670. *The Crystal Structure of Potassium Methylenedisulphonate.*

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Potassium methylenedisulphonate, $K_2[CH_2(SO_3)_2]$, has been investigated by three-dimensional *X*-ray crystal-structure analysis. Refinement of the co-ordinates and anisotropic thermal-motion parameters reduced the agreement index to 0·10. The bond lengths in the methylenedisulphonate ion, corrected for rotational oscillations, are S–C = 1·770 ± 0·007 Å, and S–O 1·461 ± 0·005 Å, the mean of three independent values; the S–C–S angle is 119·7° ± 0·7°.

The approximate stereochemistry of the methylenedisulphonate ion can be deduced from its formula, $CH_2(SO_3)_2^{2-}$, as a tetrahedral carbon atom bonded to two tetrahedral sulphur atoms, the sulphur being in the oxidation state VI. This investigation was undertaken to determine the precise dimensions of the anion for comparison with those in (*a*) the hydroxymethanesulphinate ion, $HO{\cdot}CH_2{\cdot}SO_2^-$, in which a tetrahedral carbon atom is bonded to a sulphur atom in the oxidation state IV and (*b*) the isoelectronic pyrosulphate, $S_2O_7^{2-}$ and iminodisulphonate, $NH(SO_3)_2^{2-}$ ions.

The structure of sodium hydroxymethanesulphinate dihydrate was determined[1] in 1955 by three-dimensional methods with allowance for isotropic thermal motion. To provide results comparable with those in this paper, the structure has been refined anisotropically as described in the following paper.[2]

In 1955 Jones[3] showed that potassium iminodisulphonate ($a = 12{\cdot}43$, $b = 7{\cdot}46$, $c = 7{\cdot}18$ Å, $\beta = 91{\cdot}2°$) and potassium methylenedisulphonate ($a = 12{\cdot}55$, $b = 7{\cdot}75$, $c = 7{\cdot}30$ Å, $\beta = 90{\cdot}5°$) have the same space group; this, and the close similarity of the unit-cell dimensions, suggest that the compounds are isostructural. Jeffrey and Jones[4] determined the structure of potassium iminodisulphonate by three-dimensional methods with isotropic refinement; anisotropic refinement has now been carried out by Cruickshank and Jones.[5] In 1960 Lynton and Truter[6] showed that potassium pyrosulphate ($a = 12{\cdot}35$, $b = 7{\cdot}31$, $c = 7{\cdot}27$ Å, $\beta = 93{\cdot}1°$) was isostructural with the iminodisulphonate[4] and published the results of a complete anisotropic refinement.

Crystal Data.—$K_2[CH_2(SO_3)_2]$, $M = 252{\cdot}34$. Monoclinic $a = 12{\cdot}556$, $b = 7{\cdot}773$, $c = 7{\cdot}253$ all $\pm 0{\cdot}005$ Å, $\beta = 90° 30' \pm 1'$. $U = 707{\cdot}9$ Å^3, $D_m = 2{\cdot}37$,[1] $Z = 4$, $D_c = 2{\cdot}369$, $F(000) = 496$. Space group $C2/c$ (C_{2h}^6 No. 15). Cu-K_α radiation single-crystal oscillation and Weissenberg photographs, absorption coefficient $\mu = 170{\cdot}8$ cm.$^{-1}$. The anion must lie with the carbon atom on a two-fold axis or a centre of symmetry.

Refinement.—The similarity between the unit-cell dimensions of potassium pyrosulphate, potassium iminodisulphonate, and potassium methylenedisulphonate suggests that all three compounds are isostructural. Further, the fractional co-ordinates in the pyrosulphate and the iminodisulphonate are very similar. For the vibration parameters, however, lower values were found for the pyrosulphate than for the iminodisulphonate in a ratio of approximately $1 : 1{\cdot}8$. As the intensities were corrected for absorption in the present work it seemed more likely that the larger values would be more nearly correct. The anisotropy of the thermal motion was approximately the same in both compounds so the first set of struture factors was calculated by using co-ordinates which were the means for those of the other structures and thermal parameters identical with those of the iminodisulphonate. The co-ordinates corresponded to the bond lengths S–O = 1·44 Å, S–C = 1·71 Å, and R was 0·37. Four cycles of refinement reduced R to 0·13. At this stage an extinction correction was applied for planes with $\sin\theta < 0{\cdot}4$, and the hydrogen atom, having an isotropic temperature factor corresponding to a mean-square vibration of 0·04 Å^2, was inserted in a position chosen to make the H–C–H′ plane perpendicular to the S–C–S′ plane and the C–H bond length 1·00 Å. In the next cycle of refinement R was 0·11 and there was a reduction in the isotropic temperature factor for hydrogen, indicating that it had been correctly placed. Three further cycles of refinement reduced R to 0·10 and the largest shift was 0·2 of the corresponding standard deviation. Table 1 shows the observed and calculated structure factors.

