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Hydrogen Bond Studies. LXXIII.* The Crystal Structure of Trifluoromethanesulphonic Acid Monohydrate, $H_3O^+CF_3SO_3^-$, at 298 and 83°K

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The crystal structure of trifluoromethanesulphonic acid monohydrate has been determined from three-dimensional single-crystal X-ray diffraction data recorded on a Stoe–Philips two-circle Weissenberg diffractometer at 298 and 83°K. The crystals are monoclinic, space group $P2_1/c$, with four formula units in a unit cell of dimensions $a=5\cdot9634$ (3), $b=9\cdot975$ (3), $c=9\cdot708$ (1) Å, $\beta=98\cdot661$ (7)° at 298°K and $a=5\cdot8416$ (3), $b=9\cdot855$ (3), $c=9\cdot548$ (1) Å and $\beta=99\cdot711$ (7)° at 83°K. The structure comprises oxonium ions and trifluoromethanesulphonate ions hydrogen-bonded together to form layers. The oxonium ion is hydrogen-bonded to three sulphonate groups in a pyramidal bonding arrangement. The O–H···O distances obtained from a full-matrix least-squares refinement are, at 83°K, 2·546 (3), 2·588 (3) and 2·672 (3) Å. The structure at room temperature is essentially the same as that found at 83°K, with only those minor changes expected to accompany an increase in temperature.

Introduction

This study is part of a series of structure determinations of hydrates of strong acids. Previous reports from this Institute include structure determinations of various hydrates of perchloric, hydrochloric, hydrobromic and sulphuric acids as summarized by Almlöf (1972), and of several substituted benzenesulphonic acids as summarized by Lundgren (1972*a*). Trifluoromethanesulphonic acid is also of interest because it is among the strongest monoprotic acids known (Gramstad & Haszeldine, 1957). It has been suggested as a replacement for perchloric acid in applications where a strong acid is needed which is a relatively weak nucleophile, but is not also a strong oxidizing agent (Scott & Taube, 1971). The present work is based on single-crystal X-ray diffractometer data collected at 298 and at 83°K.

Crystal data

Trifluoromethanesulphonic acid monohydrate, $CF_3SO_3H.H_2O$, F.W. 168·09. Monoclinic, $a=5\cdot9634$ (3),§ $b=9\cdot975$ (3), $c=9\cdot708$ (1) Å, $\beta=98\cdot661$ (7)°, $V=570\cdot9$ Å^3, $Z=4$, $D_x=1\cdot956$ g cm^{-3} at 298°K; $a=5\cdot8416$ (3), $b=9\cdot855$ (3), $c=9\cdot548$ (1) Å, $\beta=99\cdot711$ (7)°, $V=541\cdot8$ Å^3, $Z=4$, $D_x=2\cdot060$ g cm^{-3} at 83°K. Space group $P2_1/c$.

Experimental

Commercially obtained trifluoromethanesulphonic acid was purified by vacuum distillation, equimolar amounts of the acid and distilled water were mixed and the resulting compound purified by several fractional recrystallizations. Samples of the hygroscopic compound were sealed in thin-walled glass capillary tubes in which crystals were then grown by zone melting. The observed melting point (35°C) is in good agreement with the published value (34°C, Gramstad & Haszeldine, 1957). Crystals grew with the *b* axis preferentially along the axis of the capillary tube.

Unit-cell parameters were obtained from quartz-calibrated Weissenberg oscillation photographs of two crystals in different orientations using Cu $K\alpha$ radiation [$\lambda(\text{Cu } K\alpha_1)=1\cdot54051$, $\lambda(\text{Cu } K\alpha_2)=1\cdot54433$ Å; $a(SiO_2)=4\cdot9131$ Å] in a camera modified for low-temperature work as described by Olovsson (1960). The unit-cell parameters were obtained by fitting about 50 measured θ values using a least-squares procedure.

Intensity data were collected from a cylindrical crystal of radius 0·143 mm rotated about the *b* axis which corresponded quite closely to the cylinder axis of the sample. The measurements were made with a Stoe-Philips automated two-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation ($\lambda=1\cdot54178$ Å) at a temperature of 298°K. An ω–2θ scan technique (Weissenberg geometry) was used to record layers $0\le k\le 9$ which yielded a total of 1038 independent reflexions, approximately 85% of the reflexions in the copper reflexion sphere. Of these reflexions, 943 had $I>3\sigma(I)$ where $\sigma(I)$ is based on counting statistics, and those reflexions with $I<3\sigma(I)$ were given zero weight in the refinement. Three test reflexions were checked periodically for each layer and showed only statistical fluctuations in intensity.

A comparable set of data was also taken at 83°K from the same crystal. In this case a total of 982 independent reflexions was measured of which 934 had $I>3\sigma(I)$.

The intensities were corrected for Lorentz and polarization effects, and for absorption using the method

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

devised by Van den Hende (1962) for cylindrical samples. The linear absorption coefficient for Cu $K\alpha$ radiation is 56·20 cm^{-1} and the range of transmission factors was 0·211 to 0·340.

It was found in the course of refinement that the observed structure factors for reflexions with low $\sin\theta/\lambda$ values in the upper layers were systematically smaller than the calculated structure factors. These reflexions were given zero weight in the final refinements. It is thought that the intensities of these reflexions were underestimated because of the distortion affecting low-angle reflexions in upper layers using the Weissenberg method. The number of reflexions given zero weight for this reason was 51 (298 °K data) and 44 (83 °K data).

Space group and structure determination

Film and diffractometer data were consistent with the space group $P2_1/c$ (No. 14, *International Tables for X-ray Crystallography*, 1952) which is uniquely determined by systematic absences.

A program devised by Long (1965) was used to predict the signs of 136 reflexions with $|E| > 1{\cdot}50$. A starting set of seven signs was used with the program to predict the signs of the remaining E factors. From the 16 solutions thus obtained, the one showing the best consistency and convergence was used to produce a three-dimensional Fourier synthesis. This then clearly revealed all nine non-hydrogen atoms. All predicted signs in this set were subsequently found to agree with those obtained at the completion of the refinement.

The structure was then refined by a full-matrix least-squares procedure using the program *UPALS* (Lundgren, 1972*b*). The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ with each reflexion assigned a weight w inversely proportional to the estimated variance of the observation,

$$w^{-1} = \sigma^2(F^2) = k\sigma_c^2(F^2) + (0{\cdot}01F^2)^2$$

where $\sigma_c^2(F^2)$ is based on counting statistics. The constant k was given the value 2·0 for the 170 weakest reflexions of the 83 °K data to obtain an adequate weighting scheme. In all other cases k was 1·0. An overall scale factor, positional and isotropic thermal parameters were first refined for all nine non-hydrogen atoms with the refinement converging to give agreement values

$$\begin{aligned} R_{298} &= \textstyle\sum||F_o|^2 - |F_c|^2|/\sum|F_o|^2 = 0{\cdot}190\ (0{\cdot}190) \\ R_{83} &= 0{\cdot}128\ (0{\cdot}140) \\ R_{w,298} &= |\textstyle\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4|^{1/2} = 0{\cdot}312 \\ R_{w,83} &= 0{\cdot}249\,. \end{aligned}$$

The R value in parentheses includes those reflexions given zero weight in the refinement.

