θ values of 33 axial reflexions measured at 85 K with Ni-filtered Cu $K\alpha$ radiation [$\lambda(\text{Cu } K\alpha_1)=1.54051$, $\lambda(\text{Cu } K\alpha_2)=1.54433$ Å]. Cell parameters at 225 K were similarly determined using 31 measured 2θ values from both crystals. The diffraction symmetry and systematic absences were consistent with the monoclinic space group $P2_1/c$ (No. 14).

Table 1. *Crystal data*

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

Trifluoromethanesulphonic acid dihydrate $\text{CF}_3\text{SO}_3\text{H} \cdot 2\text{H}_2\text{O}$, F.W. 186.10 Space group $P2_1/c$; monoclinic		
	225 K	85 K
a	10.1192 (5) Å	9.9431 (6) Å
b	8.8700 (3)	8.8680 (5)
c	7.7545 (3)	7.6159 (3)
β	97.556 (6)°	97.083 (5)°
V	689.99 Å ³	666.41 Å ³
D_x	1.791 g cm ⁻³	1.855 g cm ⁻³
Z	4	4
$\mu(\text{Cu } K\alpha)$	45.91 cm ⁻¹	47.53 cm ⁻¹

Intensity data for layers $0kl$ to $9kl$ were recorded for crystal *A* at 85 K which yielded 1272 independent reflexions (80% of the reflexions within the unique quadrant of the Cu $K\alpha$ sphere). Three standard re-

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flexions monitored periodically during data collection decreased by 11% in intensity for which a correction was applied to all intensities. A complementary set of 914 reflexions was similarly obtained for crystal *B* (layers *h0l* to *h5l*) also at 85 K. These intensities were corrected for an 8% decrease in intensity during data collection.

A partial set of 199 intensities was similarly obtained for crystal *A* at 225 K (layers *0kl* and *1kl*). This data set could not be completed because of instability in the mounting of the capillary containing the crystal. The crystal melted and was thus lost during an attempt

to remount the capillary. A complete data set of 1262 independent reflexions was collected for crystal *B* (layers *h0l* to *h8l*) at 225 K. These intensities were also corrected for an 8% decrease in intensity during data collection.

For each data set the raw integrated peak intensities were corrected for background which was assumed to vary linearly throughout the scan range. Standard deviations $\sigma_c(I)$ were assigned to the corrected intensities as based on Poisson counting statistics (Jönsson & Liminga, 1971). The values of I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects ($\mu = 47.53 \text{ cm}^{-3}$ at 85 K for $\text{Cu } K\alpha$) with the program *DATAPW*. Crystal data are given in Table 1.

Structure determination and refinement

Direct methods were used to determine the structure. Using the F^2 values obtained for crystal *A* at 85 K, the normalized structure-factor amplitudes ($|E|$) were calculated with the program *EFAK*.

Phases were determined for 180 reflexions with $|E| \geq 1.5$ by iterative use of Sayre's equation with the program *REL*. Four plausible trial solutions were obtained, each having a high consistency index and a fast rate of convergence. The approximate geometry of the CF_3SO_3^- ion could be recognized from the positions of the peaks in an E map which was calculated for each of the four solutions.

Atomic coordinates for the non-hydrogen atoms from the E map with the most distinct features, isotropic temperature factors for these atoms, and one scale factor were refined in a full-matrix least-squares refinement using the program *UPALS*. The refinement was based on data from only crystal *A* at 85 K. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F) = \sigma_c^2(F^2)/4F^2 + (0.01F)^2$ with $\sigma_c^2(F^2)$ based on counting statistics. Reflexions with $F^2 < 2\sigma(F^2)$ were assigned zero weight. The refinement converged at $R(F) = 0.097$. After two additional cycles of refinement with anisotropic temperatures ($R = 0.045$), a Fourier difference synthesis clearly revealed the positions of all

