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The Crystal Structure of Trimethyloxosulfonium Fluoborate $[(CH_3)_3SO]^+BF_4^-$

BY IRMELA C. ZIMMERMANN, MALCOLM BARLOW AND J. D. MCCULLOUGH

Department of Chemistry, University of California at Los Angeles, Los Angeles 24, California, U.S.A.

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Crystals of $[(CH_3)_3SO]^+BF_4^-$ are orthorhombic with unit cell dimensions

$$a = 11{\cdot}49 \pm 0{\cdot}01,\ b = 11{\cdot}80 \pm 0{\cdot}01,\ c = 11{\cdot}58 \pm 0{\cdot}01\ \text{Å}\ .$$

The space group is *Pbcn* with $Z = 8$. Although the $[(CH_3)_3SO]^+$ ion is not required crystallographically to have any symmetry, it approximates closely to symmetry $3m$. The fluoborate ions are crystallographically of two types and both are required to have the symmetry 2. However, these ions achieve this symmetry in a statistical (disordered) manner.

Bond distances and angles in the trimethyloxosulfonium ion are: S–C(1) = 1·77 ± 0·02 Å, S–C(2) = 1·78 ± 0·02 Å, S–C(3) = 1·78 ± 0·02 Å, S–O = 1·45 ± 0·01 Å, C(1)–S–C(2) = 106·8 ± 0·8°, C(1)–S–C(3) = 107·2 ± 0·8°, C(2)–S–C(3) = 105·1 ± 0·8°, C(1)–S–O = 112·6 ± 0·7°, C(2)–S–O = 112·1 ± 0·7°, C(3)–S–O = 112·7 ± 0·7°.

Because of the disorder, it was not possible to obtain accurate bond distances and angles in the fluoborate ions.

Introduction

The crystal structure of trimethyloxosulfonium perchlorate has been reported by Coulter, Gantzel & McCullough (1961, 1963). At the time it became apparent that the perchlorate is disordered, the study of the fluoborate salt was undertaken with the hope that it would be ordered and thus permit a more accurate determination of the distances and angles in the $(CH_3)_3SO^+$ ion. Although it was found that the fluoborate salt was even more disordered than the perchlorate, the distances and angles in the $(CH_3)_3SO^+$ ion are in excellent agreement with the values found in the perchlorate and the structure reported for this interesting ion in the previous paper is confirmed.

Experimental

The preparation of trimethyloxosulfonium fluoborate has been described by Smith (1959) who kindly supplied the analyzed sample used in this study. Crystals suitable for the X-ray work were grown by the slow evaporation of solutions of the salt in acetone, in which it is only slightly soluble.

Weissenberg and precession photographs about the *c* axis of the unit appear much like those of the perchlorate. However, on closer inspection it was apparent that the fluoborate has orthorhombic rather than tetragonal symmetry. The lattice constants are:

$$a = 11{\cdot}49 \pm 0{\cdot}01,\ b = 11{\cdot}80 \pm 0{\cdot}01,\ c = 11{\cdot}58 \pm 0{\cdot}01\ \text{Å}$$

based on Cu $K\alpha = 1{\cdot}5418$ Å. The only systematic absences are $0kl$ with k odd, $h0l$ with l odd and $hk0$ with $h+k$ odd. The space group was accordingly assumed to be *Pbcn*. The flotation density of the crystals was found to be 1·52 g.cm^{-3} while that calculated for $Z = 8$ is 1·523 g.cm^{-3}.

The intensity data were obtained from sets of multiple-film Weissenberg photographs about the *b* and *c* axes prepared with Cu $K\alpha$ radiation. The crystals were about 0·18 mm by 0·20 mm in cross-section and the corresponding value of μR for copper radiation was 0·36. No corrections for absorption were made. The intensities were estimated visually by use of a calibrated intensity strip prepared with the same crystal and were corrected and correlated in the usual manner to give $k|F_o|$ values. Some 520 unique reflections were observed. Within this range there were some 280 lattice points other than space group absences for which intensities were below the observational limit.

Structure determination and refinement

Unsharpened and sharpened three-dimensional Patterson summations were computed. On the assumption that the strongest maxima were due to sulfur–sulfur interaction, these atoms were placed at 0·21, 0·20, 0·05. Although further information might have been obtained from the Patterson summations at this stage through considerable expenditure of time and effort, a three-dimensional Fourier synthesis was computed in which the phases were based on sulfur. If the anticipated similarity of the fluoborate salt to the perchlorate were fulfilled, then BF_4^- ions should be found near to 0, 0 $\frac{1}{4}$ and 0, $\frac{1}{2}$, $\frac{1}{4}$, and to positions related to these by symmetry. This would require the BF_4^- ions to be of two types crystallographically, *i.e.* in two sets of the fourfold positions 4*c* (0, *y*, $\frac{1}{4}$, *etc.*) with symmetry 2 and with *y* values for boron near to zero and to one-half respectively. Actually the Fourier synthesis did show maxima which accounted for half of the fluorine atoms, two in each BF_4^- ion in positions consistent with the above suggestion. These atoms (later designated F(3) and F(6)) were added to sulfur to determine the phases for the second Fourier synthesis. Maxima in reasonable positions for the three carbons and oxygen about sulfur developed, but further three-dimensional Fourier refinement made it evident that the remaining fluorine atoms and the boron atoms are disordered. The nature of the disorder is such that the individual BF_4^- ions are not required to have any symmetry, but the crystallographically required symmetry, 2, is satisfied in a statistical manner. The fluorine atoms F(3) and F(6) appear to occupy nearly the same positions in the two alternatives but the positions of the remaining fluorine atoms are quite different.