Continued refinement with anisotropic thermal parameters reduced the R values to $R_{298} = 0{\cdot}087$ (0·101) and $R_{83} = 0{\cdot}081$ (0·098), $R_{w,298} = 0{\cdot}139$ and $R_{w,83} = 0{\cdot}124$ for 82 parameters varied. At this point a difference Fourier synthesis revealed two reasonably well resolved peaks and one rather diffuse peak at positions expected for the three hydrogen atoms of the oxonium ion. These hydrogen atoms were then included with fixed positional parameters and a Debye–Waller factor of 5·0 Å^2 (298 °K data) and 2·0 Å^2 (83 °K data), for the final cycles of refinement. The final R values obtained were $R_{298} = 0{\cdot}075$ (0·092) and $R_{83} = 0{\cdot}070$ (0·091), $R_{w,298} = 0{\cdot}135$ and $R_{w,83} = 0{\cdot}116$. The conventional R values based on F were $R_{298} = 0{\cdot}049$ and $R_{83} = 0{\cdot}046$. Shifts in all parameters during the last cycle of refinement were less than 10% of the estimated standard deviation for that parameter. The final refinement was based on 886 reflexions (298 °K data) and 883 reflexions (83 °K data) with non-zero weight.

Atomic scattering factors used in the calculations were those for neutral S, F, O and C given by Hanson, Herman, Lea & Skillman (1964) and the spherical scattering factor for hydrogen proposed by Stewart, Davidson & Simpson (1965). Anomalous dispersion correction was included for S, F and O atoms (*International Tables for X-ray Crystallography*, 1962). All calculations were carried out on the IBM 370/155 computer in Uppsala except for data reduction which was done on the IBM 1800 computer at the Institute.

Atomic coordinates obtained from the final refinements, or from the difference Fourier syntheses in the case of the hydrogen atoms, are given in Table 1 and the thermal parameters in Table 2. Observed and calculated structure factors are given in Table 3.

Table 1. *Atomic coordinates* ($\times 10^5$)

	x	*y*	*z*	
S	−29677 (14)	23410 (8)	47809 (8)	298 °K
	−28490 (13)	23355 (8)	48247 (7)	83 °K
F(1)	4886 (49)	36345 (37)	41618 (37)	
	5810 (33)	37557 (22)	42012 (22)	
F(2)	7781 (55)	30905 (49)	62938 (33)	
	9956 (35)	31563 (24)	64069 (20)	
F(3)	12026 (55)	16144 (39)	47682 (43)	
	14689 (34)	16870 (22)	48065 (21)	
O(1)	−39746 (46)	36065 (28)	50416 (26)	
	−39664 (39)	35920 (23)	51018 (21)	
O(2)	−34640 (50)	19499 (30)	33358 (26)	
	−33684 (41)	19434 (24)	33370 (22)	
O(3)	−32056 (52)	12964 (30)	57541 (28)	
	−29952 (39)	12506 (23)	58157 (23)	
O(*W*)	43261 (59)	45717 (33)	25383 (27)	
	42774 (39)	45280 (25)	25263 (20)	
C	751 (77)	26852 (50)	50306 (50)	
	2455 (59)	27660 (38)	50759 (33)	
H(1)	47000	40000	34000	
	49000	42000	35000	
H(2)	56000	5000	26000	
	61000	5000	28000	
H(3)	48000	40000	19000	
	53000	41000	20000	

Description of the structure

The structure is illustrated in Figs. 1 and 2 and the bond distances and angles are given in Figs. 3 and 4, and in Table 4. Interatomic distances and angles were calculated with the program *ORFFE* (Busing, Martin & Levy, 1964) using the variance-covariance matrix from the final cycle of refinement and the standard deviations of the unit-cell parameters to obtain standard deviations in the distances and angles. All figures were prepared with the plotting program *ORTEP*-II (Johnson, 1965).

The chemical equivalence of the three sulphonate oxygen atoms, apparent from the geometry of the sulphonate group, and the appearance of peaks in the difference synthesis at positions consistent with the transfer of a proton from the acid to the water molecule support the formulation of this monohydrate of a strong acid as $H_3O^+CF_3SO_3^-$. The X-ray data, however, do not allow more detailed conclusions to be drawn from the hydrogen atom positions obtained.

The structure is composed of oxonium ions and trifluoromethanesulphonate ions hydrogen-bonded together to form layers parallel to the *bc* plane at $x = 0{\cdot}5$, with the CF_3 groups in a given layer projecting alternately in the positive and negative **a** directions. The shortest non-bonded contacts occur between a sulphonate oxygen and a fluorine atom of an adjacent anion (2·92 Å),* and between a sulphonate oxygen and the oxygen of an oxonium ion to which it is not hydrogen bonded (2·94 Å).

The trifluoromethanesulphonate ion

The $CF_3SO_3^-$ ion is in a staggered conformation having a symmetry very close to C_{3v}. The geometry of the sulphonate group with an average S–O bond distance of 1·449 Å, an average O–S–O bond angle of 114·4°, an average O–S–C bond angle of 104·0° and a C–S bond distance of 1·833 Å agrees with that found in other sulphonates as summarized by Arora & Sundaralingam (1971). The $-CF_3$ group is tetrahedral with an average

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* The distances and angles refer to the 83°K data unless stated otherwise.

Table 2. *Anisotropic thermal parameters* (× 10⁴)