The corrections for rotational oscillation[7] were determined from an analysis[8] of the rigid-body vibrational motion of the anion.

Results.—The structure as a whole is shown in Fig. 1; the carbon atoms lie on the two-fold axes by which the two SO_3^- groups in each anion are related. Figs. 1 and 2 show the numbering of the atoms. The atomic co-ordinates are shown in Table 2 both as fractions and in Å, where X', Y', and Z' refer to orthogonal axes parallel to a, b, and c^*, respectively; the standard deviations are also shown. Table 3 shows the vibration parameters and their standard deviations; U_{11}, U_{22}, and U_{33} are mean-square amplitudes of vibration parallel to

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[1] Truter, *J.*, 1955, 3064.
[2] Truter, following paper.
[3] Jones, *Acta Cryst.*, 1955, **8**, 66.
[4] Jeffrey and Jones, *Acta Cryst.*, 1956, **9**, 283.
[5] Cruickshank and Jones, unpublished work.
[6] Lynton and Truter, *J.*, 1960, 5112.
[7] Cruickshank, *Acta Cryst.*, 1961, **14**, 896.
[8] Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

TABLE 1.

Observed and calculated structure factors (× 10). (Reflections which are too weak to be observed have been omitted.)

l	$\lvert F_o \rvert$	F_c
	00*l*	
2	415	−353
4	812	−808
6	496	473
8	465	364
	02*l*	
0	1061	−1218
1	1139	1418
2	228	199
3	770	832
4	91	98
5	753	−754
6	381	−345
8	260	−186
9	279	314
	04*l*	
0	461	−428
1	136	−142
2	248	246
3	346	−347
4	414	411
5	605	627
6	190	−195
8	73	−77
	06*l*	
0	342	331
1	128	−111
2	144	−129
3	258	243
4	244	−254
6	238	209
	08*l*	
0	291	−311
	0,10,*l*	
0	148	233
	20*l*	
2	2461	2203
4	56	72
6	630	−621
8	580	459
$\bar{2}$	1785	−1797
$\bar{4}$	620	555
$\bar{6}$	864	816
$\bar{8}$	391	−330
	22*l*	
0	382	−407
1	951	1113
2	837	−822
3	867	−951
4	329	284
5	317	−307
6	301	271
7	435	418
8	285	−212
9	88	−79
$\bar{1}$	967	1097
$\bar{2}$	213	−167
$\bar{3}$	1418	−1550
$\bar{4}$	206	−169
$\bar{6}$	496	−456
$\bar{7}$	332	376
$\bar{8}$	205	147
$\bar{9}$	104	−97
	24*l*	
0	301	295
1	50	34
2	451	−448
3	880	995
4	94	101
6	260	255
7	281	−235
8	123	−119
$\bar{1}$	347	−338
$\bar{2}$	620	630
$\bar{3}$	612	620
$\bar{4}$	413	−393
$\bar{7}$	341	−296
$\bar{8}$	226	227
	26*l*	
1	223	−216
2	369	384
3	124	−130
4	248	−223
6	126	−128
7	103	−113
$\bar{1}$	279	252
$\bar{2}$	184	−177
$\bar{3}$	107	−84
$\bar{5}$	264	−231
$\bar{6}$	264	190
	28*l*	
0	177	−179
1	145	138
$\bar{2}$	144	123
$\bar{4}$	160	155
	40*l*	
0	2126	−1955
2	87	−21
4	648	630
6	365	−318
8	335	−264
$\bar{2}$	868	893
$\bar{4}$	1116	1160
$\bar{6}$	444	−426
$\bar{8}$	172	−128
	42*l*	
0	749	768
1	50	52
2	860	−888
3	683	682
4	236	−203
5	691	−687
6	216	199
8	188	134
$\bar{1}$	1043	−1315
$\bar{2}$	42	22
$\bar{3}$	518	−493
$\bar{4}$	334	−306
$\bar{5}$	596	641
$\bar{7}$	136	−132
$\bar{8}$	138	117
	44*l*	
0	383	360
1	460	−446
2	345	321
3	36	35
4	332	−452
5	594	654
8	134	136