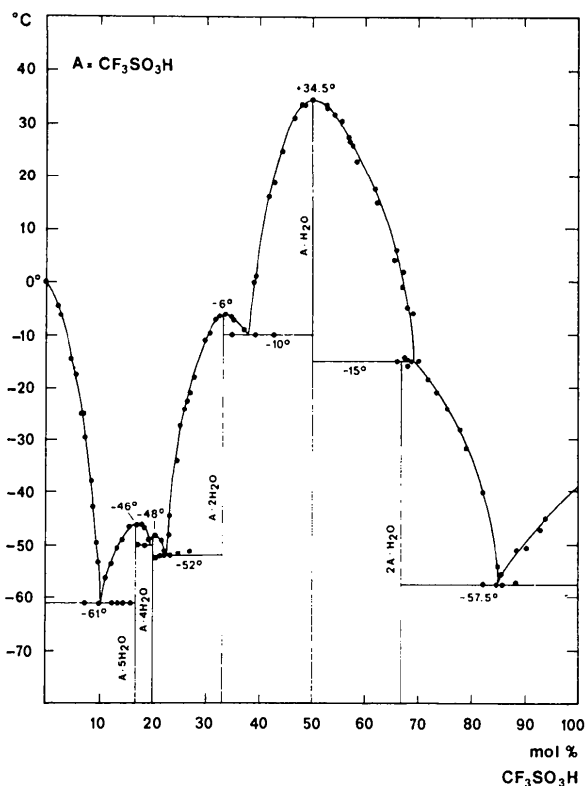


Fig. 1. The phase diagram for the binary system $\text{CF}_3\text{SO}_3\text{H}-\text{H}_2\text{O}$.

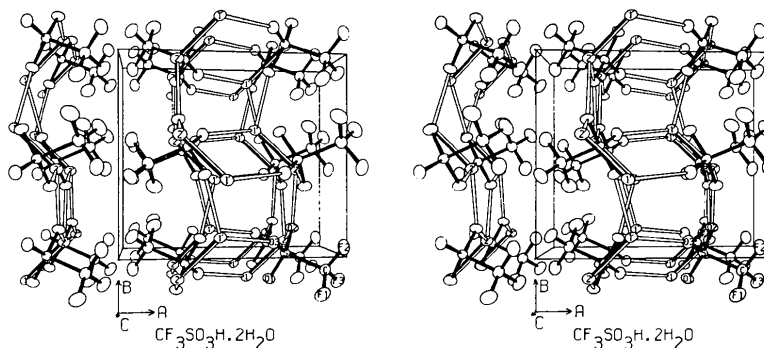


Fig. 2. Stereoscopic illustration of the crystal structure of trifluoromethanesulphonic acid dihydrate at 85 K. Covalent bonds are filled; hydrogen bonds are open. The short $\text{O} \cdots \text{O}$ bond in the H_3O_2^+ ion is half filled. Thermal ellipsoids are scaled to enclose 50% probability.

five hydrogen atoms which agreed with those positions expected from chemical considerations. At this stage, interlayer scale factors were refined by least-squares techniques with the program *INTERSCALE*; this refinement was based on 740 reflexions common to the data sets from crystals *A* and *B* at 85 K. A subsequent refinement of the structure which included variable coordinates and isotropic temperature parameters for the hydrogen atoms reduced the *R* value to 0.036. A final refinement of 112 variables included an isotropic extinction correction with a variable extinction parameter (Coppens & Hamilton, 1970). All parameter shifts were less than 0.1σ in the last cycle of refinement. Separate parallel refinements were effected with the reflexions measured from crystal *B* at 85 K and 225 K, respectively. The final *R* values are summarized in Table 2. *R* values including reflexions given zero weight are given within parentheses. The corresponding atomic parameters derived from both data sets measured at 85 K are in good agreement. The largest difference was $5(\sigma_A^2 + \sigma_B^2)^{1/2}$ where σ_A and σ_B are the standard deviations of the same parameter for crystals *A* and *B*, respectively. The parameters obtained from the data for crystal *A* were preferred since the data set for crystal *B* was not complete. The data sets were not combined because of apparent differences in extinction effects in both crystals. All subsequent results for the structure at 85 K have been derived from the parameters for crystal *A*.