The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \ldots 2\beta_{12}hk + \ldots)]$. The r.m.s. components (R_l) of thermal displacement of the atoms along the ellipsoid axes are also listed (× 10³ Å).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3	
S	268 (3)	81 (1)	69 (1)	−3 (1)	33 (1)	0 (1)	175 (1)	202 (1)	218 (1)	298°K
	92 (3)	40 (1)	22 (1)	−1 (1)	8 (1)	0 (1)	99 (2)	124 (2)	140 (2)	83°K
F(1)	416 (10)	189 (5)	218 (5)	−73 (5)	108 (5)	30 (4)	213 (3)	325 (3)	338 (4)	
	137 (6)	60 (3)	64 (2)	−10 (3)	29 (3)	8 (2)	135 (4)	169 (3)	181 (3)	
F(2)	444 (11)	270 (7)	161 (4)	−77 (6)	−51 (5)	−21 (4)	220 (3)	323 (4)	380 (4)	
	146 (6)	84 (3)	46 (2)	−15 (3)	−11 (3)	−10 (2)	123 (4)	176 (3)	207 (3)	
F(3)	387 (10)	192 (6)	302 (7)	98 (6)	100 (6)	1 (4)	216 (3)	337 (4)	377 (4)	
	124 (6)	60 (3)	74 (2)	17 (3)	28 (3)	2 (2)	133 (4)	175 (3)	185 (3)	
O(1)	334 (8)	108 (3)	95 (3)	33 (4)	26 (4)	−6 (2)	206 (3)	219 (3)	259 (3)	
	118 (6)	45 (3)	33 (2)	9 (3)	3 (3)	1 (2)	120 (4)	140 (4)	155 (4)	
O(2)	462 (11)	107 (3)	81 (3)	−26 (4)	36 (4)	−15 (2)	186 (3)	233 (3)	289 (3)	
	159 (7)	50 (3)	24 (2)	−7 (3)	10 (3)	−4 (2)	102 (5)	154 (4)	168 (4)	
O(3)	451 (11)	104 (4)	109 (3)	6 (4)	86 (5)	18 (2)	195 (3)	236 (3)	291 (3)	
	146 (7)	44 (3)	37 (2)	2 (3)	25 (3)	3 (2)	121 (4)	148 (4)	160 (4)	
O(*W*)	542 (12)	109 (4)	107 (3)	66 (5)	71 (5)	8 (2)	213 (3)	218 (3)	324 (4)	
	145 (7)	47 (3)	35 (2)	16 (3)	16 (3)	5 (2)	123 (4)	138 (4)	169 (4)	
C	292 (12)	148 (6)	129 (5)	5 (6)	36 (6)	4 (4)	225 (5)	246 (5)	273 (5)	
	113 (10)	56 (4)	36 (3)	4 (4)	8 (5)	3 (2)	127 (6)	139 (6)	166 (5)	

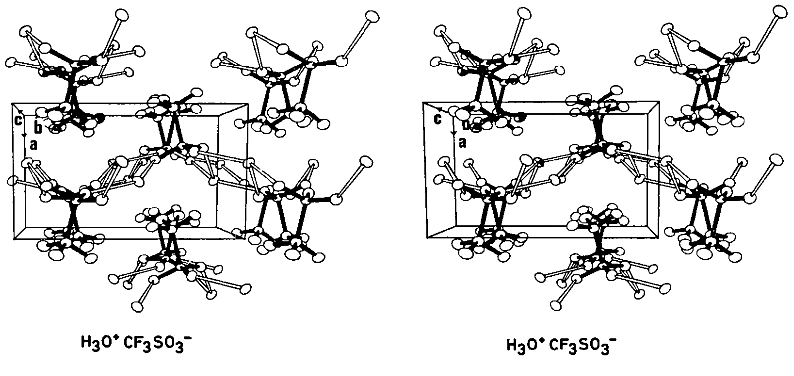


Fig. 1. Stereoscopic drawing of the crystal structure of $H_3O^+CF_3SO_3^-$ at 83°K. Covalent bonds are filled and hydrogen bonds are open. The asymmetric unit whose coordinates are given in Table 1 is drawn with shaded thermal ellipsoids. The thermal ellipsoids are scaled to enclose 50% probability.

Table 3. *Observed and calculated structure factor amplitudes*

The columns are in order *l*, $10|F_o|$, $10|F_c|$ (at 298°K), $10|F_o|$, $10|F_c|$ (at 83°K). Reflexions marked with an asterisk were given zero weight in the refinements.