$\bar{1}$	275	231
$\bar{2}$	433	−412
$\bar{3}$	484	468
$\bar{4}$	78	−77
$\bar{5}$	131	−136
$\bar{6}$	336	370
	46*l*	
0	413	−381
1	57	−42
2	299	290
3	259	−273
4	184	187
5	179	−151
6	113	−89
7	125	155
$\bar{1}$	136	122
$\bar{2}$	62	61
$\bar{3}$	539	−572
$\bar{4}$	97	93
$\bar{5}$	120	−118
$\bar{6}$	83	−88
	48*l*	
0	129	134
2	265	−276
4	78	94
5	81	96
$\bar{2}$	257	249
$\bar{3}$	201	193
$\bar{4}$	248	−235
	60*l*	
0	843	789
2	998	−1108
4	248	153
6	245	218
8	316	−270
$\bar{2}$	424	413
$\bar{4}$	322	−305
$\bar{6}$	552	−487
$\bar{8}$	259	247
	62*l*	
0	521	506
1	750	−796
2	635	631
3	249	220
4	326	−226
7	326	−275
8	226	177
$\bar{1}$	291	−241
$\bar{2}$	62	−79
$\bar{3}$	648	716
$\bar{4}$	254	−228
$\bar{5}$	174	−145
$\bar{6}$	254	225
$\bar{7}$	326	−287
	64*l*	
0	539	−508
1	47	−48
2	248	238
3	373	−381
4	180	147
6	273	−254
7	242	234
$\bar{1}$	986	1008
$\bar{2}$	167	−132
$\bar{3}$	171	−128
$\bar{4}$	449	447
$\bar{7}$	156	122
	66*l*	
0	185	−173
1	325	331
2	243	−221
3	73	57
4	107	103
$\bar{1}$	727	−625
$\bar{2}$	237	183
$\bar{3}$	118	−116
	68*l*	
0	244	294
1	63	−67
2	38	26
3	25	−29
4	146	−284
$\bar{1}$	197	188
$\bar{2}$	79	−91
$\bar{3}$	107	90
$\bar{4}$	281	−309
	80*l*	
0	218	147
2	376	−332
4	263	−206
8	160	127
$\bar{2}$	619	−589
$\bar{4}$	459	−392
$\bar{6}$	159	153
	82*l*	
0	176	−166
2	506	504
3	260	−220
4	249	221
5	216	196
$\bar{1}$	470	446
$\bar{2}$	329	−321
$\bar{3}$	280	−272
$\bar{4}$	384	366
$\bar{5}$	172	−197
$\bar{6}$	108	98
	84*l*	
0	201	−165
1	496	468
2	459	−425
3	122	95
4	175	169
5	331	−292
7	129	131
$\bar{1}$	135	140
$\bar{2}$	487	472
$\bar{3}$	378	−383
$\bar{4}$	245	−217
$\bar{6}$	241	−240
$\bar{7}$	205	180
	86*l*	
0	143	139
1	351	−325
2	97	−97
3	343	359
4	103	−112
$\bar{1}$	343	−287
$\bar{2}$	149	127
$\bar{3}$	410	399
$\bar{4}$	146	−128
	88*l*	
0	36	−46
1	151	131
2	398	443
$\bar{1}$	73	67
$\bar{2}$	315	−285
$\bar{3}$	52	−76
	10,0,*l*	
0	361	−276
2	143	−83
4	237	−226
6	134	−118
$\bar{2}$	103	22
$\bar{4}$	47	19
$\bar{6}$	68	−84
	10,2,*l*	
0	58	−67
2	219	−161
3	134	100
4	286	272
7	99	100
$\bar{1}$	71	−62
$\bar{2}$	208	191
$\bar{3}$	143	−147
$\bar{4}$	379	394
$\bar{5}$	187	211
$\bar{6}$	79	−92
	10,4,*l*	
0	335	295
1	87	72
2	82	−51
3	150	128
4	301	−298
6	97	118
$\bar{1}$	529	−479
$\bar{2}$	195	−136
$\bar{3}$	114	−92
$\bar{4}$	326	−329
$\bar{5}$	290	256
$\bar{6}$	181	194
	10,6,*l*	
1	424	−391
2	117	105
3	153	−148
4	64	−83
$\bar{1}$	609	476
$\bar{3}$	92	89
$\bar{4}$	169	−140
	12,0,*l*	
0	325	300
2	114	31
4	107	−54
$\bar{2}$	267	−219
$\bar{4}$	126	−137
	12,2,*l*	
0	57	84
1	125	−107
2	136	−119
3	52	39
4	81	83
$\bar{1}$	191	176
$\bar{2}$	342	314
$\bar{3}$	226	221
$\bar{4}$	112	−92
$\bar{5}$	133	−106
	12,4,*l*	
0	97	−110
1	299	−253
2	289	260
3	113	78
4	37	−42
$\bar{1}$	109	−86
$\bar{2}$	310	−271
$\bar{4}$	211	190
$\bar{5}$	105	143
	12,6,*l*	
$\bar{1}$	303	223
$\bar{2}$	60	−57
	14,0,*l*	
0	76	−70
2	182	146
