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The Disordered Crystal and Molecular Structure of Tris(methylsulfonyl)methane

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The structure of the tris(methylsulfonyl)methane molecule $(CH_3 . SO_2)_3CH$, and of the disordered crystal, has been determined by X-ray methods. The crystal is rhombohedral, with $a_H = 12·89 \pm 0·02$, $c_H = 9·53 \pm 0·02$ Å and six molecular weights in the unit cell. Three-dimensional Fourier series and least-squares refinement were used to obtain the atom positions, thermal parameters and quantitative measure of the packing disorder. The bond configuration at the central carbon atom in $(CH_3 . SO_2)_3CH$ is tetrahedral, with S–C–S = 110·8 ± 0·4°. The central carbon–sulfur bonds are formally single with C–S = 1·83 ± 0·01 Å; the other bond lengths are S–O = 1·43 ± 0·01 Å and S–C(methyl) = 1·73 ± 0·02 Å. The remarkable temperature-independent diffuse scattering as well as the intensities of the sharp reflections have been explained on the basis of ordered columns of molecules along the trigonal axes of this rhombohedral crystal: two differently oriented columns are distinguished, related by pseudo twofold axes perpendicular to the trigonal axis. It is the packing of the columns that causes the diffuse scattering. There is 61 % of one orientation of column, 39 % of the other orientation, in the crystal. A packing scheme has been postulated that gives an optical diffractometer transform closely matching the X-ray diffuse scattering pattern.

Introduction

The tris(sulfonyl)methanes $(R . SO_2)_3CH$ have long been known as acids comparable in strength to trichloroacetic acid (Fromm, 1889; Samen, 1941, 1942, 1947). Doering & Levy (1955) suggested that the ease with which the central hydrogen atom is lost as a proton might be attributable to the resonance stabilization of a planar carbanion. A test for lack of planarity would be the observation of optical activity in such a molecule with all three R groups different. Three independent attempts to resolve tris(sulfonyl)methanes optically have been made without success (Gibson, 1931; Kipping, 1935, Böhme & Marx, 1941).

An initial X-ray investigation of tris(methylsulfonyl) methane (TMSM) was made by Abrahams & Speakman (1956), who found a remarkable diffuse X-ray scattering pattern given by the crystal. This scattering pattern includes intense diffuse spots at points in reciprocal space forbidden by the symmetry of the sharp Bragg reflections. These diffuse spots are linked by strong diffuse ridges, forming a planar honeycomb of diffuse hexagons around the sharp spots. Since the diffuse scattering was as pronounced at 78 °K as at room temperature, it was assumed due to displacement disorder rather than to thermal motion. Confirmation of the disorder hypothesis was provided by a heat capacity study (Staveley & Davies, 1956), in which no phase transitions were found between room temperature and 14 °K.

An X-ray investigation of the ammonium salt of tris(methylsulfonyl)methane has been reported by Hoogsteen (1957). He found the central carbon atom to lie in the plane of the three sulfur atoms. Hoogsteen gave an explanation in terms of hindered rotation about the central carbon–sulfur bonds for the failure to resolve optically $(R . SO_2)_3CH$ molecules, with three different R groups. Six instead of two stereoisomeric configurations could then result, leading to a considerable increase in the difficulty of achieving optical resolution.

The present study reports the configuration about the central carbon atom in TMSM, the structure of the whole molecule, and also postulates the nature of the disorder producing the diffuse scattering.

Crystal data

Tris(methylsulfonyl)methane, $(CH_3 \cdot SO_2)_3CH$: rhombohedral, with hexagonal lattice constants $a_H = 12·89 \pm 2$, $c_H = 9·53 \pm 2$ Å* at 291 °K (Abrahams & Speakman, 1956); six molecular weights per hexagonal unit cell; $D_x = 1·82$ g.cm^{-3}; $D_m = 1·83$ g.cm^{-3}; Laue group $\bar{3}m$, $hkil$ present only for $-h+k+l=3n$, $h\bar{h}0l$ only for $l=2n$. The space group is hence most probably $R3c$ (C_{3v}^6) or $R\bar{3}c$ (D_{3d}^6). The molecular symmetry is no higher than 3. The space group $R\bar{3}c$ is unlikely on stereochemical grounds, unless the general 36-fold positions are statistically half-occupied. $R3c$ is regarded as the more reasonable choice. The volume of the unit cell is 1370·3 Å^3. The absorption coefficient for Cu $K\alpha$ X-radiation ($\lambda = 1·5418$ Å) = 7·24 mm^{-1}, for Mo $K\alpha$ X-radiation ($\lambda = 0·7107$ Å) = 0·79 mm^{-1}.

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* In this, and subsequent numerical values, errors listed without decimal point correspond to the least significant digits in the function value.

Experimental

Fine, hexagonal prismatic crystals were grown by very slow cooling of aqueous solutions of TMSM. The very low solubility of TMSM required large volumes of hot water in this process. Initial intensity measurements were made visually on films exposed using Cu *Kα* X-radiation with a modified Weissenberg (Abrahams, 1954) camera, and Mo *Kα* radiation with a precession camera. The crystal dimensions were 0·15 × 0·15 × 0·60 mm. Later, complete *hkl* data were recorded on the modified Weissenberg camera, with Mo *Kα* X-radia-