0,0,l				
2	1053	1101	1085	1113
4	528	528	628	616
6	248	256	402	408
8	216	212	370	373
10	29	30	102	100
1,0,l				
-10	172	174	213	213
-8	224	238	284	244
-6	18	21	13	6*
-4	648	612	818	759
-2	573	562	571	565
0	16	8	38	31
2	260	262	329	324
4	189	190	19	13
6	115	121	23	13
8	246	241	352	375
10	102	105	143	153
2,0,l				
-10	64	56	93	90
-8	110	116	138	128
-6	365	353	514	515
-4	121	133	223	226
-2	337	346	430	435
0	181	173	122	111
2	173	187	341	340
4	95	87	46	53
6	42	41	30	24
8	156	158	77	86
10	16	18	88	89
3,0,l				
-10	46	52	45	46
-8	72	70	132	134
-6	62	66	211	210
-4	178	172	260	255
-2	366	366	308	304
0	619	591	478	475
2	311	323	225	235
4	253	254	283	314
6	299	304	357	391
8	93	96	102	113
4,0,l				
-10	156	161	376	376
-8	219	215	368	374
-6	71	62	72	70
-4	67	60	85	77
-2	53	43	164	168
0	114	97	127	124
2	41	43	76	91
4	57	64	212	229
6	46	52	117	131
8	102	99	250	274
5,0,l				
-8	33	21	168	157
-6	31	27	30	21
-4	15	9	177	184
-2	192	177	272	281
0	179	178	791	296
2	129	110	89	82
4	33	41	29	11
6	32	26	164	174
6,0,l				
-8	84	82		
-6	28	36	17	13
-4	68	64	106	107
-2	12	3*	59	58
0	19	9	88	93
2	52	42	60	63
4	59	65	22	23
7,0,l				
-4	112	106	233	244
-2	78	82	153	156
0	75	70	216	233
0,1,l				
1	33	33	68	68
2	187	185	111	115
3	12	12	14	5*
4	111	115	142	148
5	12	20	57	63
6	309	306	361	357
7	51	53	41	42
8	229	231	231	232
9	74	72	47	47
10	98	97	108	107
11	2	0*	25	27
1,1,l				
-11	2	6*	15	18
-10	82	85	196	195
-9	91	94	127	127
-8	151	149	224	220
-7	74	80	119	123
-6	197	194	135	126
-5	202	204	242	272
-4	16	23	102	82
-3	32	17	25	23
-2	537	522	505	503
-1	34	0*	49	40
0	642	617	577	569
1	172	196	218	216
2	297	293	288	276
3	412	403	486	451
4	522	508	622	591
5	204	185	201	173
6	308	294	389	368
7	30	32	87	78
8	69	71	95	98
9	11	10*	4	7*
10	11	19*	72	62
11	8	3*	5	5*
2,1,l				
-11	8	14*	74	75
-10	107	111	200	201
-9	102	100	233	234
-8	168	165	234	237
-7	17	14	20	25
-6	107	110	210	206
-5	51	45	50	48
-4	159	161	189	190
-3	189	190	192	178
-2	576	568	589	576
-1	509	520	640	672
0	1200	1148	1238	1233
1	148	107	181	171
2	629	613	632	610
3	143	153	265	256
4	69	64	28	37
5	26	32	54	53
6	272	286	504	509
7	5	3*	71	64
8	219	225	456	447
9	90	46	176	164
10	119	124	282	280
3,1,l				
-11	35	34	87	85
-10	78	82	56	53
-9	33	33	91	91
-8	198	202	269	270
-7	105	105	175	165
-6	69	75	50	56
-5	77	79	173	163
-4	21	12	102	91
-3	142	150	203	190
-2	353	350	460	458
-1	87	103	155	149
0	490	482	694	683
1	126	147	246	233
2	101	97	136	135
3	5	13*	144	144
4	19	15	184	178
5	80	78	261	249
6	69	65	86	77
7	13	11*	74	71
8	49	54	14	6*
9	14	15	14	8
4,1,l				
-10	58	57	114	108
-9	12	13*	32	27
-8	5	4*	34	31
-7	77	78	138	133
-6	88	88	154	157
-5	29	26	72	69
-4	118	109	191	184
-3	71	74	132	127
-2	102	104	85	79
-1	98	111	58	53
0	124	128	233	223
1	37	42	136	126
2	127	128	184	181
3	20	8	99	90
4	220	208	248	238
5	41	39	53	39
6	76	78	134	127
7	23	14	57	50
8	19	16	124	126
5,1,l				
-9	16	17	16	11
-8	148	154	291	283
-7	37	41	57	52
-6	165	163	324	314
-5	27	30	76	78
-4	167	167	281	273
-3	55	56	83	74
-2	44	45	145	140
-1	63	60	34	29
0	89	88	19	10
1	110	113	176	165
2	22	20	182	180
3	61	61	118	116
4	12	12*	49	49
5	70	66	153	147
6	88	90	104	105
7	3	2*		
6,1,l				
-8	60	61		
-7	8	3*	14	12
-6	28	25	9	6*
-5	4	4*	36	31
-4	31	32	52	45
-3	33	36	125	122
-2	117	115	289	273
-1	37	32	142	139
0	97	95	203	188
1	25	26	70	64
2	55	57	152	144
3	19	18	95	87
4	56	58	217	210
5	9	1*		
7,1,l				
-4	15	15		
-3	15	12	50	48
-2	5	11*	103	97
-1	15	17	106	101
0	32	32		
1	11	5		
0,2,l				
1	57	90*	61	77*
2	892	924*	877	953*
3	99	85	111	109
4	204	123	264	230
5	242	233	315	311
6	434	444	649	681
7	168	170	332	366
8	109	90	218	202
9	104	109	280	306
10	60	59	143	143
11	50	53	145	159
1,2,l				
-11	21	15	35	34
-10	101	104	100	99
-9	80	84	197	218
-8	292	297	371	396
-7	29	30	58	59
-6	17	23	30	32
-5	223	220	235	226
-4	239	108*	227	111*
-3	207	191	217	214
-2	250	178	254	218
-1	89	64*	94	90*
0	391	390*	372	404*
1	256	290*	317	350*
2	374	372	403	401
3	310	316	535	549
4	71	14*	138	126
5	136	130	283	293
6	232	239	154	164
7	107	110	141	154
8	132	106	147	110
9	21	23	35	38
10	122	116	180	188
11	8	9*		
2,2,l				
-11	20	20	19	19
-10	35	31	60	62
-9	110	112	97	103
-8	180	175	218	234
-7	82	84	87	95
-6	240	228	315	315
-5	6	7*	22	23
-4	311	312	343	362
-3	15	24	70	72
-2	179	157	195	172
-1	26	34	161	179
0	282	293	424	449
1	118	123	53	64
2	61	13*	148	114
3	57	47	22	21
4	180	186	227	239
5	70	63	148	155
6	87	93	40	43
7	35	41	22	23
8	79	42	41	14
9	37	41	13	13*
10	35	37	25	11
3,2,l				
-11	41	46	82	85
-10	59	56	67	73
-9	100	108	150	161
-8	23	14	50	33
-7	137	148	164	173
-6	35	36	50	3*
-5	68	69	85	79
-4	70	41	82	11*
-3	95	97	82	78
-2	224	199	186	183
-1	121	114	71	72
0	429	398	331	320
1	105	102	122	105
2	154	118	97	73
3	343	356	467	501
4	264	271	311	320
5	199	217	265	287
6	261	250	340	353
7	9	9*	9	7*
8	109	112	170	184
9	17	18	11	8*
4,2,l				
-10	120	117	218	221
-9	4	2*	35	36
-8	204	200	319	326
-7	17	12	64	68
-6	138	140	154	160
-5	50	56	54	60
-4	177	181	285	303
-3	79	82	204	217
-2	195	209	318	340
-1	244	309	534	592
0	37	10*	61	58
1	171	179	291	308
2	33	15	30	14
3	22	27	46	47
4	55	46	169	175
5	5	5*	30	29
6	40	36	66	67
7	11	15*	10	8*
8	64	65	106	96
5,2,l				
-9	66	67	163	178
-8	40	40	62	54
-7	21	22	12	7*
-6	32	37	24	16
-5	5	3*	71	75
-4	69	61	45	11*
-3	28	32	67	67
-2	122	119	118	97
-1	83	85	225	242
0	190	173	283	289
1	28	33	126	138
2	48	47	92	90
3	19	12	181	205
4	78	75	176	194
5	16	10	78	85
6	32	40	168	185
7	3	3*		
6,2,l				
-7	17	21	38	40
-6	42	35	92	99
-5	26	20	63	69
-4	18	4*	29	13
-3	7	6*	23	12
-2			108	116
-1	5	8*	67	76
0	43	39	42	36
1	9	1*	14	7*
2	32	38	17	2*
3	41	46	26	24
4	82	78	80	85
7,2,l				
-4	93	96		
-3	6	17*	11	3*
-2	105	102	219	241
-1	58	60	97	107
0	58	61		
0,3,l				
1	62	66*	44	56*
2	102	102*	84	74*
3	9	38*	100	110
4	149	138	108	104
5	137	138	187	182
6	235	228	216	216
7	62	57	37	41
8	180	176	208	213
9	84	84	63	57
10	85	83	135	140
11	1	3*	49	48
1,3,l				