4	129	107
$\bar{2}$	372	−359
$\bar{4}$	217	194
	14,2,*l*	
0	118	98
1	211	185
2	74	−75
3	97	−71
4	83	−92
$\bar{1}$	171	181
$\bar{3}$	248	−231
$\bar{4}$	149	−156
	14,4,*l*	
0	176	−184
1	212	−226
$\bar{1}$	107	106
$\bar{2}$	192	179
	16,0,*l*	
0	211	−237
	11*l*	
1	365	402
2	74	72
3	507	−524
4	312	−320
5	126	90
7	223	−141
8	162	143
$\bar{1}$	719	−789
$\bar{2}$	56	−52
$\bar{3}$	393	−358
$\bar{4}$	356	287
$\bar{5}$	231	189
$\bar{6}$	336	334
$\bar{8}$	77	−118
$\bar{9}$	104	−74
	13*l*	
0	470	−493
1	157	−177
2	286	−275
3	479	−494
4	372	−338
5	386	378
7	438	341
8	67	−35
$\bar{1}$	557	644
$\bar{2}$	87	87
$\bar{3}$	296	−295
$\bar{4}$	298	−243
$\bar{5}$	484	−490
$\bar{6}$	95	−101
$\bar{7}$	429	328
$\bar{8}$	117	111
	15*l*	
	243	−236
1	124	−134
2	424	−449
3	293	307
4	846	913
5	72	−29
6	67	67
7	110	−102
8	170	−218
$\bar{1}$	585	−618
$\bar{2}$	702	764
$\bar{3}$	170	171
$\bar{4}$	410	401
$\bar{5}$	145	160
$\bar{6}$	471	−387
	17*l*	
0	352	327
1	52	51
2	337	327
3	393	327
4	484	−465
5	89	−98
6	42	−55
$\bar{1}$	629	−600
$\bar{2}$	666	−635
$\bar{3}$	61	60
$\bar{4}$	226	−204
$\bar{5}$	378	337
$\bar{6}$	180	196
	19*l*	
0	130	138
1	134	−116
2	134	123
3	274	−310
$\bar{1}$	558	581
$\bar{3}$	148	−148
	31*l*	
0	434	−445
1	743	−798
2	673	610
3	227	197
4	200	193
5	329	−313
6	165	−155
7	270	−226
8	125	−116
$\bar{1}$	629	−694
$\bar{2}$	683	705
$\bar{3}$	141	−103
$\bar{4}$	150	154
$\bar{5}$	394	376
$\bar{6}$	267	−241
$\bar{7}$	100	−325
$\bar{8}$	103	−111
$\bar{9}$	110	−124
	33*l*	
0	670	721
1	1072	1199
2	58	56
3	361	−314
4	306	−288
5	335	−333
6	125	−110
7	236	179
8	83	60
$\bar{1}$	182	−165
$\bar{2}$	810	−797
$\bar{3}$	43	−36
$\bar{4}$	104	−122
$\bar{5}$	315	294
$\bar{6}$	236	218
$\bar{7}$	343	242
	35*l*	
0	415	413
1	424	−410
2	448	−487
3	274	−281
4	191	−177
5	187	172
6	409	388
7	98	−68
$\bar{1}$	376	352
$\bar{2}$	674	650
$\bar{3}$	319	317
$\bar{4}$	505	−502
$\bar{5}$	279	−254
	37*l*	
0	422	−404
1	590	−567
2	205	194
3	99	103
4	221	207
5	179	182
6	253	−291
$\bar{1}$	91	80
$\bar{2}$	484	−433
$\bar{3}$	320	331
$\bar{4}$	443	424
	39*l*	
0	124	−135
1	487	500
3	95	−111
$\bar{3}$	260	−310
	51*l*	
0	100	−79
1	918	−1092
2	397	−354
3	60	41
4	84	56
5	218	202
6	326	333
7	151	−165
$\bar{1}$	286	−241
$\bar{2}$	207	199
$\bar{3}$	581	657
$\bar{4}$	465	−496
$\bar{5}$	729	−717
$\bar{7}$	213	−257
$\bar{8}$	253	249
	53*l*	
0	694	−656
1	440	420
2	626	575
3	591	593
4	368	368
6	293	−376
7	303	−239
1	299	−282
$\bar{2}$	416	−362
$\bar{3}$	303	275
$\bar{4}$	542	504
$\bar{5}$	265	228
$\bar{7}$	208	−178
$\bar{8}$	213	−328
	55*l*	
0	648	533
1	524	502
2	203	188
3	270	−227
4	492	−485
$\bar{1}$	169	136
$\bar{2}$	579	−498
$\bar{3}$	472	−427
$\bar{4}$	136	−103
	57*l*	
0	110	−130
1	112	−107
2	265	−270
3	205	−214
4	276	322
$\bar{1}$	394	330
$\bar{2}$	449	399
$\bar{3}$	81	−76
	59*l*	
1	92	91
2	99	−95
$\bar{1}$	276	−246
$\bar{2}$	105	105
	71*l*	
0	403	350
1	97	90
3	844	−960