Table 1. *Observed and calculated structure factors for the sharp reflections in tris (methylsulfonyl) methane*

h	*k*	*l*	*Fmeas*	*Fcalc*	*α*
1	1	0	166	161	0
2	2	0	157	150	180
3	0	0	110	105	199
3	3	0	44	47	180
4	1	0	20	23	281
4	4	0	58	51	0
5	2	0	39	36	2
5	5	0	32	28	0
6	0	0	74	67	353
6	3	0	62	54	11
6	6	0	41	39	180
7	1	0	39	36	9
7	4	0	14	15	157
7	7	0	13*	2	180
8	2	0	7	9	37
8	5	0	16	10	174
8	8	0	6	3	180
9	0	0	11*	6	65
9	3	0	12	11	201
9	6	0	16	15	5
9	9	0	12	13	180
10	1	0	32	28	188
10	4	0	30	31	358
11	2	0	17	14	329
11	5	0	20	25	7
12	0	0	8	12	210
12	3	0	35	32	359
12	6	0	10	10	6
13	1	0	16	14	5
13	4	0	10	11	353
15	0	0	15	15	142
15	3	0	11	11	200
16	1	0	11	11	159
18	0	0	16	15	3
19	1	0	16	16	360
1	3	1	58	58	8
1	6	1	22*	8	124
1	9	1	29	30	186
2	1	1	52	50	12
2	4	1	61	53	15
2	7	1	85	78	173
2	10	1	19*	7	258
3	2	1	78	82	22
3	5	1	55	52	170
3	8	1	39	45	179
4	3	1	41	31	2
4	6	1	55	45	171
4	9	1	16	9	334
5	1	1	55	54	7
5	4	1	36	30	224
5	7	1	50	48	6
6	2	1	45	43	323
6	5	1	41	42	357
6	8	1	34	31	4
7	3	1	28	26	220
7	6	1	65	68	7
7	9	1	17*	17	175
8	1	1	14	10	218
8	4	1	17*	9	151
9	2	1	40	44	174
9	5	1	17*	4	68
10	3	1	34	37	173
0	1	2	140	129	203
0	4	2	59	68	359
0	7	2	58	62	356
0	10	2	15*	10	60
0	13	2	19*	11	0
1	2	2	91	91	359
1	5	2	24	28	348
1	8	2	23	22	169
1	11	2	33	37	357
2	0	2	62	65	182
2	3	2	13	15	25
2	6	2	35	34	188
2	9	2	15*	11	174
2	12	2	19*	9	217
3	1	2	126	111	164
3	4	2	41	38	188
3	7	2	65	58	179
3	10	2	17*	8	228
4	2	2	39	37	174
4	5	2	93	86	182
4	8	2	17*	6	29
5	0	2	126	125	173
5	3	2	18	15	233
5	6	2	7	6	128
5	9	2	17*	12	179
6	1	2	27	27	346
6	4	2	24	20	200
6	7	2	28	30	11
6	10	2	19	20	184
7	2	2	27	29	341
7	5	2	22	20	9
7	8	2	19*	3	12
8	0	2	43	46	357
8	3	2	13*	1	254
8	6	2	17*	14	8
9	1	2	14	8	29
9	4	2	17*	17	173
10	2	2	24	29	170
10	5	2	19*	15	202
11	0	2	30	26	166
11	3	2	31	36	185
12	1	2	25	21	176
14	0	2	27	30	358
15	1	2	35	34	358
1	1	3	9	11	87
1	4	3	9	10	0
1	7	3	42	42	9
1	10	3	15	15	143
2	2	3	38	31	15
2	5	3	35	37	358
2	8	3	51	48	15
2	11	3	40	36	170
3	3	3	31	32	331
3	6	3	73	70	2
3	9	3	25	19	150
4	1	3	26	20	327
4	4	3	11*	4	194
4	7	3	28	26	353
4	10	3	15	22	175
5	2	3	61	60	183
5	5	3	13*	13	201
5	8	3	15*	8	214
6	3	3	75	81	171
6	6	3	25	26	215
7	1	3	59	62	173
7	4	3	20	17	181
7	7	3	13*	11	248
8	2	3	19	19	150
8	5	3	15*	8	307
9	3	3	42	44	11
10	1	3	21	19	17
10	4	3	22	28	7
11	2	3	32	34	12
0	2	4	59	64	177
0	5	4	20	22	223
0	8	4	32	35	355
0	11	4	28	28	195
0	14	4	33	39	356
1	0	4	49	47	33
1	3	4	62	65	192
1	6	4	11*	9	353
1	9	4	29	34	353
1	12	4	18	17	184
1	15	4	28	31	357
2	1	4	52	49	1
2	4	4	9*	3	178
2	7	4	42	44	11
2	10	4	22	20	181
3	2	4	34	34	2
3	5	4	25	23	30
3	8	4	15	13	18
4	0	4	142	152	359
4	3	4	30	35	164
4	6	4	20	18	22
4	9	4	17*	3	194
5	1	4	64	65	2
5	4	4	35	32	166
5	7	4	15*	9	321
6	2	4	35	34	174
6	5	4	15*	5	342
6	8	4	26	24	350
7	0	4	44	40	352
7	3	4	31	31	173
7	6	4	23	27	344
7	9	4	15	17	6
8	1	4	14	9	240
8	4	4	15*	11	354
8	7	4	19*	11	345
10	0	4	21	20	345
10	3	4	17*	10	24
12	2	4	19*	7	31
13	0	4	18	20	355
14	1	4	20	14	204
1	2	5	21	16	341
1	5	5	13	11	181
1	8	5	17*	9	297
1	11	5	28	30	3
2	3	5	20	20	138
2	6	5	37	29	220
2	9	5	48	46	359
3	1	5	11*	7	145
3	4	5	33	29	174
3	7	5	17*	13	233
3	10	5	45	49	3
4	2	5	25	27	138
4	5	5	22	23	210
4	8	5	19*	9	14
5	3	5	28	32	4
5	6	5	29	34	176
5	9	5	21*	7	163
6	1	5	35	33	8
6	4	5	17*	19	7
6	7	5	39	42	171
7	2	5	78	75	2
7	5	5	32	26	167
8	3	5	29	28	2
8	6	5	21*	20	167
9	1	5	30	33	0
9	4	5	19*	11	208
10	2	5	19*	16	330
0	0	6	147	163	353
0	3	6	18	24	128
0	6	6	13	13	4
0	9	6	24	27	184
1	1	6	47	48	351
1	4	6	39	41	157
1	7	6	21	21	331
1	10	6	23	24	168
2	2	6	64	59	177
2	5	6	13*	4	263
2	8	6	16	19	200
3	0	6	97	82	188
3	3	6	18	16	182
3	6	6	15*	12	316
3	9	6	19*	11	171
4	1	6	55	50	193
4	4	6	29	31	4
4	7	6	17*	7	211
5	2	6	36	31	353
5	5	6	17*	6	27
5	8	6	19*	13	180
6	0	6	16	18	221
6	3	6	41	37	8
6	6	6	32	30	181
7	1	6	15*	1	186
7	4	6	17	18	175
7	7	6	20	19	187
8	2	6	17*	3	90
8	5	6	19	23	179
9	0	6	20	23	165
9	3	6	19*	8	192
10	1	6	26	24	187
12	0	6	28	25	197
1	3	7	37	36	9
1	6	7	18	16	150
1	9	7	14	14	189
2	1	7	23	26	21
2	4	7	36	37	3
2	7	7	40	44	168
3	2	7	78	74	3
3	5	7	33	38	165
3	8	7	23	20	186
4	3	7	24	29	350
4	6	7	30	29	169
5	1	7	28	34	356
5	4	7	29	25	193
5	7	7	34	32	4
6	2	7	23*	12	244
6	5	7	23	19	356
6	8	7	38	31	3
7	6	7	36	40	6
0	1	8	64	65	196
0	4	8	68	64	357
0	7	8	12	13	192
0	10	8	20	24	7
1	2	8	30	34	1
1	5	8	29	29	353
1	8	8	26*	12	168
1	11	8	16	22	358
2	0	8	16	13	173
2	3	8	43	40	9
2	6	8	24*	18	178
3	1	8	13	16	93
3	4	8	24*	2	4
3	7	8	27	21	166
4	2	8	14	18	161
4	5	8	35	24	187
5	0	8	38	36	165
5	3	8	23*	17	203
8	0	8	44	37	353
8	1	8	23*	0	357
1	1	9	8*	6	324
1	4	9	13	9	344
1	7	9	26	23	1
2	2	9	21	16	323
2	5	9	26	27	355
2	8	9	30	26	15
3	3	9	11*	5	296
3	6	9	39	41	360
4	1	9	9*	7	236
4	4	9	13*	2	149
5	2	9	33	37	181
5	5	9	15*	8	177
6	3	9	39	39	169
6	6	9	22	19	204
7	1	9	23	24	173
8	2	9	15*	7	107
9	3	9	23	22	5
10	1	9	15	14	8
11	2	9	18	22	4
0	2	10	28	28	178
0	5	10	28	23	194
0	8	10	14	13	356
1	0	10	14	12	123
1	3	10	26	26	195
1	6	10	11	9	192
1	9	10	13*	8	343
2	1	10	8*	6	328
2	4	10	19	17	190
2	7	10	18	15	5
3	2	10	20	21	350
3	5	10	11*	5	121
4	0	10	54	62	358
4	3	10	9*	7	157
4	6	10	13*	13	10
5	1	10	24	26	359
5	4	10	11*	10	142
6	2	10	22	22	179
7	0	10	27	24	190
8	1	10	21	17	192
10	0	10	11	9	350
1	2	11	6*	2	141
1	5	11	9*	7	197
1	8	11	24*	6	308
1	11	11	19	17	1
2	3	11	8	13	174
2	6	11	10	13	202
2	9	11	18	20	349
3	1	11	8*	8	156
3	4	11	14	15	183
3	7	11	24*	11	209
3	10	11	20	19	4
4	2	11	9*	7	127
4	5	11	15	13	188
5	3	11	21	20	6
5	6	11	13*	12	169
6	1	11	20	20	10
6	4	11	12	12	3
6	7	11	24*	13	160
7	2	11	33	33	2
7	5	11	13*	9	159
8	3	11	13	10	349
0	0	12	24	31	347
1	1	12	18	19	357
3	0	12	19	18	188
4	1	12	22	28	189
6	0	12	12	10	197
1	3	13	11	9	5