The final three-dimensional least-squares refinement and the structure factor calculations were performed on the IBM 7090 by means of ACA Computer Program No. 317 (UCLALS1) written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood. This program minimizes the weighted sum of the squares of the quantity $(KF_o - G|F_c|)$ by a full-matrix routine, where K and G are scale factors. The program provides for several weighting options and for either isotropic or anisotropic temperature factors on the individual atoms. The options selected were the weighting scheme of Hughes (1941) and individual anisotropic temperature factors of the form

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right].$$

Unobserved reflections were omitted from the refine-

Table 1. *Atomic positional parameters and their standard deviations*

All values have been multiplied by 10^4

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
S	2175	03	2028	04	0439	04
O	2929	10	2812	11	−0146	11
C(1)	0702	16	2302	15	0180	16
C(2)	2431	14	0619	13	0014	15
C(3)	2375	14	2034	17	1947	13
B(1)*	0108	50‡	4935	33	2466	50‡
	0049†		4883		2495	
B(2)*	4857	50‡	4556	31	2435	50‡
	4942†		4530		2493	
F(1)*	0701	50	4081	41	2692	47
F(2)*	1110	40	4595	36	2245	46
F(3)	0090	18	5560	18	3377	18
F(4)*	4380	40	3670	28	2570	38
F(5)*	3856	44	4371	38	2299	51
F(6)	4895	18	5157	20	3396	18

* In the indicated general positions, these atoms must be given a statistical weight of $\frac{1}{2}$.

† Coordinates which place the B atom equidistant from the four F atoms in its group.

‡ Estimated values.

Table 2. *Vibrational parameters and their standard deviations*

All values have been multiplied by 10^4. The temperature factor has the form:

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right]$$

Atom	B_{11}	$\sigma(11)$	B_{22}	$\sigma(22)$	B_{33}	$\sigma(33)$	B_{12}	$\sigma(12)$	B_{13}	$\sigma(13)$	B_{23}	$\sigma(23)$
S	067	033	067	033	081	004	−013	007	013	007	006	010
O	119	012	114	013	143	014	−082	023	044	023	047	026
C(1)	119	018	104	019	121	022	024	029	−023	034	028	035
C(2)	106	016	065	013	117	016	034	023	015	032	−080	031
C(3)	110	016	124	018	065	013	−027	035	−064	027	−029	036
B(1)	132	040	067	025	040	033	*		−038	065	*	
B(2)	145	053	060	030	057	049	*		−026	083	*	
F(1)	330	084	203	058	239	073	243	100	−219	119	062	097
F(2)	211	042	171	053	257	068	244	075	251	079	106	080
F(3)	274	024	413	035	292	031	088	055	−077	048	−474	057
F(4)	386	106	197	039	120	034	−436	101	041	151	021	112
F(5)	203	045	257	061	356	088	−236	095	−251	090	179	107
F(6)	303	027	377	031	292	031	−235	054	180	047	−472	056

* Held at zero during final stages of refinement.

Table 3. *Comparison of observed and calculated structure factors for* $[(CH_3)_3SO]^+BF_4^-$

Within each group, the numbers are (left to right) h, F_o, and F_c. Those labeled with an asterisk correspond to the maximum permitted value for an unobserved reflection, while those labeled E are believed to have been subject to extinction. Reflections labeled * or E were not used to obtain the parameters given in Tables 1 and 2