TABLE 1. (*Continued.*)

	$\lvert F_o \rvert$	F_c
4	511	−519
5	219	254
7	155	206
8	131	146
$\bar{1}$	461	453
$\bar{2}$	415	381
$\bar{3}$	444	−438
$\bar{4}$	102	−101
$\bar{5}$	521	−601
$\bar{6}$	352	404
$\bar{7}$	321	351
	73l	
0	647	−572
1	451	−406
2	270	−264
3	102	70
4	407	405
5	258	263
6	172	170
8	98	−160
$\bar{1}$	102	74
$\bar{2}$	791	985
$\bar{3}$	283	235
$\bar{4}$	233	206

	$\lvert F_o \rvert$	F_c
$\bar{6}$	419	−457
	75l	
0	114	−88
1	93	61
2	120	95
3	248	241
4	72	58
$\bar{1}$	682	−573
$\bar{2}$	639	−519
$\bar{4}$	207	192
	77l	
0	245	255
1	174	170
2	37	−26
3	140	−138
$\bar{2}$	77	65
$\bar{3}$	227	−208
$\bar{4}$	157	−150
	91l	
0	405	−362
1	707	750

	$\lvert F_o \rvert$	F_c
2	573	516
3	143	−106
4	78	68
5	294	−389
6	187	−267
7	128	142
$\bar{1}$	110	−84
$\bar{2}$	167	−138
$\bar{3}$	667	−740
$\bar{4}$	257	253
$\bar{5}$	382	469
$\bar{7}$	188	213
	93l	
0	883	852
1	171	139
2	420	−364
3	290	−268
4	174	−175
6	324	335
$\bar{1}$	51	51
$\bar{2}$	331	294
$\bar{3}$	196	150
$\bar{4}$	174	−175
$\bar{6}$	324	335

	$\lvert F_o \rvert$	F_c
	95l	
0	436	−362
1	358	−332
2	81	−67
3	55	37
4	62	73
$\bar{1}$	133	98
$\bar{2}$	60	−24
$\bar{3}$	427	394
$\bar{4}$	72	61
	97l	
0	135	120
1	57	67
2	32	45
$\bar{1}$	100	−22
$\bar{2}$	133	−116
$\bar{3}$	114	−74
$\bar{4}$	140	151
	11,1,l	
0	378	−400
2	244	−202
3	620	657
4	216	232

l	$\lvert F_o \rvert$	F_c
$\bar{1}$	563	−572
$\bar{2}$	286	296
$\bar{3}$	352	365
$\bar{5}$	309	328
$\bar{6}$	232	−234
	11,3,l	
0	402	387
1	154	73
2	356	351
4	242	−240
$\bar{1}$	130	−94
$\bar{2}$	553	−552
$\bar{3}$	45	8
$\bar{4}$	67	−61
$\bar{6}$	430	457
	11,5,l	
0	159	−153
1	136	127
2	88	−82
3	190	−170
4	46	48
$\bar{1}$	317	257
$\bar{2}$	68	58

	$\lvert F_o \rvert$	F_c
$\bar{3}$	338	−174
$\bar{4}$	92	85
	11,7,l	
0	83	108
$\bar{1}$	81	−57
	13,1,l	
0	260	246
1	254	328
2	174	−212
3	64	61
4	151	−185
5	224	326
$\bar{1}$	126	84
$\bar{3}$	501	512
$\bar{4}$	219	−216
$\bar{5}$	201	−240
	13,3,l	
0	429	−405
2	320	284
3	159	−126
4	99	94
$\bar{2}$	87	−71

	$\lvert F_o \rvert$	F_c
$\bar{3}$	125	−84
$\bar{4}$	362	365
	13,5,l	
0	91	95
2	202	−212
$\bar{1}$	244	−174
$\bar{2}$	93	84
	15,1,l	
0	79	91
1	197	56
2	167	215
3	176	−235
$\bar{1}$	254	364
$\bar{2}$	139	−138
$\bar{3}$	103	−94
	15,3,l	
0	120	−145
1	117	145
2	105	−148
$\bar{1}$	108	−71
$\bar{2}$	162	219

the a^*-, b^*-, and c^*-axes, respectively, and, with U_{12}, U_{23}, and U_{13}, define the magnitude and orientation of the ellipsoid of vibration with respect to the crystallographic axes.