* unobserved

tion. Sheets of 0·0008 in. nickel foil were interleaved between films, resulting in an intensity reduction of 2·7:1 for exposures at normal incidence. Polarization, Lorentz and rotation factors were applied manually. Neither absorption nor extinction corrections were used. The complete set of 337 independent structure factors, on the final absolute scale, is given in Table 1 under F_{meas}.

Analysis of the structure

The initial set of $F^2(hk{\cdot}0)$ data were used as coefficients in evaluating the Patterson function projected along the *c* axis. Sulfur atom positions were thereby deduced. Both F_{meas} and $F_{\text{meas}}-F_{\text{calc}}$ two-dimensional Fourier series methods were used to locate the carbon and oxygen atoms. The best fit, with conventional $R=0{\cdot}18$, contained many unsatisfactory discrepancies, and the difference maps showed unduly large residual electron densities. The position of the principal residual density was related to the sulfur atom by means of a twofold axis perpendicular to **c** and lying in the glide plane. Introduction of a statistical center, *i.e.* using $R\bar{3}c$ instead of $R3c$, increased R to 0·21. Overlap in the *a* axis projection was sufficiently serious to preclude use of the $h0{\cdot}l$ intensities in purely two-dimensional methods.

The complete $hk{\cdot}l$ data were thereupon used as input terms in a three-dimensional Patterson summation. A preliminary one-dimensional summation was computed on an IBM 650 machine, and a set of sections in three dimensions was obtained in 1958 on the X-Ray Analog Computer at State College, Pa., through the courtesy of Professor R. Pepinsky. The Patterson function contained more peaks than could be accounted for by the assumption of an ordered structure in $R3c$. The *positions* of the additional peaks could be explained on the basis of $R\bar{3}c$; the *heights* of these peaks were, however, inconsistent with the centrosymmetric arrangement.

Attempts to refine the ordered structure in $R3c$ were not very successful, and the atomic coordinates obtained corresponded to unreasonable bond lengths and angles. Further consideration of the Patterson function, together with use of vector convergence methods, indicated that there must be some appreciable electron density in real space at a position related to the ordered sulfur atom by a twofold axis perpendicular to the trigonal *c* axis. The distance between sulfur and this position was 1·8 Å, approximately a C–S bond distance. However, a methyl carbon atom at this position was incompatible with the distribution of other peaks in the Patterson function.