K= 0, L= 0		
2	13.0	-8.5
4	171.9	169.9
6	40.9	-41.6
8	18.4	16.6
10	24.8	17.2
12	10.8	-13.0
14	18.4	13.6
K= 1, L= 0		
1	14.4	13.6
3	23.6	-27.1
5	30.6	30.2
7	25.1	-23.6
9	14.6	14.1
11	11.3	-9.9
13	11.0*	4.0
K= 2, L= 0		
0	7.1	-1.8
2	152.4E	212.2
4	32.5	-28.6
6	47.3	47.9
8	38.9	34.8
10	12.5*	-10.6
12	17.7	15.8
14	17.0	-12.7
K= 3, L= 0		
1	41.1	-39.8
3	53.2	58.8
5	40.6	-42.2
7	50.3	52.6
9	32.1	-30.5
11	16.3	16.4
13	10.6*	-7.3
K= 4, L= 0		
0	105.3	122.2
2	26.1	-27.9
4	40.9	44.0
6	9.7*	12.1
8	11.2*	3.1
10	12.4	10.7
12	11.5*	-6.7
K= 5, L= 0		
1	47.3	46.6
3	25.0	-29.6
5	68.1	72.1
7	51.5	-56.3
9	28.3	31.3
11	21.4	-19.9
13	11.9	8.4
K= 6, L= 0		
0	16.6	-21.5
2	8.8*	2.7
4	18.0	20.8
6	18.3	19.4
8	9.7	9.7
10	12.3*	-0.7
12	10.1*	-3.1
K= 7, L= 0		
1	10.8*	-13.6
3	43.9	44.3
5	40.3	-44.0
7	34.7	35.9
9	22.5	-27.8
11	17.2	14.4
K= 8, L= 0		
0	47.1	-45.6
2	50.4	51.0
4	28.7	-30.8
6	17.6	22.2
8	11.3	-12.9
10	11.2*	-1.7
K= 9, L= 0		
1	7.4	7.2
3	22.3	-20.9
5	6.4	6.9
7	20.3	-23.5
9	4.1	6.9
K= 10, L= 0		
0	31.7	27.2
2	29.6	-30.5
4	22.0	20.3
6	7.9	-6.9
8	11.4*	-1.0
K= 11, L= 0		
1	12.5*	-11.3
3	12.3*	-3.0
5	12.0*	-5.9
7	11.2*	3.2
K= 12, L= 0		
0	25.3	-25.7
2	22.6	21.2
4	13.4	-13.8
6	5.8	7.4
K= 13, L= 0		
1	11.2*	-2.6
3	10.5*	2.6
K= 14, L= 0		
0	13.0	12.4
K= 1, L= 1		
1	8.2	11.5
2	47.5	-42.8
3	33.7	36.0
4	9.9	3.3
5	19.7	-17.2
6	41.1	-38.3
7	26.2	25.1
8	33.0	34.2
9	9.3	-11.7
10	17.1	-19.6
11	8.8	8.4
12	17.3	15.4
13	7.7*	-4.0
K= 2, L= 1		
0	17.5	18.3
1	75.5	-70.9
2	46.4	43.8
3	53.5	53.5
4	54.4	-56.5
5	29.8	-30.8
6	16.2	-12.3
7	14.4	13.9
8	7.7*	-5.0
9	8.6*	-1.9
10	8.8*	2.0
11	8.8*	-2.3
12	8.8*	1.4
13	8.9	5.6
K= 3, L= 1		
1	28.1	28.8
2	27.4	23.8
3	4.8*	-2.0
4	17.8	12.8
5	23.5	24.8
6	20.2	19.1
7	7.4*	-5.3
8	17.1	-17.8
9	14.8	11.4
10	8.8	9.1
11	10.6	-4.8
12	8.4*	-8.5
13	7.4*	2.4
K= 4, L= 1		
0	66.1	66.5
1	28.1	36.0
2	55.3	-54.0
3	5.6*	-3.3
4	19.8	-17.4
5	24.1	20.3
6	29.2	-31.5
7	7.4*	1.2
8	10.1	8.3
9	8.7	-9.2
10	8.8*	3.6
11	13.6	11.1
12	7.9*	-2.3
13	12.5	-11.4
K= 5, L= 1		
1	8.7	-10.5
2	6.1	-6.1
3	6.1	6.3
4	16.7	-13.5
5	7.4	9.2
6	7.4*	-1.4
7	10.2	12.2
8	8.5	5.7
9	8.8*	0.5
10	8.8*	-0.5
11	8.6*	0.5
12	7.9*	3.5
K= 6, L= 1		
0	35.0	-34.4
1	56.3	-54.1
2	16.2	15.4
3	41.0	38.9
4	33.7	-35.0
5	28.4	-30.6
6	12.5	13.2
7	13.2	12.9
8	8.8*	5.5
9	9.1*	1.6
10	8.6*	2.1
11	8.4*	-4.3
K= 7, L= 1		
1	6.8*	-0.3
2	7.9	-7.5
3	8.9	12.2
4	25.8	25.0
5	7.9*	6.4
6	14.5	-16.3
7	8.8*	6.8
8	13.2	13.7
9	8.8*	-5.6
10	10.2	-10.5
11	7.7*	1.8
K= 8, L= 1		
0	22.6	20.1
1	20.1	20.8
2	7.7	-10.0
3	7.9	-7.2
4	14.1	10.5
5	14.6	15.3
6	8.8*	1.5
7	12.5	-3.4
8	8.8*	4.5
9	10.3	-2.6
10	7.9*	1.0
K= 9, L= 1		
1	8.4*	3.5
2	8.3	9.1
3	8.4*	-1.0
4	19.2	-21.3
5	10.7	7.6
6	19.7	19.9
7	8.7	-10.3
8	15.8	-14.9
9	7.9*	1.9
K= 10, L= 1		
0	8.8*	-0.4
1	8.8*	4.6
2	8.8*	4.7
3	8.8	-9.3
4	8.8*	-1.7
5	8.8*	0.7
6	8.8*	1.7