An analysis of the vibrational motion of the anion, assumed to be a rigid body, was carried out. First, the position of its mass centre and the direction cosines of the axes of inertia were determined; they are shown in Fig. 2; then, two ellipsoids were calculated, one for the translatory vibrations and one for the rotational oscillations. The directions of the principal axes of these ellipsoids and the corresponding root-mean-square (r.m.s.) amplitudes of vibration

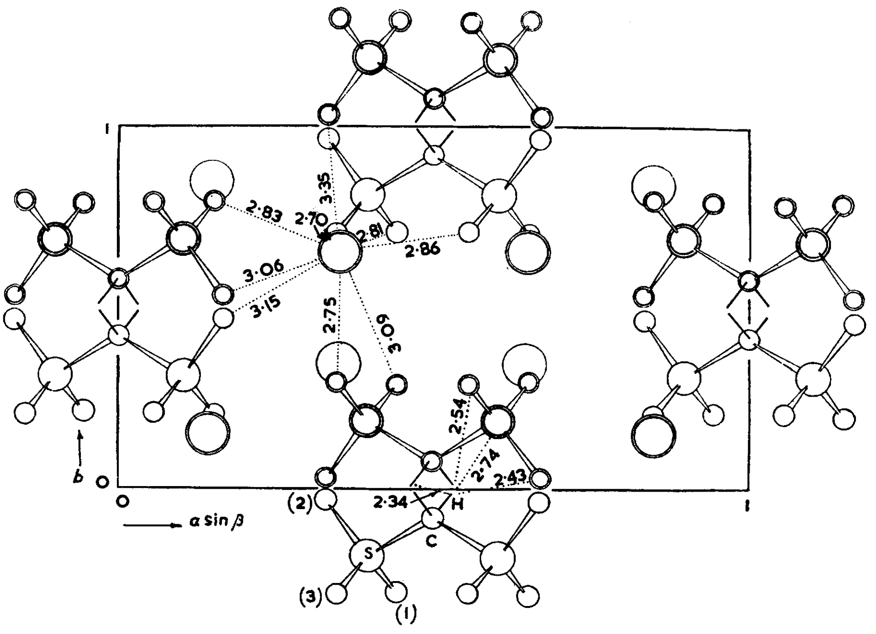

FIG. 1. The structure projected along [001]. Large circles represent potassium ions, medium circles sulphur atoms, small circles oxygen atoms, and the hydrogen atoms are situated at the ends of the short lines. Atoms which lie between $z/c = 0$ and $z/c = \frac{1}{2}$ are shown as single circles and those between $z/c = \frac{1}{2}$ and $z/c = 1$ as double circles with the exception that O(1) is just on the other side of the boundary. The numbers are distances in Å between the atoms indicated by the dotted lines.

are shown in Fig. 2. It can be seen that the ellipsoids have different orientations and neither coincides with the axes of inertia. However, the direction of maximum rotational oscillation is found to be fairly close to the axis, I, with the minimum moment of inertia. Cruickshank's revised procedure [7] was used to calculate the corrections in the atomic co-ordinates required for rotational oscillation; the maximum correction in any one co-ordinate was 0·0065 Å. The revised co-ordinates with respect to the orthogonal system are shown in Table 4.

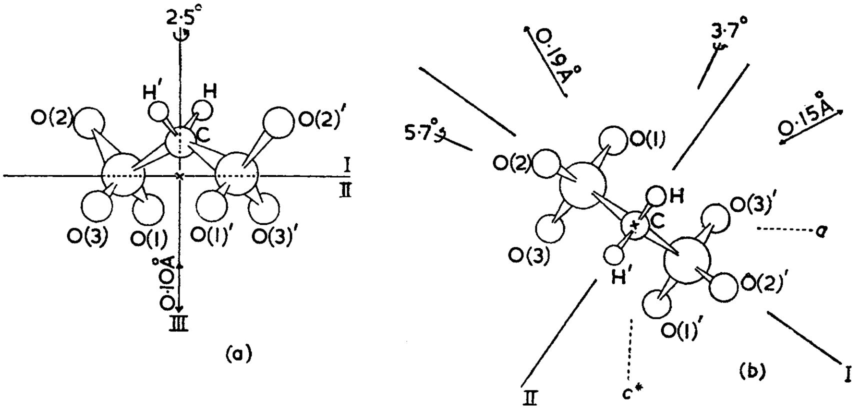

FIG. 2. A methylenedisulphonate ion viewed (a) along the *c*-axis and (b) down the *b*-axis of the crystal. The mass centre is marked ×. The directions of the axes of inertia (I, II, and III in order of increasing moment of inertia) are shown by full lines, and in (b) the orientation of the crystallographic axes is indicated by broken lines. The direction of the principal axes of the ellipsoid of translational vibration are shown by ◄—► with the corresponding r.m.s. amplitudes in Å. The directions of the principal axes of rotation are indicated by the curved arrows and the r.m.s. amplitudes of oscillation are given in degrees.

