Acta Cryst. (1964). **17**, 465

The Crystal Structure of Dimethylphenylsulphonium Perchlorate

BY AMPARO LOPEZ-CASTRO AND MARY R. TRUTER

Department of Inorganic and Structural Chemistry, The University, Leeds 2, England

(*Received* 7 *May* 1963)

Crystals of $[(CH_3)_2C_6H_5S]^+ClO_4^-$ are monoclinic with four formula units in a unit cell, space group $P2_1/c$, of dimensions

$$a = 12{\cdot}81,\ b = 10{\cdot}06,\ c = 9{\cdot}33\ \text{Å};\ \beta = 110{\cdot}7°.$$

The structure was determined by three-dimensional Patterson and Fourier syntheses from observations made with Cu $K\alpha$ radiation. Isotropic and anisotropic refinement was carried out by the method of least squares.

The structure consists of perchlorate anions and sulphonium cations, each ion being surrounded by six of the opposite charge. The bonds round the sulphur atom are pyramidal with C–S–C angles of 102°, 103° and 105° each ± 1°; the bond lengths are S–C(methyl), 1·81 and 1·83 Å, each ± 0·02 Å; and S–C(phenyl), 1·82 ± 0·02 Å. The perchlorate ion undergoes large vibrational motion and the apparent Cl–O bond lengths vary from 1·38 to 1·60 Å.

Introduction

Sulphur is remarkable for the variety of the oxidation states it displays and for the number of atoms to which it may be attached: one, two, three, four and six covalency being known. A sulphonium ion R_3S^+ contains sulphur in the oxidation state II with a covalency of three, and, as shown by classical optical resolution experiments, the three R groups are not coplanar.

We have examined a simple member of this class of compounds, dimethylphenylsulphonium perchlorate, in which two methyl groups and one phenyl group are attached to the sulphur atom.

Experimental

Dimethylphenylsulphonium perchlorate was prepared by the method of Bordwell & Boutan (1956). Colourless crystals were obtained after recrystallization from acetone. Chemical analyses were not reproducible because the compound explodes on combustion; the average values were in fair agreement with the calculated ones except for carbon (observed 38%, calculated 40·2%). The crystals melted at 156 °C without decomposition.

The unit-cell dimensions were measured from Weissenberg photographs. For intensity measurements a crystal 0·15 × 0·25 × 0·35 mm was set about each of the three principal axes in turn. Equi-inclination multiple-film Weissenberg photographs were taken from the zero to the fourth layer about each axis. Of the 2560 possible reflexions only 823 gave measurable intensities; when the crystal was cooled a superlattice formed and so we were not able to increase the number of observations by reducing the temperature. Correction factors were applied to the visually estimated intensities on the Leeds University Pegasus computer with a program written by Dr F. M. Lovell. For the ($h0l$) reflexions the approximate scale factor was obtained by Wilson's (1942) method; the remaining observations were correlated with these.

Crystal data

$$a = 12{\cdot}81,\ b = 10{\cdot}06,\ c = 9{\cdot}33,\ \text{all} \pm 0{\cdot}03\ \text{Å};$$
$$\beta = 110{\cdot}7 \pm 0{\cdot}3°;$$
$$V = 1124{\cdot}7\ \text{Å}^3,\ F(000) = 496\ .$$
$$Z = 4,\ D_x = 1{\cdot}41\ \text{g.cm}^{-3},$$
$$D_m\,(\text{flotation}) = 1{\cdot}40\ \text{g.cm}^{-3}.$$

The systematic absences are $0k0$ absent for k odd and $h0l$ for l odd so that the space group is uniquely determined as $P2_1/c$. No symmetry is required in the molecules or ions. The absorption coefficient for Cu $K\alpha$ radiation is 46 cm^{-1}.

Structure determination

Fourteen atoms other than hydrogen were to be located, one chlorine atom and four oxygen atoms (designated O(1) ⋯ O(4)) in the perchlorate ion and one sulphur atom and eight carbon atoms in the sulphonium ion; the carbon atoms of the phenyl group were designated C(1) ⋯ C(6), with C(1) attached to sulphur, and the methyl carbon atoms were designated C(7) and C(8). It proved necessary to use a three-dimensional Patterson synthesis to obtain trial coordinates for chlorine and sulphur. Structure factors calculated for ($hk0$), ($h0l$), and ($0kl$) with these coordinates gave R values of 0·34, 0·31, and 0·38 respectively, indicating that the heavy atoms were correctly placed. In the corresponding projections of the electron density, peaks were obtained which could be assigned to some of the