7	8.8*	-3.0
8	7.9*	1.0
9	6.8*	3.8
K= 11, L= 1		
1	8.8*	-3.5
2	8.8	-8.0
3	8.8*	2.6
4	13.7	14.6
5	8.5	-8.7
6	11.5	-14.5
7	7.7*	2.4
8	9.8	11.9
K= 12, L= 1		
0	8.6*	-1.9
1	8.6*	-3.4
2	8.6*	2.3
3	8.4*	5.1
4	8.2*	-2.6
5	7.9*	1.8
6	7.4*	2.2
K= 13, L= 1		
1	7.4*	-1.7
2	7.4*	5.0
3	6.8*	-4.0
4	6.8*	-7.8
5	6.3*	1.9
6	5.9	9.2
K= 0, L= 2		
1	89.7	-77.8
2	221.9	-218.3
3	47.7	48.1
4	60.9	58.3
5	20.6	-22.1
6	37.0	-34.1
7	15.1	21.3
8	15.2	-25.0
9	10.8*	4.6
10	32.4	9.4
11	12.5*	-4.3
12	12.5*	-14.0
13	10.8*	5.9
14	9.9	11.9
K= 1, L= 2		
1	14.9	16.5
2	5.8	-5.7
3	16.2	-18.7
4	7.4	7.0
5	17.8	18.3
6	9.7	-9.6
7	18.3	-18.5
8	10.5*	6.0
9	12.9	11.8
10	12.5*	-4.2
11	12.5*	-5.6
12	12.0*	2.4
13	10.8*	3.2
14	8.8*	-0.8
K= 2, L= 2		
0	165.5	-206.8
1	56.6	53.8
2	36.5	-13.0
3	33.4	-31.6
4	10.9	-13.9
5	31.1	29.9
6	10.7	-2.6
7	9.7*	-0.6
8	10.8*	11.7
9	11.9*	1.0
10	22.3	-22.2
11	12.5*	3.3
12	11.0	14.5
13	10.5*	-5.5
14	12.6	-11.7
K= 3, L= 2		
1	13.2	-13.4
2	17.0	19.0
3	27.7	29.8
4	15.4	-15.6
5	44.1	-44.6
6	21.9	21.0
7	35.3	33.9
8	15.4	-15.7
9	18.1	-18.3
10	8.4	10.9
11	8.2	11.4
12	11.7*	-5.7
13	10.1*	-3.8
K= 4, L= 2		
0	74.1	69.4
1	20.6	-19.9
2	16.2	-14.6
3	12.0	9.1
4	14.1	9.6
5	9.9	-10.2
6	17.4	-22.5
7	10.8*	3.9
8	23.5	-23.3
9	12.5*	0.1
10	12.5*	7.0
11	12.5*	-1.9
12	11.5*	-5.7
13	9.5*	2.3
K= 5, L= 2		
1	20.1	20.9
2	7.9	-9.9
3	51.3	-50.6
4	25.5	23.6
5	34.9	33.3
6	20.2	-20.6
7	38.4	-39.8
8	19.3	18.6
9	24.4	25.5
10	12.0	-11.2
11	13.4	-12.3
12	6.9	7.1
13	8.8*	4.5
K= 6, L= 2		
0	11.9	-13.1
1	12.0	-9.2
2	8.7	5.8
K= 7, L= 2		
1	23.2	-23.1
2	11.8	11.6
3	25.5	23.4
4	10.4	-10.4
5	24.4	-26.9
6	16.1	16.0
7	41.6	39.7
8	11.9	-11.6
9	11.7	-14.0
10	11.9*	8.6
11	10.8*	9.2
12	8.8*	-4.1
K= 8, L= 2		
0	24.2	-27.5
1	20.8	19.4
2	30.8	32.7
3	17.1	-15.6
4	27.3	-28.8
5	11.7*	8.7
6	12.5*	10.5
7	12.5*	-4.2
8	12.5*	-3.5
9	12.0*	-0.8
10	11.2*	0.6
K= 9, L= 2		
1	17.7	16.7
2	11.3	-4.4
3	12.5*	-2.6
4	12.5*	4.3
5	22.2	20.2
K= 1, L= 3		
1	35.0	-33.9
2	21.6	-21.6
3	23.9	27.6
4	20.5	-14.0
5	34.5	-37.1
6	16.0	-16.8
7	32.0	33.5
8	16.7	17.2
9	21.3	-21.3
10	6.5	-8.4
11	12.3	12.3
12	10.8	8.2
K= 2, L= 3		
0	77.6	-88.4
1	36.4	-34.6
2	4.0*	4.6
3	4.8*	1.4
4	4.8*	2.0
5	21.3	-20.1
6	17.7	18.8
7	7.4*	5.4
8	7.9*	1.0
9	8.4*	1.6
10	8.8*	-6.7
11	9.3*	-3.2
K= 3, L= 3		
1	19.8	20.1
2	13.6	7.7
3	16.9	-15.4
4	17.4	14.8
5	22.2	22.1
6	6.8*	4.1
7	25.3	-26.3
8	8.6	-8.2
9	17.0	12.0
10	9.1*	1.9
K= 4, L= 3		
0	16.5	18.0
1	26.7	-18.5
2	39.2	-36.8
3	6.0	5.2
4	48.5	46.5
5	10.4	-11.5
6	7.1*	-1.8
7	7.7*	9.6
8	11.9	-8.6
9	12.5	-11.9
10	9.1*	4.5
K= 5, L= 3		
1	16.1	12.4
2	5.9*	-5.1
3	12.9	12.0
4	17.8	-16.2
5	8.2	-7.7
6	7.7*	-2.8
7	8.2*	2.6
8	8.6*	1.1
9	9.1*	-1.4
K= 6, L= 3		
0	51.8	-49.1
1	27.4	-25.6
2	34.7	34.2
3	6.8*	0.7
4	17.1	-17.0
5	18.1	-19.7
6	8.2*	4.0
7	8.4*	2.7
8	8.8*	-6.0
9	9.1*	2.7
K= 7, L= 3		
1	7.1*	4.9
2	7.4*	-3.8