Table 2. Final unweighted and weighted *R* values

$R(F) = (\sum |F_o| - |F_c|) / \sum |F_o|$ and $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. *N* is the number of reflexions with non-zero weight. Values within parentheses include reflexions with zero weight.

Refinement	<i>N</i>	<i>R</i> (<i>F</i>)	<i>R_w</i> (<i>F</i>)
Crystal <i>A</i> at 85 K	1157 (1272)	0.029 (0.035)	0.038
Crystal <i>B</i> at 85 K	870 (914)	0.038 (0.043)	0.049
Crystal <i>B</i> at 225 K	1120 (1262)	0.040 (0.045)	0.050

The atomic parameters from the final cycle of refinement are given in Tables 3 and 4. The final value of the extinction parameter *g* as defined and scaled by Coppens & Hamilton (1970) is 2364(209) and 955(171) for the 85 and 225 K data sets, respectively. Atomic scattering factors for S, F, O and C were those given by Hanson, Herman, Lea & Skillman (1965). Spherical scattering factors for hydrogen atoms were used (Stewart, Davidson & Simpson, 1965). An anomalous dispersion correction was included for the non-hydrogen atoms (Cromer & Liberman, 1970). The programs used for all computations with IBM 370/155 and IBM 1800 computers have been described by Lundgren (1974b).*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31008 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Atomic coordinates ($\times 10^5$ for heavy atoms, $\times 10^4$ for hydrogen atoms) from crystal *A* at 85 K (lower numbers) and crystal *B* at 225 K (upper numbers)

	<i>x</i>	<i>y</i>	<i>z</i>
S	70953 (7)	2927 (9)	12900 (9)
	71232 (5)	3085 (5)	12378 (5)
C	86802 (34)	-4019 (45)	23499 (45)
	87226 (24)	-4381 (23)	23419 (25)
F(1)	84892 (29)	-14604 (30)	34811 (33)
	84738 (15)	-14938 (15)	34930 (16)
F(2)	93591 (25)	6837 (35)	31939 (36)
	94171 (14)	6607 (16)	32057 (17)
F(3)	93772 (25)	-9860 (32)	11974 (36)
	94415 (15)	-10443 (15)	11816 (17)
O(1)	64813 (26)	-9666 (25)	3708 (30)
	64832 (16)	-9638 (15)	3001 (18)
O(2)	74604 (26)	14547 (26)	1369 (25)
	75389 (16)	14737 (14)	695 (16)
O(3)	64672 (25)	8630 (29)	27110 (29)
	64745 (15)	9024 (16)	26692 (17)
O(w1)	58150 (25)	-11911 (31)	-40538 (32)
	58345 (18)	-11923 (16)	-41283 (19)
O(w2)	74881 (28)	6839 (31)	-32831 (32)
	75469 (16)	6984 (15)	-33661 (18)
	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	6553 (36)	-61 (40)	-3683 (46)
	6705 (34)	-113 (36)	-3705 (40)
H(2)	6008 (40)	-2126 (49)	-4056 (50)
	6047 (36)	-2039 (43)	-4175 (43)
H(3)	5175 (49)	-1140 (47)	-3357 (60)
	5249 (31)	-1133 (31)	-3520 (37)
H(4)	7527 (43)	1384 (52)	-3755 (56)
	7531 (33)	1403 (37)	-3975 (42)
H(5)	7572 (43)	965 (49)	-2173 (63)
	7514 (30)	930 (31)	-2329 (41)

Description of the structure

The crystal structure is illustrated in Fig. 2; the bond distances and angles are given in Table 5 and included in Fig. 3. All illustrations were drawn with the plotting program *ORTEP-II*. Interatomic distances and angles were calculated with the program *ORFFE*. Standard deviations were estimated using the variance-covariance matrix from the final cycle of refinement. Effects of the standard deviations of the unit-cell parameters were included.