-11	40	38	50	50
-10	24	21	45	41
-9	70	76	73	78
-8	145	140	208	203
-7	172	177	185	188
-6	240	240	297	293
-5	106	106	167	157
-4	411	415	492	500
-3	309	294	350	335
-2	442	449*	460	492*
-1	168	186*	212	237*
0	305	353*	327	364*
1	145	132*	74	70*
2	137	125	166	124
3	417	386	498	462
4	157	149	179	167
5	250	244	297	273
6	126	115	167	155
7	83	83	102	100
8	18	7	81	74
9	17	18	64	54
10	14	18	30	26
11	13	14		
2,3,l				
-11	64	61	177	182
-10	112	112	163	167
-9	82	84	231	241
-8	50	47	23	14
-7	192	189	346	355
-6	53	46	22	12
-5	162	162	172	159
-4	139	120	130	112
-3	102	107	247	252
-2	375	365	447	474
-1	498	483	672	674
0	200	218	183	184
1	316	326	405	401
2	149	147	166	180
3	20	33	16	3*
4	233	233	362	368
5	110	112	239	234
6	202	209	315	317
7	45	43	145	145
8	152	150	244	251
9	37	37	135	145
10	47	55	58	64
3,3,l				
-11	6	8*		
-10	108	107	174	177
-9	128	129	292	303
-8	187	186	289	290
-7	17	18	37	40
-6	310	304	441	498
-5	47	52	42	41
-4	181	182	252	261
-3	57	49	155	156
-2	349	353	466	479
-1	95	104	205	207
0	121	111	121	127
1	60	64	67	62
2	112	110	191	188
3	97	99	364	374
4	7	20*	170	173
5	16	12	123	130
6	36	34	269	280
7	18	14	6	8*
8	35	29	36	35
9	17	15	81	81
4,3,l				
-10	13	17	13	7
-9	81	78	98	97
-8	14	4*	46	41
-7	50	42	93	94
-6	124	122	147	147
-5	54	55	70	67
-4	117	117	39	35
-3	13	18*	62	67
-2	252	247	234	229
-1	13	3*	144	142
0	150	161	173	173
1	67	68	41	37
2	200	194	289	290
3	58	64	19	21
4	143	143	158	157
5	40	34	110	106
6	115	111	215	219
7	16	13	18	10
8	39	47	78	84
5,3,l				
-9	44	48	62	57
-8	82	81	137	142
-7	43	41	13	3*
-6	56	59	72	74
-5	31	32	38	30
-4	129	121	202	206
-3	61	53	63	57
-2	83	84	144	148
-1	159	163	196	194
0	48	50	145	155
1	88	87	99	100
2	5	4*	23	30
3	132	132	276	281
4	39	44	32	8*
5	88	91	178	185
6	87	83	135	139
6,3,l				
-7	15	19	13	14
-6	101	102	184	183
-5	9	7*	43	46
-4	129	129	241	247
-3	5	10*	48	53
-2	131	130	233	231
-1	68	69	215	225
0	93	91	160	154
1	30	27	61	60
2	59	63	123	125
3	13	10	83	83
4	71	70		
7,3,l				
-3	26	30		
-2	10	13		
-1	35	33		
0,4,l				
1	349	450*	433	606*
2	149	114*	145	123*
3	16	13	77	79
4	283	274	367	364
5	22	24	34	28
6	211	204	339	335
7	95	93	163	161
8	117	110	210	209
9	124	124	274	281
10	15	10	6	6*
11	6	11*		
1,4,l				
-11	6	7*	40	43
-10	116	114	180	177
-9	5	7*	62	59
-8	139	143	196	197
-7	76	71	77	76
-6	319	298	411	402
-5	82	90	136	136
-4	313	303	440	429
-3	305	302	501	489
-2	383	369*	399	417*
-1	277	297*	211	236*
0	138	131*	137	150*
1	28	35*	11	17*
2	183	210*	242	258
3	14	19	29	17
4	235	229	249	246
5	50	48	99	90
6	91	86	74	73
7	47	41	164	162
8	108	103	101	99
9	35	31	25	30
10	49	48	68	69
2,4,l				
-11	20	20		
-10	75	67	143	138
-9	67	66	55	60
-8	118	119	180	176
-7	73	69	148	144
-6	228	225	240	239
-5	110	119	170	167
-4	175	172	160	159
-3	23	13	43	48
-2	325	313	304	306
-1	167	163	173	178
0	216	240	234	255
1	27	30	29	23
2	204	192	233	226
3	114	103	234	226
4	33	26	143	140
5	117	120	140	132
6	11	24*	126	125
7	95	90	124	127
8	22	24	15	5*
9	28	23	29	32
10	16	15		
3,4,l				
-10	41	43	66	66
-9	59	63	54	57
-8	11	13*	55	53
-7	108	110	88	84
-6	157	155	248	248
-5	87	82	99	80
-4	188	191	244	241
-3	218	207	279	288
-2	182	184	147	147
-1	114	116	124	119
0	56	62	90	95
1	12	4*	50	52
2	102	104	140	134
3	146	147	240	238
4	145	182	220	230
5	121	121	192	185
6	187	190	283	242
7	61	55	82	88
8	88	83	193	194
9	14	16		
4,4,l				
-10	77	81		
-9	21	16	79	73
-8	130	129	185	179
-7	58	56	175	170
-6	225	223	305	355
-5	20	22	84	87
-4	355	357	511	514
-3	22	19	63	62
-2	346	339	511	517
-1	230	228	388	388
0	155	157	265	260
1	113	110	135	131
2	49	47	101	104
3	10	4*	10	10*
4	20	24	71	75
5	57	57	202	205
6	12	19*	104	103
7	48	48	128	132
8	17	15		
5,4,l				
-8	64	60	139	136
-7	58	54	149	146
-6	104	97	206	199
-5	8	2*	11	9*
-4	78	78	109	112
-3	92	85	285	281
-2	97	91	110	107
-1	49	49	166	161
0	94	96	110	105
1	27	23	54	52
2	104	96	227	227
3	14	10	86	79
4	81	87	266	273
5	4	12*	131	133
6	60	63		
6,4,l				
-7	38	33		
-6	11	8	83	84
-5	7	11*	21	19
-4	8	11*	108	104
-3	44	42	45	43
-2	46	39	25	16
-1	4	7*	24	17
0	42	44	12	11*
1	21	16	77	80
2	64	63	4	47*
3	18	26	19	13
4	61	67		
0,5,l				
1	128	180*	165	267*
2	47	51*	84	104*
3	112	110	210	214
4	114	108	56	54
5	177	187	242	231
6	139	139	79	80
7	83	84	69	72
8	101	97	142	130
9	15	16	12	10*
10	95	96	172	170
1,5,l				
-10	45	46	120	116
-9	28	28	19	11
-8	63	62	143	135
-7	13	7*	128	127
-6	238	242	416	414
-5	31	33	114	113
-4	322	320	416	415
-3	118	119	141	139
-2	393	427*	425	466
-1	2	9*	24	25*
0	125	152*	179	228*
1	189	211*	130	150*
2	106	115	211	216
3	18	9	72	69
4	13	6	26	20
5	123	121	192	180
6	45	38	99	89
7	208	201	305	300
8	21	19	98	90
9	40	45	19	15
10	3	8*	19	15
2,5,l				
-10	53	54	46	40
-9	60	61	121	119
-8	82	83	128	118
-7	176	175	338	329
-6	26	21	69	58
-5	144	144	251	246
-4	226	222	304	289
-3	186	186	312	316
-2	197	187	225	213
-1	306	314	421	430
0	293	295	452	452
1	45	47	150	157
2	73	79	72	71
3	65	60	104	94
4	145	146	174	163
5	120	116	302	297
6	167	165	193	187
7	24	27	138	127
8	52	54	17	12
9	12	9	4	1*
3,5,l				
-10	62	65	152	151
-9	34	38	117	122
-8	184	179	326	325
-7	21	19	11	7*
-6	216	209	340	330
-5			13	12*
-4	352	344	580	567
-3	130	127	374	369
-2	100	106	159	157
-1	21	19	101	101
0	107	105	189	187
1	107	102	143	183
2	10	10*	75	71
3	58	61	81	80
4	84	83	266	256
5	76	71	91	90
6	10	2*	52	46
7	53	52	122	111
8	7	5*	103	97
4,5,l				
-9	35	34	63	63
-8	42	42	73	67
-7	52	51	148	137
-6	22	24	71	62
-5	7	11*	18	17
-4	142	136	97	96
-3	42	47	14	16*
-2	125	123	54	52
-1	11	6*	30	9*
0	231	227	268	258
1	19	14	29	20
2	138	143	100	97
3	23	21	41	42
4	142	138	235	234
5	72	68	68	63
6	64	73	128	130
7	55	59	65	63
5,5,l				
-8	30	35	37	36
-7	46	50	46	45
-6	41	43	72	69
-5	46	39	75	69
-4	9	10*	25	13
-3	88	90	154	150
-2	62	59	152	151
-1	67	63	98	96
0	28	29	24	21
1	3	3*	12	7*
2	4	6*	11	3*
3	44	38	93	88
4	73	72	112	108
5	63	67	162	158
6,5,l				
-6	99	102		
-5	35	37	103	94
-4	130	132	228	216
-3	44	40	183	169
-2	120	120	207	198