3	7.4*	2.8
4	17.4	17.1
5	14.9	-14.4
6	15.5	-13.2
7	8.8*	6.6
8	9.1*	6.7
K= 8, L= 3		
0	15.2	13.2
1	7.9*	3.8
2	25.0	-20.8
3	7.9*	-0.3
4	8.4*	6.1
5	8.4*	4.4
6	13.0	-9.7
7	9.1*	-0.1
K= 9, L= 3		
1	8.4*	1.4
2	8.4*	6.7
3	14.2	-11.8
4	14.4	-12.6
5	14.6	13.6
6	9.2	10.7
K= 0, L= 4		
0	189.8	176.8
1	29.7	-36.4
2	77.5	-70.2
3	7.2	12.7
5	28.4	-27.7
6	38.2	-37.4
7	10.5	-15.5
8	7.9*	-2.6
9	5.7	6.4
10	9.8	7.8
11	10.2	-10.9
12	7.9*	-6.8
13	13.6	12.5
K= 1, L= 4		
1	5.2	6.0
2	9.9	-10.1
3	10.2	-11.1
4	7.1	7.2
5	12.5	13.6
6	10.3	-9.3
7	10.7	-12.8
8	9.4	7.5
9	8.6*	6.0
10	9.1*	-5.3
11	8.8*	-4.8
12	7.9*	2.4
K= 2, L= 4		
0	64.8	-63.0
1	23.5	27.9
2	4.0	3.2
3	8.2	-8.6
4	47.0	-42.0
5	8.4	4.5
6	6.5	-2.5
7	7.4*	-5.4
8	20.5	20.4
9	9.9	-11.7
10	8.3	-10.0
11	9.8	10.4
K= 3, L= 4		
1	32.6	-33.8
2	11.2	10.6
3	15.7	14.9
4	26.0	-24.8
5	20.6	-22.7
6	22.7	23.0
7	19.7	20.3
8	18.9	-19.6
9	13.3	-13.0
10	10.6	11.6
11	8.6*	5.7
K= 4, L= 4		
0	10.6	10.0
1	9.8	-10.1
2	47.4	-42.8
3	5.6*	5.1
4	9.4	-5.4
5	4.6	-5.6
6	5.0	0.8
7	8.2*	0.0
8	8.4*	-4.3
9	9.1*	4.8
10	9.1*	5.3
K= 5, L= 4		
1	4.0	5.0
2	24.4	-22.2
3	25.9	-25.0
4	19.7	18.2
5	21.2	24.0
6	27.2	-28.6
7	28.9	-30.5
8	19.6	20.9
9	9.2	10.9
10	12.0	-14.9
11	11.1	-7.6
12	9.6	6.8
K= 6, L= 4		
0	29.8	-26.6
1	13.3	-9.9
2	4.6	-3.2
3	12.6	13.9
4	7.4*	2.9
5	7.7*	0.1
6	11.0	9.9
7	8.8*	3.1
8	9.1*	2.3
9	8.8*	2.0
K= 7, L= 4		
1	20.8	-20.6
2	11.2	9.7
3	8.9	10.7
4	17.8	-15.9
5	26.1	-27.2
6	16.2	18.0
7	11.7	13.0
8	14.3	-15.0
9	13.8	-12.6
K= 8, L= 4		
0	22.5	-21.5
1	19.2	16.3
2	22.3	24.5
3	17.5	-17.3
4	15.0	-17.4
5	8.2	6.5
6	8.3	9.0
7	8.8*	0.4
8	8.6*	-8.9
K= 9, L= 4		
1	7.9*	-3.0
2	8.4*	-4.7
3	17.4	-15.9
4	8.4*	5.8
5	8.4*	-3.0
6	5.8	-6.8
7	13.8	-12.7
K= 10, L= 4		
0	8.2	6.7
1	17.6	-17.5
2	11.7	-10.4
3	14.4	13.0
4	8.8*	4.6
5	8.6*	-5.2
K= 11, L= 4		
1	10.0	-10.4
2	8.6*	1.0
3	8.8*	-3.9
K= 12, L= 4		
0	10.9	-10.8
1	13.3	14.0
2	10.7	7.8
3	10.4	-11.5
K= 1, L= 5		
1	20.1	-21.2
2	5.6	-7.5
3	35.7	37.8
4	12.6	-12.2
5	41.0	-43.6
6	6.6*	-4.8
7	44.6	43.9
8	4.9	7.1
9	22.0	-26.6
K= 2, L= 5		
1	20.7	-18.3
2	57.7	59.7
3	20.2	22.3
4	22.8	-19.8
5	13.8	-14.2
6	6.6	7.8
7	8.2*	6.3
8	8.4*	4.5
9	8.8*	-5.3
K= 3, L= 5		
1	10.5	11.0
2	4.8*	4.6
3	32.1	-29.6
4	15.4	15.9
5	22.5	25.3
6	6.8*	1.5
7	25.5	-29.1
8	7.9*	-2.0
9	16.6	16.0
K= 4, L= 5		
0	90.4	91.5
1	3.2	2.8
2	32.9	-26.3
3	15.5	15.6
4	30.2	29.1
5	7.4*	4.6
6	8.6	-9.6
7	7.9*	-0.9
8	8.8	3.6
K= 5, L= 5		
1	18.6	-19.6
2	6.3*	-2.1
3	6.3*	-0.2
4	10.2	-6.3
5	6.8*	-4.0
6	7.7*	1.5
7	9.6	8.0
8	9.1*	4.1
K= 6, L= 5		
0	40.4	-34.4
1	11.5	-13.4
2	53.7	50.0
3	12.3	14.2
4	20.8	-21.6
5	12.6	-12.1
6	19.9	21.7
7	8.4*	7.5
8	10.3	10.1
K= 7, L= 5		
1	7.4*	0.4
2	7.4*	-2.6
3	13.2	12.1
4	8.4*	8.8
5	8.8*	-7.7
6	9.1*	-3.8
K= 8, L= 5		
0	37.5	35.5
1	7.9*	3.6
2	12.9	-9.3
3	7.9*	3.7
4	18.2	18.4
5	9.1*	5.8
K= 9, L= 5		
1	7.2	6.1
2	8.4*	-0.6
3	7.2	-9.2