The structure is composed of discrete H_2O_2^+ and CF_3SO_3^- ions linked together by hydrogen bonds. This formulation is based on the positions of the hydrogen atoms as revealed by the difference Fourier synthesis and the successful refinement of this structural model. Furthermore, the similarity of the three S-O bonds, 1.441 (1), 1.456 (1) and 1.434 (1) Å,* indicates that no hydrogen atom is attached to any of the three sulphonate oxygen atoms; a typical S-OH bond distance in a hydrogen sulphate ion is 1.57 Å, which is about 0.1 Å longer than the other three S-O bonds (Brown, 1973).

The structure consists of an infinite series of double layers parallel to the *bc* plane, separated by normal van der Waals contact distances; the shortest such distances are between two fluorine atoms of opposite CF_3SO_3^- groups (2.898 Å). The double-layer contains two single layers connected by hydrogen bonds of the type

O(w1)–H···O(3). Within each single layer alternating H_5O_2^+ and sulphonate groups are interlinked by hydrogen bonds in both the **b** and **c** directions. Both H_5O_2^+ and CF_3SO_3^- groups in a single layer are related by centres of symmetry to corresponding groups in the second single layer.

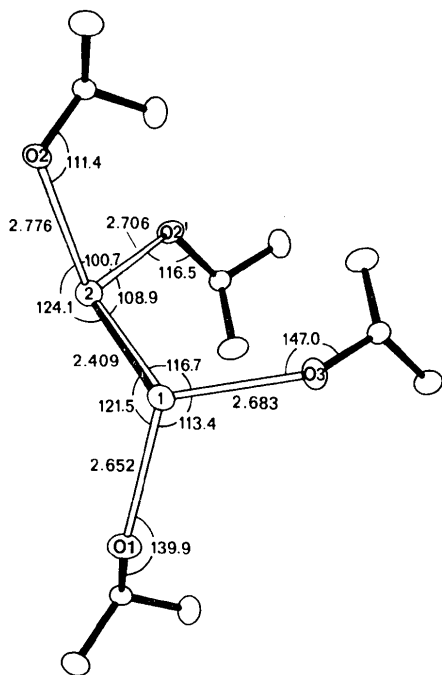


Fig. 3. Hydrogen-bond distances and angles at 85 K.

The H_5O_2^+ ion

The geometry and immediate environment of the H_5O_2^+ ion are shown in Figs. 3 and 4. The ion is hydrogen bonded to four acceptor atoms O(1), O(3), O(2) and O(2') belonging to different sulphonate groups. The internal O(w1)···O(w2) hydrogen bond with a length of 2.409 Å is much shorter than any of the outer hydrogen bonds to the sulphonate oxygens. Thus the formulation of the H_5O_2^+ ion here is quite distinct. The ion has a *gauche* conformation with a dihedral angle of 94.8° as defined by the angle between the two planes formed by the O(w1)···O(w2) bond with the bisector of the pair of outer O···O bonds at each end. The bonding arrangement around each oxygen atom in H_5O_2^+ is pyramidal. Typically, the bond angles O(1)···O(w1)···O(3) and O(2)···O(w2)···O(2') are less than the other two angles involving the O(w1)···O(w2) bond at each end of the ion.

The distances and angles of bonds involving hydrogen are included in Table 5. As the outer hydrogen bonds around O(w1) differ from those around O(w2), the O(w1)···H(1)···O(w2) hydrogen bond is expected to be non-centred. The coordinates of H(1) obtained from the least-squares refinement, which also agree well with those determined from the Fourier difference synthesis, show the proton to be slightly nearer O(w2) than O(w1). This is opposite to the expected position nearer O(w1). However, the low precision of the coordinates for the hydrogen atoms as determined by X-ray diffraction does not permit any definite conclusions to

* All distances and angles in the text unless stated otherwise refer to the structure at 85 K.