TABLE 2.

Atomic co-ordinates.

	x/a	y/b	z/c	X' (Å)	$\sigma(X)$ (Å)	Y' (Å)	$\sigma(Y)$ (Å)	Z' (Å)	$\sigma(Z)$ (Å)
K	0·152	0·132	−0·146	1·912	0·002	1·026	0·002	−1·060	0·002
S.........	0·396	−0·194	0·140	4·962	0·002	−1·505	0·002	1·013	0·002
O(1) ...	0·443	−0·295	−0·008	5·568	0·007	−2·290	0·008	−0·062	0·008
O(2) ...	0·327	−0·057	0·075	4·105	0·007	−0·445	0·008	0·545	0·009
O(3) ...	0·347	−0·300	0·281	4·339	0·008	−2·334	0·008	2·039	0·009
C	0·500	−0·080	0·250	6·262	—	−0·622	0·013	1·813	—
H	0·536	−0·004	0·150	6·71	0·15	−0·03	0·14	1·09	0·12

TABLE 3.

Vibration parameters (all units are 10^{-3} Å^2).

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	σ
K	35	1	35	1	31	1	3	1	−5	1	−8	1
S	27	1	19	1	31	1	0	1	1	1	−6	1
O(1)	39	4	32	4	46	5	−2	3	−10	3	2	3
O(2)	27	3	39	4	53	5	−6	3	13	4	0	3
O(3)	41	4	32	4	50	5	8	3	3	3	−5	3
C	27	6	22	6	42	8	0	—	0	—	−8	5
H	Isotropic $\bar{U}$ = 30											

TABLE 4.

Atomic co-ordinates of the anion corrected for rotational oscillation (all in Å).

	S	O(1)	O(2)	O(3)	C	H
X'	4·959	5·568	4·099	4·333	6·262	6·716
Y'	−1·505	−2·294	−0·439	−2·340	−0·616	−0·020
Z'................	1·010	−0·070	0·541	2·041	1·813	1·086

This treatment differs from that published for the pyrosulphate ion in which the vibrations with respect only to the axes of inertia were determined. For comparison with the present results the additional calculations have been carried out according to Cruickshank's revised procedure. For the pyrosulphate ion the principal axes of both ellipsoids are nearer the axes of inertia than in the methylenedisulphonate; for rotational oscillation the axis of maximum vibration makes an angle of 2° with I and the r.m.s. amplitude is 6·4° while the axis of minimum vibration is along III, the 2-fold axis of the ion, and the r.m.s. amplitude is 2·8°. There is no significant difference between these amplitudes of rotational oscillation and those for the methylenedisulphonate ion. For translatory motion the maximum r.m.s. amplitude of vibration is 0·11 Å in a direction at 17° to I and the minimum is again along III with an r.m.s. amplitude of 0·08 Å. These values are smaller than the corresponding ones in potassium methylenedisulphonate probably because no absorption correction was applied to the observations on potassium pyrosulphate. Revision of the co-ordinate correction increases the average S–O bond length from 1·437 to 1·440 Å but the S–O– bond length (1·645 Å) remains unchanged.

Interatomic Distances and Angles.—Table 5 shows the bond lengths and bond angles, and their standard deviations, together with the mean length of the chemically indistinguishable bonds; these values have been calculated from the corrected co-ordinates given by the computer to four decimal places, not from the rounded-off values in Table 4. In Fig. 1 the distances of less than 3·5 Å from a potassium ion to its neighbours are shown together with the distances of less than 3·0 Å from a hydrogen atom to atoms in the nearest anion.

TABLE 5.

Bond lengths (Å) and angles in the methylenedisulphonate ion.

S–O(1)	1·470 ± 0·009	1·461 ± 0·005 Å	O(1)–S–O(2)	113·8°	all ± 0·5°
S–O(2)	1·448 ± 0·008		O(1)–S–O(3)	112·8	
S–O(3)	1·467 ± 0·009		O(2)–S–O(3)	113·2	
S–C	1·770 ± 0·007		C–S–O(1)	107·3	
C–H	1·04 ± 0·14		C–S–O(2)	102·4	
			C–S–O(3)	106·3	
			S–C–S	119·7 ± 0·7	
			H–C–S	107 ± 8	
			H–C–H	110 ± 10	

Discussion.—Some months before this refinement was completed Dr. D. W. J. Cruickshank predicted the bond lengths "C–S at least 1·76 Å and S–O 1·43—1·46 Å." He has now published[9] his theoretical treatment of XO_4^{n-} and related ions and his essentially correct prediction lends support to his theory. According to Cruickshank there is π-bonding between d-orbitals on sulphur and the p-orbitals on nitrogen or oxygen in the iminodisulphonate or pyrosulphate ions: in both ions the π-bond order is 3/15 so that the S–N and S–O bond lengths 1·662 and 1·645 Å represent partial double bonds. In the methylenedisulphonate ion no π-bonding is possible to the carbon atom, so that the S–C bond length of 1·770 Å represents a single bond. Further discussion of the significance of the bond lengths is deferred to the following paper on sodium hydroxymethanesulphinate.