4	8.4*	-6.1
5	14.5	16.6
K= 0, L= 6		
0	36.7	35.0
1	75.4	-66.6
2	22.6	-21.5
3	43.8	39.8
4	37.5	34.9
5	30.1	-26.5
6	13.3	-8.7
7	14.0	17.5
8	8.8*	-3.6
K= 1, L= 6		
1	6.3*	1.5
2	6.3*	-3.8
3	6.8*	-4.7
4	11.3	10.7
5	7.4*	3.1
6	11.3	-11.3
7	8.4*	-1.8
8	8.8*	8.9
K= 2, L= 6		
0	12.3	-15.8
1	43.9	45.5
2	16.4	12.6
3	29.3	-31.1
4	17.0	17.0
5	28.2	26.8
6	8.2*	0.6
7	8.4*	-2.4
8	8.8*	3.8
K= 3, L= 6		
1	9.7	12.0
2	18.1	20.3
3	8.4	11.1
4	18.8	-20.6
5	7.4*	2.3
6	24.7	27.3
7	7.9*	5.8
8	19.0	-21.6
K= 4, L= 6		
0	28.3	27.9
1	20.6	-21.3
2	6.8*	5.7
3	6.8*	3.4
4	7.4*	2.2
5	12.3	-15.5
6	11.9	-8.7
7	8.8*	1.5
8	9.1*	-8.3
K= 5, L= 6		
1	22.1	22.3
2	18.5	-15.9
3	6.8*	4.9
4	30.0	27.2
5	7.9*	8.7
6	33.7	-29.9
7	7.4*	0.2
8	28.8	25.4
9	6.8*	1.2
10	19.3	-15.2
K= 1, L= 7		
1	21.6	-22.9
2	9.7	8.0
3	24.5	24.2
4	24.4	-26.0
5	31.5	-32.8
6	16.8	17.1
7	32.4	34.4
8	7.4*	-13.1
9	20.8	-20.3
10	8.4*	10.2
11	12.4	12.4
K= 2, L= 7		
0	59.4	-64.0
1	9.9	8.7
2	13.1	7.3
3	8.5	-10.9
4	23.1	-24.8
5	8.4*	3.8
6	8.4*	8.0
7	8.8*	2.6
8	9.1*	-3.5
K= 3, L= 7		
1	11.6	9.6
2	7.4*	-6.3
3	18.5	-19.3
4	17.3	17.7
5	17.7	20.3
6	13.2	-14.5
7	23.4	-23.6
K= 4, L= 7		
0	26.8	25.6
1	32.5	-35.6
2	48.5	-53.8
3	27.2	28.2
4	27.1	23.1
5	12.6	-15.5
6	19.3	-19.7
K= 0, L= 8		
0	12.2	6.5
1	24.6	-21.3
2	33.8	30.7
3	15.6	13.0
4	8.4*	-13.1
5	15.2	-13.8
6	15.6	11.3
7	9.1*	-1.0
8	9.1*	-0.9
K= 1, L= 8		
1	7.7*	2.3
2	7.7*	-4.6
3	7.9*	3.1
4	8.2*	3.7
5	8.4*	-3.3
6	8.8*	-4.1
7	9.1*	0.8
8	9.1*	4.0
K= 2, L= 8		
0	36.1	33.1
1	17.9	18.6
2	14.3	-20.7
3	7.9*	-2.8
4	28.6	25.5
5	12.5	10.5
6	6.8*	-6.3
7	7.4*	-0.3
8	14.7	13.8
K= 3, L= 8		
1	7.9*	-8.2
2	8.2*	7.1
3	8.2*	-12.1
4	8.4*	-10.1
5	8.8*	7.5
6	9.1*	13.4
7	9.3*	-11.5
8	9.5*	-10.0
K= 4, L= 8		
0	7.9*	3.2
1	7.9*	-6.3
2	18.0	16.9
3	7.9*	6.3
4	8.4*	0.5
5	8.4*	-2.9
6	12.6	11.5
K= 5, L= 8		
1	7.9*	-8.3
2	9.5	-10.1
3	7.9*	2.9
4	11.8	10.9
5	11.5	-14.4
6	13.5	-15.0
7	7.9	7.1
8	12.6	11.1
9	9.9	-11.0
10	6.1	-7.4
K= 1, L= 9		
1	8.4*	-5.0
2	8.4*	8.2
3	12.6	13.0
4	16.5	-19.1
5	10.5	-11.7
6	15.8	17.0
7	14.6	14.8
8	11.1	-12.5
9	8.4*	-6.6
10	9.9	9.2
K= 2, L= 9		
0	8.4*	2.6
1	10.7	10.4
2	11.8	12.9
3	8.6*	-9.9
4	8.8*	-1.4
5	9.1*	1.3
6	9.1*	1.1
K= 3, L= 9		
1	8.6*	12.7
2	8.6*	-5.8
3	8.8*	-3.6
4	8.8*	14.6
5	9.1*	9.6
K= 4, L= 9		
0	20.7	19.4
1	26.0	-27.7
2	8.4*	-5.3
3	26.3	24.1
4	8.4*	6.3
5	15.4	-14.5
K= 0, L= 10		
0	28.9	-21.9
1	8.8*	-5.8
2	8.8*	-1.1
3	8.8*	-2.2
4	16.1	-11.8
K= 1, L= 10		
0	8.8*	0.0
1	8.8*	-1.6
2	9.1*	-0.7
3	9.1*	1.9
4	9.1*	1.9
K= 2, L= 10		
0	8.8*	3.2
1	8.8*	1.6
2	24.0	-22.5
3	9.1*	1.1
K= 4, L= 11		
1	18.0	-18.2
2	7.9*	-5.5
3	13.4	15.5
K= 0, L= 12		
0	10.7	-7.8
1	8.4*	-0.8
2	19.7	21.1
K= 2, L= 12		
0	16.1	21.5
1	7.9*	0.1
2	11.7	-10.2
3	7.9*	3.0
4	11.0	14.7
K= 4, L= 13		
1	13.1	-14.8
2	6.3*	5.5
3	9.9	12.1
K= 0, L= 14		
0	9.0	-11.4
1	12.1	10.1
2	5.6*	1.9
3	10.8	-10.1