The only explanation for the Patterson vector arrangement thus appeared to be a partial approach to $R\bar{3}c$. In this space group, the centrosymmetrically related positions are occupied by two sets of TMSM molecules, with an equal number of molecules in sites corresponding to xyz and to $y, x, \frac{1}{2}-z$. By comparing peak heights in the Patterson function, the occupancy ratio for the two sets of sites appeared to lie between 0·78:0·22 and 0·5:0·5 (corresponding to $R\bar{3}c$). The greater diffuse intensity near those positions in reciprocal space that violate the condition $-h+k+l=3n$ suggested consideration of the symmetry elements in $P3c1$ (C_{3v}^{3}). This space group is also satisfied by the diffuse scattering in the $h0l$ layer, diffuse reflections of the form $l=2n+1$ not being observed. In $P3c1$, if two molecular orientations are possible with three molecules in the unit cell, the occupancy ratio would be $\frac{2}{3}:\frac{1}{3}$. Indeed, most of the Patterson peaks could be predicted on this basis.

A direct method for checking this partial occupancy model is to compute the three-dimensional Fourier series using the phases derived from a single sulfur atom in space group $R3c$. This calculation was performed on the Deuce computer, using Silverton's (1962) program. The value of R based on the input sulfur atom alone was 0·43. The resulting electron density distribution clearly indicated the sulfur atom, as well as smaller peaks in positions corresponding to those expected for the lighter atoms. In addition, a peak of height 5e.Å^{-3}, with volume comparable to the sulfur atom (at xyz) and much larger than the lighter atoms, was located at $y, x, \frac{1}{2}-z$.

An attempt to refine only the ordered atom positions based on this Fourier series was then made by the method of least squares. The lowest value of R was 0·33, with no further refinement possible. The resulting coordinates closely resembled those derived from the three-dimensional Patterson function, with unlikely bond lengths and angles, *e.g.* the central carbon–sulfur length became 2·0 Å (0·2 Å longer than expected). A three-dimensional difference Fourier series at once revealed a large electron density at the point $y, x, \frac{1}{2}-z$ corresponding to the original xyz position for sulfur, as well as indicating movement in the carbon positions. A set of coordinates based on both the F_{meas} and the $F_{\text{meas}}-F_{\text{calc}}$ Fourier series, with a partial occupancy ratio of the sites at xyz: $y, x, \frac{1}{2}-z$ of 2:1, gave an R value of 0·25. A second difference Fourier series gave coordinates with $R=0{\cdot}18$.

Three-dimensional least-squares refinement

The atom coordinates from the three-dimensional Fourier series were now refined by the method of least squares, with Rollett's (1961) program for the Deuce computer. The weights used were $w=1$ for $F_{\text{meas}}<8F_{\text{min}}$ and $w=1/F^2_{\text{meas}}$ for $F_{\text{meas}}>8F_{\text{min}}$. Four least-squares cycles reduced R to 0·102. The atoms at the two sites were refined independently, with position and temperature coordinates taken as the weighted mean of the two sets. The weights for the two sets of atoms, maintaining the xyz: $y, x, \frac{1}{2}-z$ relationship, were taken as 2:1. The resulting isotropic temperature factor at the site with smaller occupancy value was now lower than at the other site. This observation indicated the true occupancy ratio to be less, probably, than 2:1.

Because of machine and program limitations, least-squares variation of the occupancy factor was not possible on Deuce.

Additional least-squares refinement was then made on an IBM 7090 computer with the Busing & Levy (1959*a*) program. Isotropic temperature factors only were used in this refinement: although a better fit could probably be obtained with anisotropic temperature factors, the disorder in this crystal made this procedure appear unreasonable. Two least-squares cycles were then computed in which only the occupancy factors for each atomic site were varied: the individual values obtained are listed in Table 2, with a mean value of 0·613 ± 0·008. Further least-squares cycles with the occupancy factor for all atoms held constant at 0·61 led to the position coordinates of Table 2. All shifts in the final least-squares calculations were small compared with the error in each shift, except for those in the *z* coordinates. The shifts in this coordinate were generally comparable with the standard deviation (σ) and exceeded it both for S (2·4σ) and for O(2) (1·6σ). In any given cycle, all Δz values had the same sign, with a mean value of 0·0014, *i.e.* the entire molecule oscillated between refinement cycles by *ca.* 0.013 Å. There was neither a significant change in any agreement index, nor in the magnitudes of individual structure factors, for the coordinates given in Table 2 compared with those for which all *z* coordinates are 0·0014 less. Similarly, no bond length or angle differs by as much as one standard deviation, as between the two sets of coordinates.

The *xyz* values in Table 2 correspond to positions 6(*a*) for C(2) and 18(*b*) for the remaining atoms (*International Tables for X-ray Crystallography*, 1952). The corresponding *R* value is 0·091, for observed reflections. If the upper limits for unobserved F_{meas} are taken as $\frac{1}{2}F_{\text{min}}$ (corresponding to the smallest F_{meas} observed near that part of reciprocal space) and including differences for the unobserved terms only if $F_{\text{calc}} > \frac{1}{2}F_{\text{min}}$, then *R* is 0·100. Of the 75 unobserved structure factors, only three have $F_{\text{calc}} > F_{\text{min}}$. The structure factors calculated on the basis of the coordinates in Table 2 are listed under F_{calc} in Table 1. The atomic form factors given in *International Tables for X-ray Crystallography* (1962) were used.

Intramolecular bond distances and angles

Although the crystal structure of TMSM is disordered, the dimensions within individual molecules may be computed from the position coordinates given in Table 2. The intramolecular bond distances and angles, and the errors in these values, computed using Busing & Levy's (1959*b*) ORFFE program, are given in Table 3.