As is usual in $Y{-}SO_3^-$ groups electrostatic repulsion between the charged oxygen atoms causes the bond angles round sulphur to differ from those of a regular tetrahedron, the O–S–O angles being larger and the O–S–C angles smaller. The S–C–S angle is significantly larger than the tetrahedral angle or the $H_2C\lessdot$ angle (113°) found in paraffins. A similar but smaller increase in angle from the ideal of 120° is found for S–N–S (5·5°) and S–O–S in the iminodisulphonate and pyrosulphate ions.

Fig. 1 shows that the potassium ion is surrounded by nine oxygen atoms with distances

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[9] Cruickshank, *J.*, 1961, 5486.

ranging from 2·70 to 3·35 Å. The corresponding distances in potassium iminodisulphonate and potassium pyrosulphate are shown:

Comparison of interionic distances (all in Å).

										Mean
$K_2S_2O_7$	2·84	2·80	3·22	3·05	2·76	3·10	2·76	2·81	2·71	2·89
$NH(SO_3)_2K_2$	2·95	2·82	3·05	3·00	2·71	3·23	2·75	2·83	2·70	2·89
$CH_2(SO_3)_2K_2$	3·35	2·83	3·06	3·15	2·75	3·09	2·81	2·86	2·70	2·96

As the standard deviation is 0·01 Å, some of the differences in these distances are significant. The individual variations are consistent with longer central bonds and smaller central angles in the methylenedisulphonate anions and with the larger relative displacement of the anions along the *b*-axis to accommodate the hydrogen atoms. The greater volume of the anion itself gives rise to the observed larger volume for the unit cell in the methylenedisulphonate; the ratios of the volumes of the three unit cells is 1 : 1 : 1·08, and the main difference in the unit cell dimensions (given in the introduction) is a larger value of *b* as the number of hydrogen atoms increases.

Experimental.—The crystals were supplied by Dr. D. W. Jones and were part of the sample he prepared for the preliminary investigation.[3]

The unit-cell dimensions were determined by the Straumanis method. Equi-inclination photographs were taken about the three principal axes from the zero to the fourth layer lines inclusive. For photographs about the [*a*]- and [*c*]-axes the crystals used were equi-dimensional and of side 0·15 mm., while for photographs about [*b*] a crystal of side 0·4 mm. was used. The absorption correction appropriate to spherical crystals was applied to the observations about each axis. Of the 810 possible reflections 643 gave measurable intensities. A multiple-film method was used and intensities estimated visually with the aid of a calibration strip. Lorentz and polarisation corrections were applied with a computer programme written by Dr. F. M. Lovell. The intensities were correlated and their square roots extracted to give a set of relative structure amplitudes which were scaled approximately by comparison with the corresponding values for the isostructural potassium pyrosulphate. During refinement the scale factor was one of the parameters. An empirical extinction correction $I_{\mathrm{true}} = I_{\mathrm{obs}} \exp(\alpha I_{\mathrm{calc.}})$ was applied after four cycles of refinement and α was found to be $2{\cdot}65 \times 10^{-4}$.

The scattering factors used were the corrected values of Tomiie and Stam[10] for S, those of Berghuis *et al.*[11] for C, O, and K^+ and the expression $1/\left(1 + \frac{4\pi^2 \sin^2\theta}{\lambda^2}\right)^2$ for hydrogen. Refinement was carried out by the method of least squares on the Leeds University Ferranti Pegasus computer with programmes[12] devised by Dr. D. W. J. Cruickshank and Miss D. E. Pilling.

The function minimised was $R = \Sigma w\,(|F_o| - |F_c|)^2$ where the weighting factor w was $1/|F_o|$.

Analysis of the thermal motion and calculation of the corrections for rotational oscillation were carried out on the Pegasus computer with programmes written by Dr. Cruickshank and Mr. Bujosa.[12]

I am grateful to Mr. D. Holey for taking the photographs, to Mrs. P. M. E. Currie for estimating the intensities of those taken about one of the axes, to my colleagues for the use of their programmes,[12] and to the Director of the Leeds University Computing Laboratory for the use of the computing facilities. Some of the equipment was provided by the Royal Society and Imperial Chemical Industries Limited.

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[11] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[12] Cruickshank, Pilling, and, in part, Bujosa, Lovell, and Truter, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, Oxford, 1961.