ment procedures and in computing the agreement index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, but were included in the final structure factor calculations. The standard deviations of the positional and vibrational parameters were estimated from the inverse matrix of the normal equations.

The disordered trial structure was refined by the above least-squares procedures. Individual anisotropic temperature parameters were applied initially to all atoms except fluorine, which, because of the disorder, were assigned isotropic parameters. However, as the refinement progressed, anisotropic temperature parameters were assigned to these atoms, but the x and z parameters of the boron atoms were held constant. During the least-squares refinement the R value was reduced from the Fourier value of 20% down to the final value of 10·1%. A three-dimensional difference Fourier synthesis based on the final positional and vibrational parameters in Tables 1 and 2 showed no significant maxima or minima. In Table 3 the observed structure factors are compared with those calculated on the basis of the final parameters. In these calculations, the following atomic scattering factors were used without correction for anomalous dispersion: sulfur, those of Dawson (1960); fluorine and boron, those of Freeman (1959); oxygen, Hoerni & Ibers (1954), and carbon, McWeeny's values for diamond (1954).

Discussion of the structure

Projections of the structure of trimethyloxosulfonium fluoborate on (001) and (010) are shown in Figs. 1 and 2 respectively. In order to minimize the complexity of these figures, each BF_4^- ion is shown in only one of the two possible positions open to it because of the disorder. Also the projections show only half of the material in the unit cell, one layer of $(CH_3)_3SO^+$ ions and one layer of BF_4^- ions. The remaining half of the unit cell is, in each case, identical with that shown, but must be operated upon by the space group symmetry in order to be brought into coincidence with the Figure. The bond distances and angles and the structurally significant packing distances are given in Tables 4 and 5 respectively. The distances and angles in the $(CH_3)_3SO^+$ ion were corrected for librational motion (Cruickshank, 1956, 1961) and are in excellent agreement with the values found in trimethyloxosulfonium perchlorate (Coulter, Gantzel & McCullough, 1963). In view of the consistent results from the two independent studies, it appears quite certain that the free ion would have the symmetry $3m$ with the following distances and angles: S–O, 1·45 ± 0·01 Å; S–C, 1·78 ± 0·01 Å; C–S–O, 112·5 ± 0·5°; C–S–C, 106·0 ± 0·5°.

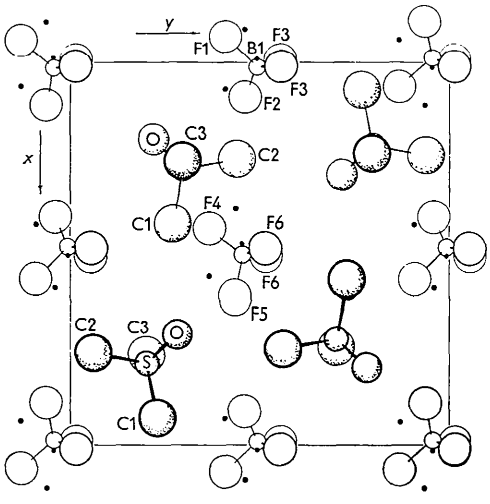

Fig. 1. Projection of the structure of $[(CH_3)_3SO]^+BF_4^-$ on (001) showing only half of the unit cell in the z direction. Alternate positions of the atoms in the fluoborate ions are shown by dots. The $(CH_3)_3SO^+$ ions are shaded and are above the mean plane of the BF_4^- ions.