Table 3. *Bond distances and angles in a TMSM molecule*

S–O(1) = 1·427 ± 17 Å
S–O(2) = 1·442 ± 12
O(1)–S–O(2) = 119·3 ± 0·9°
S′–C(2)–S = 110·8 ± 0·4
C(2)–S–O(1) = 107·2 ± 0·8
S–C(1) = 1·729 ± 17 Å
S–C(2) = 1·830 ± 10
C(2)–S–O(2) = 106·0 ± 1·4°
C(2)–S–C(1) = 104·9 ± 1·0
O(2)–S–C(1) = 111·4 ± 0·9
O(1)–S–C(1) = 106·8 ± 1·0°

Discussion of intramolecular structure

The bond angles of 110·8 ± 0·4° at the central carbon atom differ by only 3·3σ from the normal tetrahedral bond angle of 109·5°. The suggestion of Doering & Levy (1955) of a planar bond arrangement at the central carbon atom, to account for the high acid strength of TMSM, would thus indicate that the molecule is not appreciably ionized in the solid state. In case the close approach of 0·37 Å (approximately the limit of resolution of the data) between the central carbon atom at 0, 0, $\frac{1}{2}-z$ and that at 00*z* had influenced the refinement procedure, the following test was made. After refinement was complete, the *z* values of the related central carbon atoms were changed to increase the approach distance to 0·85 Å. Least-squares refinement with the central carbon atom coordinates as the sole variables, and with shifts of only $\frac{1}{4}\Delta z$ allowed between cycles, reduced the C(2)–C(2′) distance to 0·40 Å in three cycles. The validity of the close approach and of the pyramidal molecular structure is hence verified.

The dimensions of the sulfone group in TMSM are comparable with other reliable determinations. The O–S–O angle is invariably the largest sulfur bond angle in a given sulfone group (*cf.* Abrahams, 1956) and is generally in the range 115–120°. Thus, in 4,4′-dichlorodiphenyl sulfone or DCDPS (Sime & Abrahams, 1960) the O–S–O angle is 120·4 ± 0·4°, very close to the 119·3 ± 0·9° in TMSM. Similarly, the C–S–C angle of 104·9 ± 1·0° is indistinguishable from the value 104·8 ± 0·4° in DCDPS. The average of the four C–S–O angles in TMSM (107·8°) is not significantly different from the average bond angle (*cf.* Abrahams, 1956) of 107·2°, nor from the average angle in DCDPS of 107·6°. The average S–O bond length in TMSM of 1·435 Å is essentially identical with that in DCDPS and that regarded as the standard double bond distance for S–O. The

Table 2. *Coordinates of tris(methylsulfonyl)methane**

	x	*y*	*z*	*B*	Occupancy factor
S	0·1525 ± 4	0·1040 ± 3	0·3291 ± 6	1·90 ± 8 Å^2	0·604 ± 6
O(1)	0·2217 ± 14	0·0469 ± 14	0·3072 ± 14	3·55 ± 26	0·640 ± 22
O(2)	0·1415 ± 12	0·1401 ± 13	0·4690 ± 12	3·13 ± 23	0·632 ± 23
C(1)	0·2061 ± 16	0·2230 ± 15	0·2132 ± 14	2·39 ± 28	0·578 ± 31
C(2)	0	0	0·2694 ± 32	2·34 ± 42	0·606

* For every atom given at *xyz*, 1 − (occupancy factor) is located at *y*, *z*, $\frac{1}{2}-x$.

two C–S bond lengths in TMSM are very significantly different. Comparison with the standard C–S single bond distance of 1·82 Å (*cf.* Abrahams, 1956) indicates the bond formed by the central carbon atom is a good single bond. That formed by the methyl [C(1)] atom, with C–S = 1·729 Å, is even shorter than the usual aromatic carbon–sulfur distance of about 1·76 Å. It is not significantly different from the 1·726 Å found in $(CH_3 . SO_2)_2C{:}C{:}NCH_3$ by Wheatley (1954).

An interesting comparison is with the ammonium salt of TMSM, reported by Hoogsteen (1957). The three central C–S bonds in this anion $(CH_3 . SO_2)_3C^-$ appear to be planar, since the sum of the three S–C–S angles is 359·7°. The average O–S–O angle is 116·7°, the average C–S–C angle is 106·5° and the average C–S–O angle is 108·9°. The S–O bond length in the ammonium salt is identical at 1·43 Å with that in TMSM, but the C–S bonds are quite different in length. The central C–S bond is 1·70 Å, indicating very considerable double bond character, while the methyl C–S bond is 1·78 Å, closer to a single bond than that found in TMSM. Unlike TMSM, the ammonium salt does not possess C_3 symmetry. Two CH_3 groups appear to be pointing above the plane of the three sulfur atoms, the remaining CH_3 group below this plane. A noteworthy macroscopic difference between TMSM and its ammonium salt is the very sparing solubility of the former and the high solubility of the latter. This could indicate that TMSM possesses a different molecular geometry from the $(CH_3 . SO_2)_3C^-$ anion.

In crystalline TMSM, the three bulky methyl groups are all on the same side of the plane of the three sulfur atoms, conforming to the molecular C_3 symmetry. The methyl groups occupy that side of the molecule with most room. One set of oxygen atoms is on the opposite side of the molecule; the second set is approximately in the plane of the sulfur atoms.

Ordered stacking along the trigonal axis

The TMSM crystal is made up of $(CH_3 . SO_2)_3CH$ molecules stacked along the trigonal axis. The diffuse scattering is entirely in layers perpendicular to **c***, with no evidence of scattering parallel to **c***. In the *h0l* layer, the diffuse scattering consists only of sections through the planar diffuse hexagons perpendicular to **c***. The width of the diffuse scattering parallel to **c*** is identical with that of the sharp reflections, and is less than may pass through the annular opening of the layer line screen. It may hence be deduced that there is no disorder within these stacks, *i.e.* the diffuse scattering is caused only by disordered packing of stacks of ordered molecules. It may also be observed that whereas the crystals undergo excellent cleavage parallel to **c**, they do not easily fracture perpendicular to **c**, indicating strong binding forces along the ordered, trigonal axis direction. Verification of this deduction is indicated by the close approach distances given in Table 4. A macroscopic observation reflecting this packing efficiency is the unusually high density of TMSM, 1·82 g.cm^{-3}. The density of dimethyl sulfone, for example, is 1·42 g.cm^{-3}.