Table 4. Anisotropic thermal parameters ($\times 10^5$ for heavy atoms) (cf. Table 3)

The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. The r.m.s. components of thermal displacement of the atoms along the ellipsoid axis are also listed ($\times 10^3$ Å). Isotropic thermal parameters (B Å²) are given for the hydrogen atoms. Upper numbers: 225 K, lower numbers: 85 K.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
S	899 (7) 349 (7)	698 (12) 350 (6)	1149 (11) 479 (8)	-17 (7) -18 (4)	113 (6) 21 (4)	62 (9) 24 (4)	165 (1) 115 (1)	187 (1) 119 (1)	215 (1) 134 (1)
C	1075 (35) 456 (25)	1452 (58) 625 (22)	1878 (60) 800 (29)	93 (40) 47 (20)	27 (38) 41 (21)	75 (52) 42 (21)	219 (4) 143 (4)	244 (5) 156 (3)	251 (4) 162 (3)
F(1)	2011 (38) 920 (19)	2357 (47) 893 (17)	2911 (56) 1092 (21)	447 (36) 174 (14)	-144 (38) -22 (16)	1402 (44) 456 (15)	188 (3) 127 (2)	338 (3) 218 (2)	373 (3) 224 (2)
F(2)	1425 (29) 528 (17)	2708 (52) 1016 (18)	3292 (61) 1335 (24)	-253 (32) -49 (13)	-640 (35) -248 (15)	-433 (46) -214 (16)	216 (3) 133 (3)	333 (3) 198 (2)	362 (3) 227 (2)
F(3)	1434 (28) 636 (17)	2743 (52) 986 (18)	3296 (59) 1250 (22)	739 (31) 257 (13)	565 (36) 186 (16)	-190 (48) -120 (15)	218 (3) 145 (2)	318 (3) 193 (2)	360 (3) 219 (2)
O(1)	1456 (31) 579 (19)	979 (34) 468 (15)	2070 (46) 902 (22)	-264 (27) -103 (13)	-122 (32) -110 (17)	88 (32) -36 (14)	188 (4) 125 (3)	235 (3) 152 (2)	297 (3) 191 (2)
O(2)	1619 (30) 629 (18)	965 (33) 423 (14)	1290 (34) 623 (19)	-155 (25) -47 (13)	263 (26) 136 (15)	140 (26) 64 (13)	179 (3) 120 (3)	208 (3) 140 (2)	289 (3) 177 (3)
O(3)	1245 (27) 454 (18)	1635 (41) 756 (17)	1687 (40) 738 (21)	106 (26) 24 (13)	535 (28) 169 (16)	-38 (32) -55 (14)	199 (3) 131 (3)	253 (3) 159 (3)	268 (3) 175 (2)
O(w1)	1178 (27) 513 (19)	974 (41) 458 (17)	1985 (45) 865 (21)	243 (26) 86 (13)	412 (29) 146 (17)	-16 (33) 5 (14)	182 (4) 128 (3)	233 (3) 153 (3)	263 (3) 168 (3)
O(w2)	1464 (31) 612 (20)	948 (41) 498 (16)	1385 (40) 599 (21)	12 (26) 20 (13)	337 (27) 117 (16)	70 (31) 29 (14)	190 (4) 129 (2)	203 (3) 141 (2)	274 (3) 174 (3)
H(1)	3.8 (7) 3.9 (7)								
H(2)		4.3 (9) 4.1 (7)							
H(3)			6.4 (1.2) 2.3 (6)						
H(4)					4.7 (1.1) 3.4 (7)				
H(5)							5.7 (1.0) 2.7 (6)		