-1	4	5*	28	27
0	76	76	174	165
1	19	21	12	13*
2	73	75	229	225
3	3	3*		
0,6,l				
1	93	148*	129	218*
2	107	106*	87	90*
3	305	322	447	458
4	198	201	244	220
5	7	9*	35	38
6	88	78	33	14
7	125	125	160	156
8	39	42	57	55
9	3	11*	44	36
10	15	14	82	78
1,6,l				
-10	93	93	217	210
-9	10	13*	11	6*
-8	90	81	96	87
-7	236	235	365	367
-6	162	159	222	206
-5	160	149	191	184
-4	198	179	227	220
-3	111	114	43	44
-2	8	11*	18	26*
-1	61	77*	11	8*
0	59	104*	111	148*
1	215	242*	308	332*
2	89	93	22	15
3	38	36	115	108
4	132	133	195	185
5	220	214	439	419
6	102	98	220	209
7	47	44	181	166
8	82	77	187	174
9	43	41	115	107
2,6,l				
-10	65	68	125	124
-9	41	41	81	80
-8	91	86	131	122
-7	25	25	13	6*
-6	92	99	76	76
-5	48	45	53	54
-4	152	143	128	131
-3	79	80	144	145
-2	124	133	206	214
-1	45	48	69	74
0	154	162	134	138
1	172	164	273	273
2	140	143	141	133
3	63	61	92	88
4	41	42	104	101
5	212	211	247	240
6	18	11	141	133
7	103	103	106	101
8	10	10*	55	55
9	54	53	113	109
3,6,l				
-9	16	14	14	10
-8	9	3*	25	26
-7	39	38	20	15
-6	39	39	106	104
-5	59	57	69	69
-4	178	174	203	199
-3	147	160	211	206
-2	171	169	174	172
-1	103	96	173	165
0	142	142	226	220
1	116	114	122	120
2	192	182	347	338
3	30	34	26	20
4	162	165	204	201
5	50	45	64	65
6	81	74	119	113
7	60	56	92	80
8	69	72	187	185
4,6,l				
-9	20	16		
-8	75	75	160	154
-7	78	77	181	178
-6	146	146	286	281
-5	39	44	54	58
-4	169	168	233	228
-3	21	21	29	19
-2	161	161	202	196
-1	59	56	36	25
0	140	131	332	317
1	30	31	21	8
2	80	90	268	260
3	36	38	70	64
4	8	6*	75	68
5	96	92	298	295
6	9	10*	105	101
7	49	53		
5,6,l				
-7	28	29	107	102
-6	67	64	94	92
-5	61	50	186	178
-4	77	75	195	186
-3	61	59	210	203
-2	68	68	158	157
-1	36	33	130	121
0	52	48	84	83
1	31	27	120	118
2	70	69	186	179
3	6	8*	24	23
4	56	53	151	146
5	28	26		
6,6,l				
-5	37	35		
-4	15	13	133	132
-3	35	41	34	26
-2	18	18	45	45
-1	55	53	44	96
0	37	35	37	34
1	14	18	18	12
2	50	55		
0,7,l				
1	106	160*	119	205*
2	6	7*	40	53*
3	95	99	121	132
4	44	40	83	83
5	145	144	168	164
6	55	53	11	11
7	83	85	117	106
8	68	68	85	80
9	28	25	45	44
1,7,l				
-9	20	21	22	15
-8	84	82	217	212
-7	14	15	56	91
-6	64	60	180	166
-5	68	64	145	143
-4	204	208	250	265
-3	26	30	70	77
-2	125	151*	81	106*
-1	41	36*	54	54*
0	180	246*	282	375*
1	167	201*	226	257*
2	256	272*	456	465
3	156	154	215	201
4	128	125	211	144
5	227	212	336	313
6	4	5*	12	17*
7	154	156	249	266
8	31	27	128	114
9	64	62	140	130
2,7,l				
-9	29	31	51	55
-8	32	28	104	95
-7	104	104	166	167
-6	102	100	270	266
-5	158	160	226	231
-4	95	91	129	133
-3	157	154	175	174
-2	84	92	140	160
-1	166	183	231	245
0	62	57	23	6*
1	38	39	56	52
2	35	33	69	70
3	39	33	89	80
4	153	150	157	140
5	76	76	215	194
6	50	54	51	46
7	39	36	180	166
8	76	69	121	107
3,7,l				
-9	16	15	36	33
-8	35	35	17	18
-7	25	26	5	6*
-6	131	127	154	153
-5	41	42	51	45
-4	106	103	184	181
-3	42	43	136	134
-2	107	107	196	196
-1	85	79	96	101
0	17	17	70	68
1	94	97	174	169
2	91	85	262	266
3	112	104	220	205
4	20	17	34	25
5	84	83	180	165
6	4	1*	50	47
7	70	66	179	166
4,7,l				
-8	21	17	54	51
-7	55	53	124	119
-6	15	18	32	24
-5	23	27	35	21
-4	14	10	56	49
-3	62	51	93	89
-2	86	82	125	126
-1	20	25	25	19
0	71	74	11	11*
1	13	7	22	15
2	142	140	131	131
3	31	27	20	14
4	51	52	60	56
5	48	52	17	2*
6	57	54		
5,7,l				
-6	42	42	81	79
-5	36	37	57	56
-4	10	13*	50	53
-3	72	62	114	110
-2	43	39	46	44
-1	43	40	78	70
0	3	5*	27	25
1	7	2*	38	28
2	49	42	117	105
3	22	22	34	34
4	29	32		
6,7,l				
-3	53	52		
-2	51	50		
-1	22	18		
0	70	67		
0,8,l				
1	58	104*	49	77*
2	231	242*	322	404*
3	21	24*	32	34*
4	145	134	152	141
5	76	78	82	79
6	34	37	63	39
7	41	40	45	44
8	32	24	17	4*
9	59	58		
1,8,l				
-9	40	43		
-8	42	44	37	32
-7	81	83	145	143
-6	40	34	17	23
-5	170	177	267	264
-4	21	22	35	24
-3	106	104*	196	210*
-2	118	153*	230	296*
-1	165	217*	268	367*
0	9	14*	2	7*
1	95	117*	190	217*
2	24	32*	36	33*
3	150	157	270	260
4	73	66	75	74
5	78	72	182	166
6	41	86	257	234
7	60	58	165	154
8	68	63	150	147
2,8,l				
-9	27	28		
-8	40	43	82	80
-7	36	38	56	44
-6	39	33	10	12
-5	17	22	12	17*
-4	92	97	139	141
-3	16	17	66	67
-2	37	37	89	95
-1	75	82*	61	59
0	63	74*	116	123
1	62	61	61	61
2	71	79	46	53
3	107	106	91	94
4	24	21	83	77
5	85	81	68	64
6	4	6*	62	61
7	92	90	140	151
8	7	2*		
3,8,l				
-8	24	19	30	24
-7	60	59	141	132
-6	26	27	45	46
-5	42	38	74	69
-4	56	58	72	67
-3	77	75	92	84
-2	114	121	110	115
-1	40	37	74	64
0	140	133	223	218
1	13	7	41	16
2	186	184	319	316
3	22	21	34	33
4	109	103	162	152
5	23	19	20	17
6	35	34	32	33
7	44	43		
4,8,l				
-7	7	10*	49	40
-6	52	51	127	120
-5	25	30	7	2*
-4	20	24	16	12
-3	42	44	19	14
-2	25	27	92	85
-1	62	58	90	83
0	58	56	195	189
1	50	49	109	88
2	42	37	191	182
3	64	60	132	127
4	14	10	20	22
5	71	72		
5,8,l				
-5	37	40	72	70
-4	59	56	156	156
-3	51	46	115	106
-2	35	34	93	91
-1	5	5*	31	25
0	46	47	85	86
1	7	10*	38	35
2	36	34	80	78
3	15	12		
0,9,l				
1	55	100*	44	77*
2	2	5*	14	14*
3	64	13*	24	28
4	56	57	62	62
5	47	52	49	48
6	44	43	22	23
7	23	20	58	63
8	32	31		
1,9,l				
-8	38	39	78	84
-7	61	61	121	133
-6	48	45	95	106
-5	4	3*	18	15
-4	72	79	101	119
-3	18	23	52	67
-2	69	86*	66	94*
-1	65	92*	124	186*
0	71	107*	119	171*
1	61	75*	148	174*
2	174	201*	317	342
3	104	102	232	226
4	82	82	140	135
5	85	82	131	124
6	12	7	46	45
7	84	78	149	151
8	27	26		
2,9,l				
-8	30	30		
-7	68	72	102	117
-6	26	27	74	80
-5	55	56	44	41
-4	50	53	80	94
-3	112	125	132	149
-2	149	173	229	273
-1	82	94	116	127
0	65	75	43	48
1	125	129	307	322
2	100	99	111	117
3	73	71	207	194
4	69	85	142	133
5	61	57	125	121
6	51	46	55	48
7	13	8		
3,9,l				
-7	3	3*	12	4
-6	17	17	17	19
-5	6	8*	13	10
-4	61	63	110	121
-3	62	60	173	201
-2	3	6*	8	6*
-1	47	51	100	110
0	59	61	87	90
1	93	94	122	127
2	34	33	112	107
3	45	49	27	24
4	13	6	5	3*
5	71	66	140	146
6	28	26		
4,9,l				
-6	18	18		
-5	73	71	128	143
-4	30	37	34	46
-3	34	37	95	102
-2	6	7*	25	30
-1	50	45	141	156
0	37	41	37	46
1	2	10*	33	31
2	43	45	35	37
3	18	15	95	99
4	32	32		
5,9,l				
-3	42	45		
-2	2	1*		
-1	72	64		
0	11	12		
1	53	55		