Table 4. *Closest approaches between molecules in stacks, less than* 4 Å

O(2†) ··· C(1″) = 3·29 ± 2 Å	O(2†) ··· C(1′) = 3·45 ± 2 Å
O(2†) ··· O(1′) = 3·35 ± 2	O(2†) ··· S′ = 3·66 ± 2
O(2†) ··· C(2′) = 3·39 ± 3	O(1†) ··· C(1′) = 3·94 ± 2

† Atom at $\bar{y}, \bar{x}, \frac{1}{2}+z$; ′ atom at *xyz*; ″ atom at $\bar{y}, x-y, z$.

Intermolecular distances

All distances less than 4 Å in TMSM were computed, with the use of Busing & Levy's (1959*b*) ORXFE program. The values for the intermolecular contacts are given in Table 4. There are three somewhat short oxygen–carbon approaches of 3·29, 3·35 and 3·39 Å. A common estimate of the sum of oxygen–carbon van der Waals radii used to be 3·4 Å. Recent structure determinations of molecular crystals containing sulfone or sulfoxide groups [*e.g.* 4,4′-dichlorodiphenyl sulfone (Sime & Abrahams, 1960)] have indicated this radius sum should be revised to about 3·2 Å. On this basis, there are no unusually short intermolecular distances in TMSM.

Disordered packing of the stacks

The model obtained from the least-squares refinement, taken in conjunction with the over-all features of the diffuse scattering, corresponds to the existence of two kinds of ordered stacks of TMSM molecules in the crystal. One kind of stack has atoms in the *xyz* positions of Table 2, and may be regarded as in orientation *A*. The second kind has atoms in the $y, x, \frac{1}{2}-z + (\frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ positions: this corresponds to orientation *B*. The ratio of orientation *A* to that of *B* is 0·613:0·387 (see Table 2).

A complete model for the disordered structure of the TMSM crystal should possess the following features:

(*a*) The arrangement of stacks *A* and *B* should give a resultant *A*:*B* ratio of 61:39,
(*b*) A mask containing holes corresponding to orientations *A* and *B*, as given in (*a*) above, should produce an optical transform closely resembling the observed diffuse scattering pattern,
(*c*) The distances between atoms in different stacks should be reasonable, and
(*d*) The model should be unique.

In the present model, it will be shown that the first three conditions are fulfilled: no systematic attempt, however, has been made to demonstrate that the final condition is met.

The simplest arrangement, consistent with the observed *A*:*B* ratio of the two kinds of stacks, involves an *A* stack surrounded by four concentric triangles of

B stacks, *A* stacks, *B* stacks and finally *A* stacks, in that order. The various stacks are always located on the trigonal axes in *R*3*c*. This short-range ordered group of first through sixth nearest neighbors, with the identity of stacks given, contains 19 *A* and 12 *B* stacks, corresponding to 61·3% *A* stacks and 38·7% *B* stacks. It should be pointed out that increasing the number of concentric triangles gradually reduces this ratio until in the limit it becomes 50:50, and the space group is then, statistically, $R\bar{3}c$. At present, it is assumed that small triangular domains of average size as shown in Fig. 1 fill space, and maintain the necessary symmetry by twinning across the sides of the outermost triangle.

A mask was then constructed, with sulfur atom positions only being used, based upon the above triangular arrangement. An optical diffractometer (Taylor, Hinde & Lipson, 1951) then produced the optical transform reproduced in Fig. 2(*a*). For comparison, Fig. 2(*b*) contains the experimental X-ray diffuse pattern. A random arrangement of *A* and *B* stacks, present in the 61:39 ratio, produced a generally diffuse pattern, with no linear structure. Various other systematic arrangements of *A* and *B* stacks, maintaining the required ratio, also failed to give the observed diffuse scattering pattern. As a final check on the basic model that the diffuse scattering is caused by *stacking* disorder, rather than disorder *within* the molecule, a mask was constructed with open holes corresponding to the *A* stacks, and cellophane-covered holes corresponding to the *B* stacks. This would correspond to different molecules in the *A* and *B* stacks, *e.g.* a molecule with rotation about one or more of the central C–S bonds in a *B* stack as compared with the standard molecule in the *A* stacks. The resultant diffuse pattern was a continuous set of hexagons with a normal fall-off in intensity, surrounding sharp spots similarly falling off in intensity.

The distances between atoms in a stack surrounded by identical stacks are indicated in Fig. 3. Several close contacts are made, of which the shortest is a carbon–

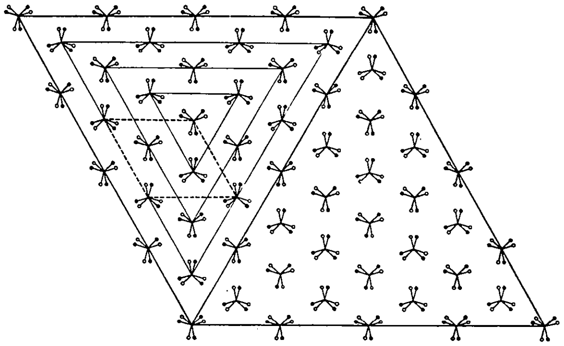


Fig. 1. Postulated disordered arrangement of ordered stacks in TMSM. The heavy lines indicate possible twin boundaries: the dashes outline one unit cell, and the light lines show the triangular surroundings about a central stack of *A* orientation, The open circles represent sulfur atoms at height z(or $\frac{1}{2}-z$):The closed circles are at height $\frac{1}{2}+z$ (or $\bar{z}$).