Table 5. *Interatomic distances (Å) and angles (°)*

(a) Covalent bonds within the trifluoromethanesulphonate ion

	225 K	85 K
S—O(1)	1.423 (2)	1.441 (1)
S—O(2)	1.444 (2)	1.456 (1)
S—O(3)	1.435 (2)	1.434 (1)
S—C	1.811 (4)	1.829 (2)
C—F(1)	1.316 (4)	1.327 (2)
C—F(2)	1.308 (4)	1.322 (2)
C—F(3)	1.316 (4)	1.318 (2)
O(1)—S—O(2)	112.4 (1)	113.2 (1)
O(1)—S—O(3)	116.9 (2)	116.9 (1)
O(2)—S—O(3)	113.5 (1)	113.1 (1)
C—S—O(1)	105.2 (2)	104.5 (1)
C—S—O(2)	103.9 (2)	104.0 (1)
C—S—O(3)	103.1 (2)	103.3 (1)
F(1)—C—F(2)	107.8 (3)	108.7 (2)
F(1)—C—F(3)	108.1 (3)	108.4 (2)
F(2)—C—F(3)	109.7 (3)	109.9 (2)
S—C—F(1)	110.3 (3)	109.7 (2)
S—C—F(2)	110.6 (3)	109.5 (1)
S—C—F(3)	110.3 (2)	110.6 (1)

(b) Hydrogen bonds

	225 K	85 K
O(w1)···O(w2)	2.395 (4)	2.409 (2)
O(w1)···O(1)	2.663 (4)	2.652 (2)
O(w1)···O(3)	2.671 (3)	2.683 (2)
O(w2)···O(2')	2.728 (3)	2.706 (2)
O(w2)···O(2)	2.824 (4)	2.776 (2)
O(1)···O(w1)···O(3)	114.8 (1)	113.4 (1)
O(1)···O(w1)···O(w2)	121.0 (1)	121.5 (1)
O(3)···O(w1)···O(w2)	116.3 (1)	116.7 (1)
O(2)···O(w2)···O(2')	101.5 (1)	100.7 (1)
O(2')···O(w2)···O(w1)	108.9 (1)	108.9 (1)
O(2)···O(w2)···O(w1)	123.1 (1)	124.1 (1)
S—O(1)···O(w1)	139.7 (1)	139.9 (1)
S—O(3)···O(w1)	146.2 (2)	147.0 (1)
S—O(2')···O(w2)	117.1 (1)	116.5 (1)
S—O(2)···O(w2)	111.0 (1)	111.4 (1)

(c) Bonds involving hydrogen

	225 K	85 K
O(w1)—H(1)	1.26 (4)	1.30 (3)
O(w1)—H(2)	0.85 (4)	0.78 (4)
O(w1)—H(3)	0.90 (5)	0.79 (3)
O(w2)—H(1)	1.17 (4)	1.11 (3)
O(w2)—H(4)	0.73 (4)	0.78 (3)
O(w2)—H(5)	0.87 (5)	0.82 (3)
H(1)—O(w1)—H(2)	130 (3)	123 (3)
H(1)—O(w1)—H(3)	106 (3)	109 (3)
H(2)—O(w1)—H(3)	104 (4)	108 (3)
H(1)—O(w2)—H(4)	116 (4)	115 (3)
H(1)—O(w2)—H(5)	114 (3)	105 (3)
H(4)—O(w2)—H(5)	105 (4)	112 (3)
O(w1)—H(1)—O(w2)	162 (3)	173 (3)
O(w1)—H(2)···O(1)	165 (4)	170 (3)
O(w1)—H(3)···O(3)	159 (4)	164 (3)
O(w2)—H(4)···O(2)	171 (5)	165 (3)
O(w2)—H(5)···O(2')	170 (4)	177 (3)

be drawn. A clear distinction between a centred or non-centred bond in the H_5O_2^+ ion is not possible either.

Neutron diffraction techniques have been used to study two compounds containing H_5O_2^+ ions free from symmetry restriction. In the structures of picrylsulphonic acid tetrahydrate (Lundgren & Tellgren, 1974) and nitranilic acid hexahydrate (Williams & Peterson,

1969), the proton is found 0.09 and 0.05 Å, respectively, from the centre of the internal $\text{O}\cdots\text{O}$ bond. The shifts are in the direction of the end of the H_5O_2^+ ion with the shorter outer hydrogen bonds. A summary of the results of seven neutron diffraction studies of short $\text{O}\cdots\text{O}$ hydrogen bonds free from symmetry restrictions suggests that the position of the hydrogen atom in these bonds is very sensitive to asymmetrical environments and even small differences in the environment can cause deviations from a centred bond (Kvick, Koetzle, Thomas & Takusagawa, 1974).