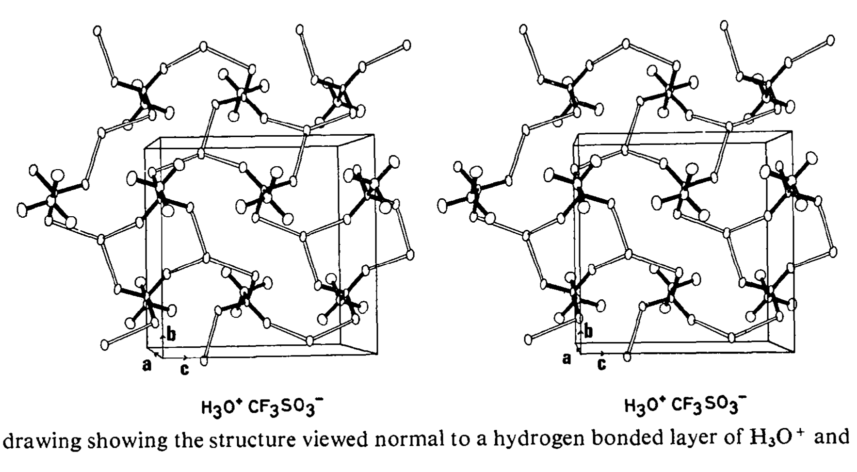


Fig. 2. Stereoscopic drawing showing the structure viewed normal to a hydrogen bonded layer of H_3O^+ and $CF_3SO_3^-$ ions (83°K).

Table 4. *Interatomic distances and angles*

(*a*) Covalent bonds

	298 °K	83 °K
S–O(1)	1·437 (3) Å	1·445 (2) Å
S–O(2)	1·443 (3)	1·459 (2)
S–O(3)	1·428 (3)	1·442 (2)
S–C	1·827 (5)	1·833 (4)
C–F(1)	1·316 (6)	1·322 (4)
C–F(2)	1·299 (6)	1·332 (4)
C–F(3)	1·307 (6)	1·334 (4)
O(1)–S–O(2)	112·3 (2)°	112·4 (1)°
O(1)–S–O(3)	116·0 (2)	115·8 (1)
O(2)–S–O(3)	114·8 (2)	114·9 (1)
C——S–O(1)	104·2 (2)	104·1 (2)
C——S–O(2)	103·5 (2)	103·2 (1)
C——S–O(3)	104·2 (2)	104·6 (2)
F(1)–C–F(2)	108·4 (4)	109·5 (3)
F(1)–C–F(3)	108·2 (4)	108·9 (3)
F(2)–C–F(3)	109·6 (4)	108·4 (3)
S——C–F(1)	109·2 (3)	109·6 (2)
S——C–F(2)	110·9 (3)	110·5 (2)
S——C–F(3)	110·5 (3)	109·9 (2)