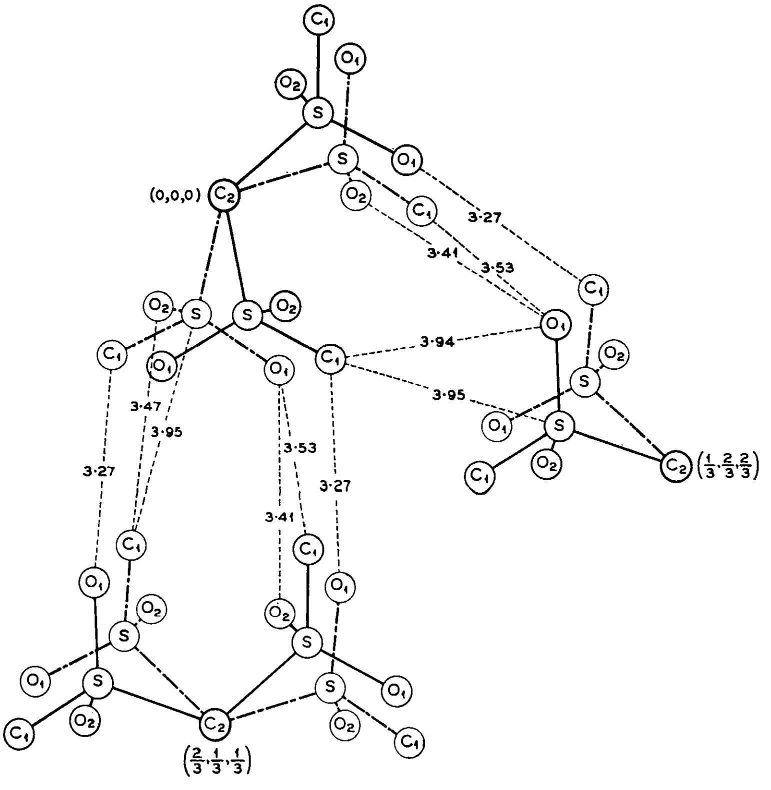
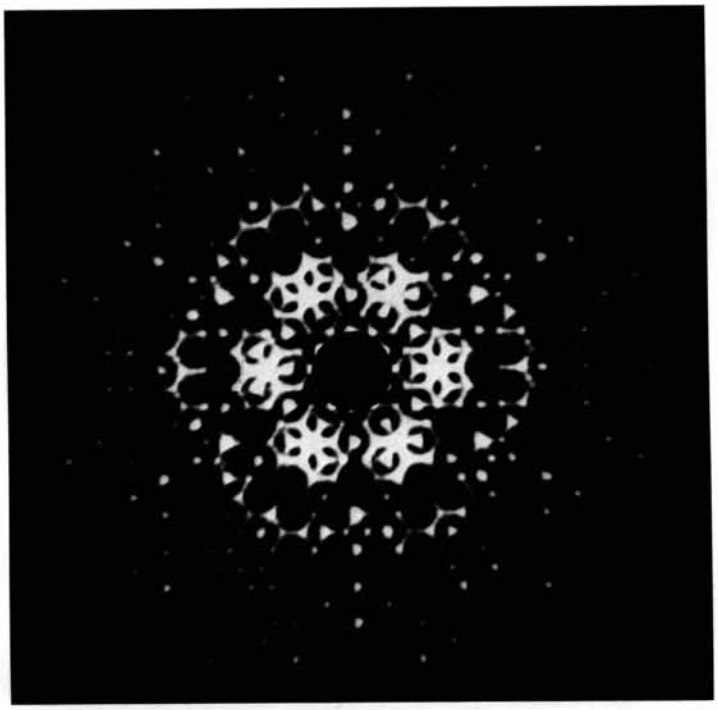
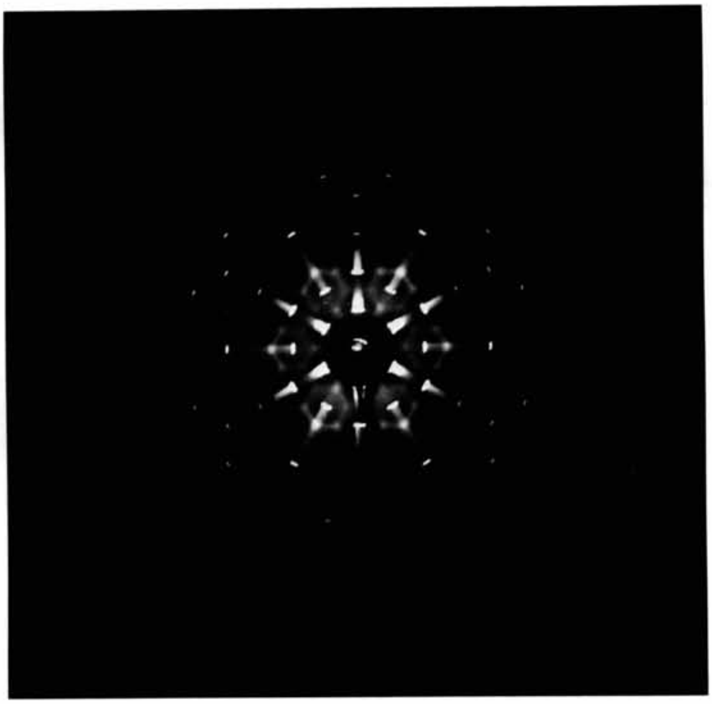


Fig. 3. Distances between atoms in one kind of stack surrounded by other stacks of the same orientation. One third of the environment is shown.



(*a*)



(*b*)

Fig. 2. (*a*) Optical transform corresponding to Fig. 1. (*b*) Observed X-ray diffuse scattering from TMSM at room temperature, using Mo$K\alpha$ radiation, at about same magnification as in (*a*). Only the inner array of diffuse hexagons is clearly visible in (*b*) because of the unfavorable Lorentz and polarization factors. The next-to-inner array of hexagons is readily observed if Cu $K\alpha$ radiation is used, as may be seen in the corresponding figure of Abrahams & Speakman (1956).

oxygen approach of 3·27 Å. This is no shorter than those found within a given stack (see *Intermolecular Distances*) and should not be regarded as unusually short. In this arrangement, the closest oxygen–oxygen approach is 3·41 Å.

Fig. 4 shows the atoms in an *A* stack surrounded by *B* stacks (which is related by an inversion center to an arrangement of *B* stacks surrounded by *A* stacks). In this arrangement, the closest oxygen–oxygen approach for three of the surrounding stacks is greater than 4·1 Å. The remaining three stacks make oxygen–oxygen contacts of 3·25 Å, which would be expected to result in a highly energetic repulsion. It might be due to such considerations that this form of packing is not observed. If it were, the crystal symmetry would correspond to $P3c1$.