The trifluoromethanesulphonate ion

The CF_3SO_3^- ion has a staggered conformation with C_{3v} symmetry. The sulphonate group has an average S—O bond distance of 1.444 Å, an average O—S—O bond angle of 114.4°, an average O—S—C bond angle of 103.9° and a C—S bond distance of 1.829 Å. The $-\text{CF}_3$ group is tetrahedral with an average C—F bond distance of 1.322 Å, the average of all bond angles about the carbon atom is 109.5°. The F—C—S—O torsional angles for F and O in the *trans* positions are 178.0 (3), 178.2 (3) and 179.5 (3)° respectively. This geometry agrees well with that of the same ion in trifluoromethanesulphonic acid monohydrate (Spencer & Lundgren, 1973). In the present structure the S—O distance involving O(2) is slightly longer than the other two; the atom O(2) is an acceptor for two hydrogen bonds whereas O(1) and O(3) each only accept a single bond. However, these differences are just marginally significant.

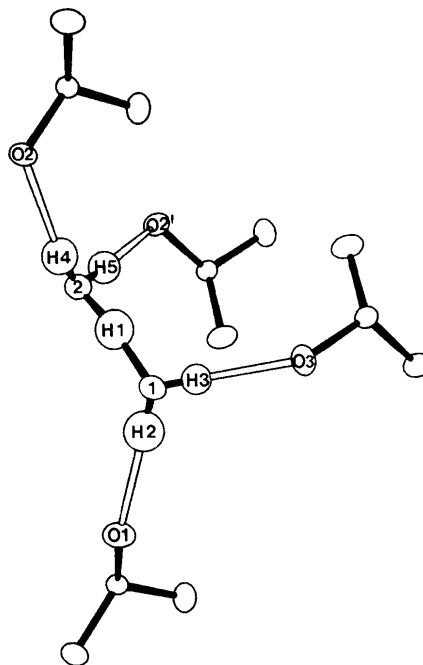


Fig. 4. Hydrogen atom positions as obtained from least-squares refinements. The thermal ellipsoids are scaled to enclose 50% probability.

Comparison of the structures at 225 and 85 K

The structures at 85 and 225 K are nearly identical; the covalent bond distances within the CF_3SO_3^- group tend to be shorter at the higher temperature as was also found for trifluoromethanesulphonic acid monohydrate at 298 and 83 K (Spencer & Lundgren, 1973). Clearly, the ellipsoidal model applied here does not adequately describe the thermal motion of the CF_3SO_3^- group and the apparent interatomic distances will then tend to decrease with increased temperature.

The thermal expansion is anisotropic and mainly confined to directions in the *ac* plane. For the temperature range 85 to 225 K the mean coefficients of linear thermal expansion (all $\times 10^6$) for $\bar{\alpha}_a$, $\bar{\alpha}_b$ and $\bar{\alpha}_c$ are 126, 2 and 130 K^{-1} , respectively. The largest principal coefficient of expansion $\bar{\alpha}_{\text{max}}$ is 153 K^{-1} and lies in the *ac* plane near the $[\bar{1}01]$ direction. A direct correlation between directions of expansion and changes in individual bond distances and angles between the two temperatures is difficult because of the complexity of the structure and the absence of a correct model for correcting these distances and angles for the effects of thermal motion. The largest thermal expansion occurs in the van der Waals distances between the double layers; the non-bonded contact $\text{F}(3)\cdots\text{F}(3')$ which lies near the direction of maximum expansion increases 0.056 (6) Å. The two weakest hydrogen bonds $\text{O}(w2)\cdots\text{O}(2)$ and $\text{O}(w2)\cdots\text{O}(2')$ are 0.022 (4) and 0.048 (5) Å respectively longer at 225 K. Smaller changes only marginally significant occur in the lengths of the three other hydrogen bonds. Differences in corresponding bond angles at the two temperatures are minimal and less than 1.5° .

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