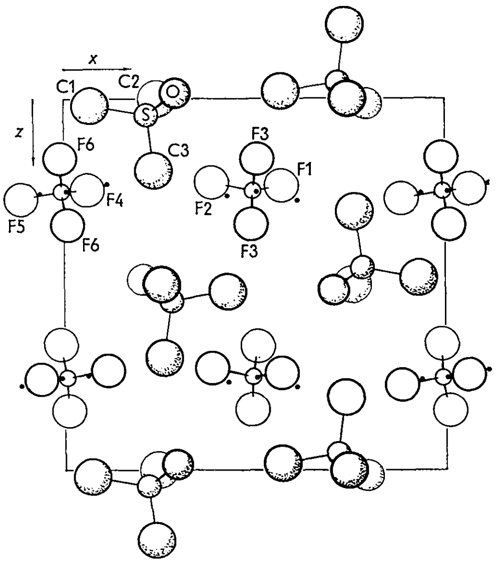

Fig. 2. Projection of the structure of $[(CH_3)_3SO]^+BF_4^-$ on (010) showing only half of the unit cell in the y direction. Alternate positions of the atoms in the fluoborate ion are shown by dots. The $(CH_3)_3SO^+$ ions are shaded and are above the mean plane of the BF_4^- ions.

Because of the disorder in the BF_4^- ions, the computed distances and angles within these groups have little significance. When the refined positions of the boron atoms are used, the computed B–F distances vary from 1·18 Å to 1·40 Å with σ 0·08 Å. However, if each boron atom is assumed to be equidistant from the four F atoms in its own ion, the B–F distances are 1·30 Å around B(1) and 1·28 Å around B(2). These values are considerably shorter than the reported values (1·40 Å and 1·43 Å) for the B–F distance in the BF_4^- ion (*Tables of Interatomic Distances*, 1958). Although some of this discrepancy may be due to librational motion of the BF_4^- ions, the data do not permit the analysis required for such corrections.

Table 4. *Bond distances and angles with standard deviations and corrections for implied librational motion*

(*a*) Trimethyloxosulfonium ion

	Uncorrected	Corrected
S–O	1·437 ± 0·013 Å	1·45 Å
S–C(1)	1·750 ± 0·019	1·77
S–C(2)	1·758 ± 0·017	1·78
S–C(3)	1·762 ± 0·016	1·78
O–S–C(1)	112·6 ± 0·7°	
O–S–C(2)	112·1 ± 0·7	
O–S–C(3)	112·7 ± 0·7	
C(1)–S–C(2)	106·8 ± 0·8	
C(1)–S–C(3)	107·2 ± 0·8	
C(2)–S–C(3)	105·1 ± 0·8	

(*b*) Fluoborate ion (I)

B–F	Range:	1·22 to 1·40 Å	Average 1·30 Å
F–B–F	Range:	90 to 125°	

(*c*) Fluoborate ion (II)

B–F	Range:	1·18 to 1·37 Å	Average 1·28 Å
F–B–F	Range:	103 to 118°	

Table 5. *Interionic packing distances in trimethyloxosulfonium fluoborate*

C(1)–O	3·19 Å	C(2)–F(5′)	3·47 Å
C(2)–O	3·34	C(2)–F(6)	3·39
C(3)–O	3·39	C(2)–F(6′)	3·49
C(1)–F(3)	3·35	C(3)–F(1)	3·21
C(1)–F(4)	3·23	C(3)–F(2)	3·37
C(1)–F(6)	3·16	C(3)–F(2′)	3·38
C(2)–F(1)	3·46	C(3)–F(4)	3·09
C(2)–F(2)	3·31	C(3)–F(5)	3·27
C(2)–F(5)	3·37	C(3)–F(5′)	3·47

Standard deviations:

C–O, 0·02 Å; C–F (for F(3) and F(6), 0·04 Å;
C–F (for other F atoms), 0·09 Å.

Sum of van der Waals radii:

CH_3–O, 3·40 Å; CH_3–F, 3·35 Å.

The observed F–B–F angles vary from 97° to 125° with standard deviations from 3° to 6°. It may be significant that the angles involving the least disturbed of the fluorine atoms (F(3)–B(1)–F(3′) = 108 ± 3° and F(6)–B(2)–F(6′) = 110 ± 3°) are close to the expected tetrahedral angle.

The packing of the ions in $[(CH_3)_3SO]^+BF_4^-$ is quite similar to that in trimethyloxosulfonium perchlorate. The similarities are especially apparent if one compares the projections of the two structures on (001). The interionic contacts in the fluoborate are mainly between methyl groups and fluorine, as would be expected. However, there are some C–O separations between different cations which are short enough to be considered as contacts. All interionic CH_3–CH_3 and F–F separations are greater than the sums of the corresponding van der Waals radii, 4·00 Å and 2·70 Å respectively. Although some of the separations in Table 5 are less than the sums of the corresponding van der Waals radii, the O or F atom may be approaching the methyl group between hydrogen atoms so that the short distance is not unreasonable. Also the standard deviations of the C–F separations are so large that the differences between the van der Waals sum and the observed separations may not be very significant.

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