Three *B* stacks can be arranged around a central *A* stack, as partly illustrated in Fig. 4, and maintain favorable interatomic contacts. The remaining three stacks required to complete the hexagonal packing will then contain unfavorably short oxygen–oxygen contacts. If these are *B* stacks, the situation will be as shown in Fig. 4: if they are *A* stacks, close contacts will be made with the original set of *B* stacks.

The disorder thus appears to be the product of a compromise between two competing processes: one leading to favorable local orientations of the stacks of TMSM molecules (not allowed by the crystal symmetry) and one giving short as well as long range order (leading to some unfavorable local orientations). The model used for the optical transform hence probably represents a typical compromise structure. It provides a considerable degree of favorable local orientations at the cost of some close oxygen–oxygen approaches. The domains of ordered packing are probably small, no larger than those shown in Fig. 1. This figure should be regarded as illustrative of a compromise packing to which the structure probably tends, but not as showing the actual packing, since it corresponds to a supercell with lattice constant $4a_H$: in fact, no such superlattice is observed.

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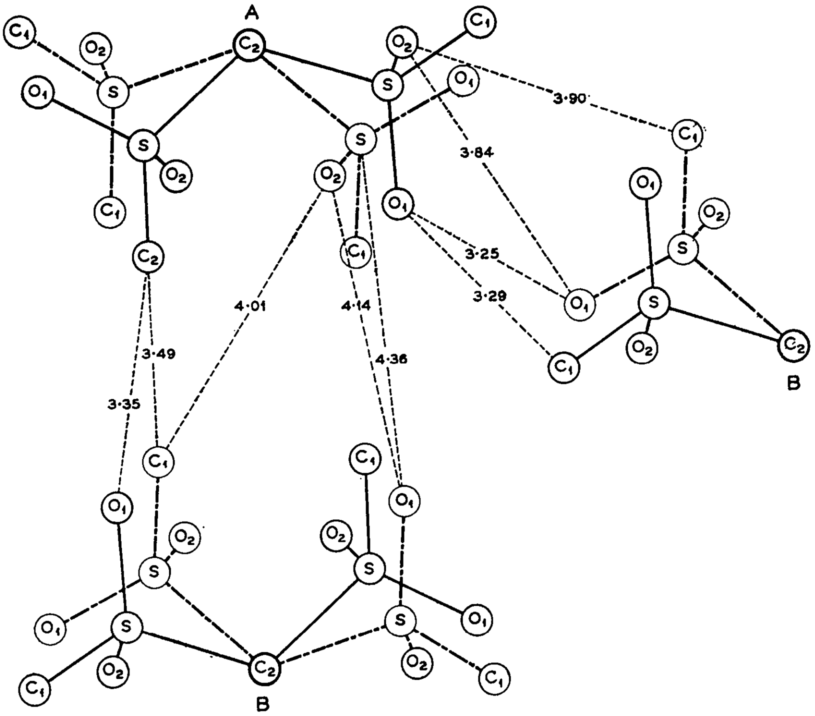

Fig. 4. Distances between atoms in stack *A* surrounded by stacks of different *B* orientation. One third of the environment is shown.

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The Crystal and Molecular Structure of Iodopentaborane-9

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The molecular configuration of 1-iodopentaborane-9 (B_5H_8I) has been determined in a partial three-dimensional X-ray crystallographic study. The unit cell is monoclinic with $a = 11·24$, $b = 10·03$, $c = 13·14$ Å, $\beta = 110°5'$, $Z = 8$ and the space group is $C2/c$. The structure refined smoothly to R (observed data only) = 13·0% for data taken at −25 °C which included 417 observed and 112 unobserved reflections in the $h0l$, $h1l$, $h2l$, and $hk0$ levels. Individual isotropic temperature factors were used for the one iodine and five boron atoms. Hydrogen atom parameters were not included.

Experimental

Iodopentaborane (B_5H_8I) forms colorless crystals melting at 54 °C. It is soluble in most common organic solvents and reacts slowly with water vapor and oxygen, forming a fuming mist and giving off odors characteristic of the boron hydrides.

Because of the high vapor pressure of iodopentaborane and its sensitivity to air, single crystals were grown from the melt in small, thin-walled, Pyrex capillary tubes. The tubes were first filled with crystallites of the compound which was prepared according to the procedure of Hall, Subbana & Koski (1964) and then sealed off in a dry box. The unit-cell parameters and space group were determined from precession photographs of the $0kl$, $1kl$, $h0l$, and $h1l$ levels taken at room temperature with Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å). The room-temperature cell dimensions were used throughout the structure analysis since the unit-cell dimensions at −25 °C agreed with the room temperature values within the estimated standard deviations. The lattice constants reported here agree well with those of Norment, Henderson & South (1960).

The systematic absences observed for this crystal are as follows:

hkl	$h+k=2n+1$
$h0l$	$l=2n+1 (h=2n+1)$
$0k0$	$(k=2n+1)$

On this basis the space group is Cc or $C2/c$. The Howells, Phillips & Rogers (1950) statistical test applied to the $0kl$ and $h0l$ data indicated that these projections are centered. Since these results are consistent only with the space group $C2/c$, it was used in the structural determination. The complete determination of the structure showed that $C2/c$ is the correct choice. The assumption of eight molecules in the unit cell gives a reasonable density, 1·80 g.cm^{-3}, a reasonable molecular volume, 174 Å^3, and allows the molecules to be in the general positions of the space group. The final structure verified this assumption. The density of the crystal was not determined because of its high solubility in suitable solvents.

Intensity data were obtained on a Buerger precession camera for the $h0l$ and $0kl$ projections at room temperature and for the $h0l$, $h1l$, $h2l$, and $hk0$ levels at −25 °C. The intensities were estimated with the aid of a densitometer. The very weak reflections were estimated by eye and the unobserved reflections were set equal to one half the minimum observed intensity.

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