(*b*) Hydrogen bonds

	298 °K	83 °K
O(*W*)···O(1)	2·668 (4) Å	2·672 (3) Å
O(*W*)···O(2)	2·546 (4)	2·546 (3)
O(*W*)···O(3)	2·585 (4)	2·588 (3)
O(1)···O(*W*)···O(2)	132·1 (1)°	130·5 (1)°
O(1)···O(*W*)···O(3)	108·2 (2)	107·5 (1)
O(2)···O(*W*)···O(3)	101·3 (1)	100·9 (1)
S———O(1)····O(*W*)	105·6 (2)	103·9 (1)
S———O(2)····O(*W*)	125·3 (2)	124·2 (1)
S———O(3)····O(*W*)	144·2 (2)	138·4 (1)

C–F bond distance of 1·329 Å. The average of all bond angles about the carbon atom is 109·5°, with a maximum deviation of 1° from the average. The F–C–S–O torsional angles for *trans* substituents are all within 1·8 (3)° of 180°.

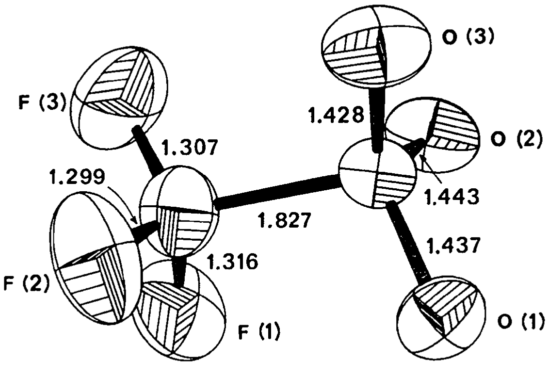
Hydrogen bonding

The O(*W*)···O hydrogen bond distances found in this compound (2·546, 2·588, 2·672 Å) are similar to those found in other monohydrates of strong acids; see, for example, $H_2SO_4.H_2O$ (Taesler & Olovsson, 1968). Two oxonium ions and two sulphonate groups related by a centre of symmetry form hydrogen-bonded rings involving O(*W*), O(2) and O(3) as can be seen in Fig. 2, with the shorter hydrogen bonds involved in this arrangement. The longer hydrogen bond, O(*W*)··· O(1), then links these rings to one another, forming the layers of the hydrogen bonded structure. The two S–O···O(*W*) hydrogen bond angles for the sulphonate oxygens involved in the ring (124·2 and 138·4°) are similar, and they differ from the angle for the sulphonate oxygen linking the rings (103·9°). The coordinates of the hydrogen atoms as obtained from Fourier difference syntheses give O–H distances for the oxonium ion in the range 0·93–1·04 Å and H–O–H angles in the range 100–131°. The O–H···O angles are in the range 161–177°. In order to determine more precisely the conformation of the oxonium ion in this somewhat asymmetric environment, a neutron diffraction investigation of this compound is being undertaken.

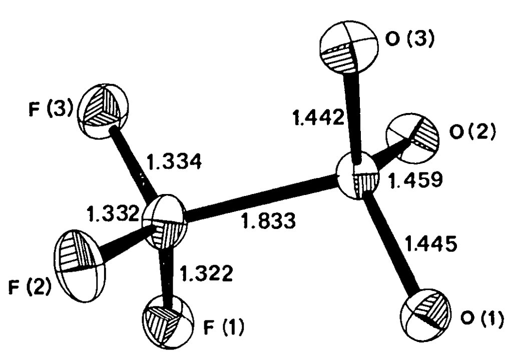
Comparison of the structure at 298 and 83 °K

The structure at room temperature is essentially the same as that found at 83 °K except for the minor changes expected to accompany an increase in temperature.

The S–O and C–F bonds are all shorter at 298 °K. This is a natural consequence of the model used to describe the thermal motion of the atoms; a model which cannot properly describe, for example, torsional vibrations around the C–S bond. Further analysis of the thermal parameters will be given elsewhere. The thermal expansion is slightly anisotropic, falling in the range 1·2–2 %, with the smallest change along the **b** direction. The hydrogen-bond lengths do not differ significantly at the two temperatures and the small rearrangements in the geometry of the hydrogen bonds at 83 °K are mainly reflected in the hydrogen-bond angles where the changes are up to 6°.



T: 298 K



T: 83 K

Fig. 3. Bond lengths (Å) in the $CF_3SO_3^-$ ion at 298 and 83 °K. The thermal ellipsoids are scaled to enclose 50 % probability.

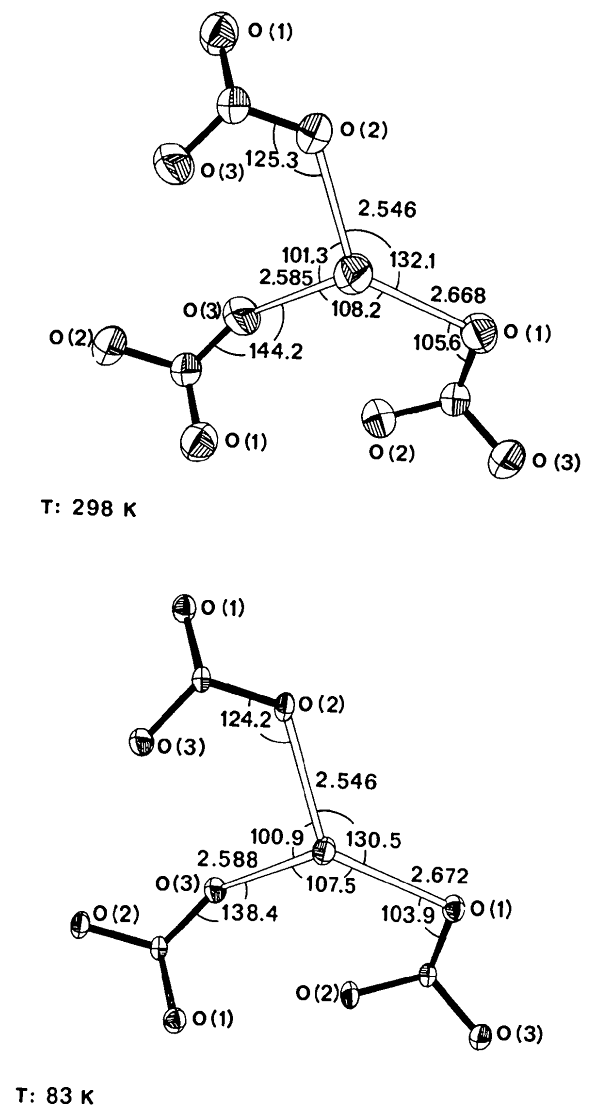


Fig. 4. Hydrogen bond distances (Å) and angles (°) at 298 and 83°K. The thermal ellipsoids are scaled to enclose 50% probability.

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