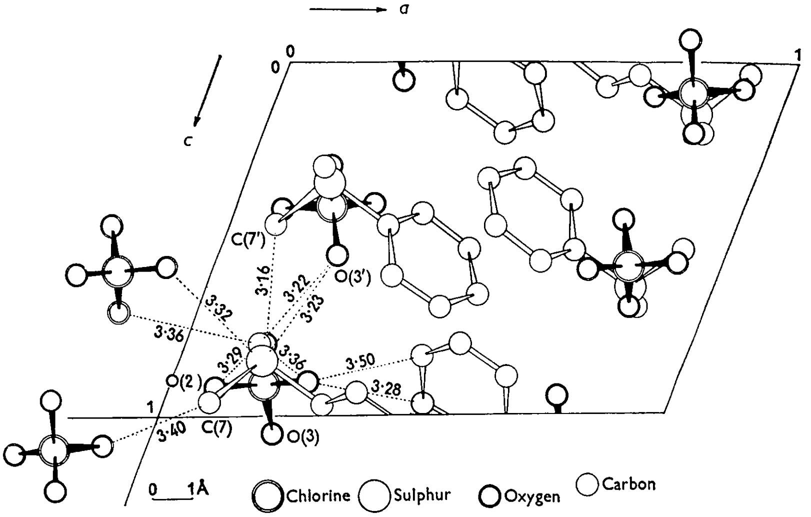

Fig. 1. The structure of dimethylphenylsulphonium perchlorate projected down [010]. The numbers are distances in Å between the pairs of atoms indicated by broken lines.

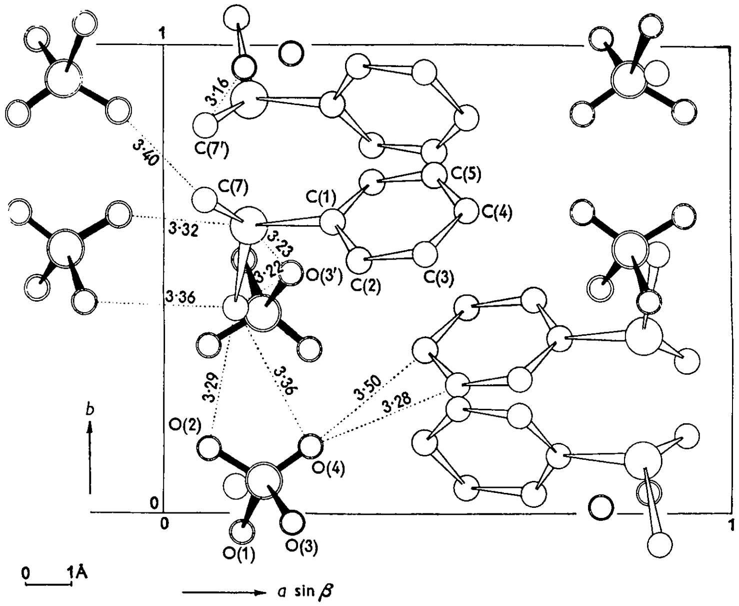

Fig. 2. The structure projected down [001]. The numbers are distances in Å between the pairs of atoms indicated by broken lines.

light atoms. In assigning positions to the light atoms, the criterion was that the positions were consistent with vectors in the three-dimensional Patterson function as well as with a chemically acceptable model. Successive structure factor calculations and Fourier syntheses were used to locate the remaining atoms and the structure found is depicted in Figs. 1 and 2.

Refinement was carried out by the method of least squares with programs written by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). The weighting factor was $1/(2{\cdot}4|F_{\min}|+|F_o|)$ where $|F_{\min}|$ was the minimum observable. The scattering factors of Tomiie & Stam (1958) were used for S and Cl and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for O and C. When isotropic refinement had been completed the value of R was 0·25. Anisotropic refinement was then started. It did not proceed smoothly; the vibration parameters of some atoms increased continuously, and it seemed possible that four atoms, O(1), O(3), O(4), and C(3), were wrongly located. Structure factors were calculated for the other ten atoms only and a three-dimensional Fourier synthesis was carried out. The results confirmed the previous positions for all fourteen

Table 1. *Observed and calculated structure factors* (×10)

Reflexions too weak to be observed have been omitted

h	k	l	$\|F_o\|$	F_c
2	0	0	643	-765
3	0	0	1148	-1388
4	0	0	427	-318
5	0	0	142	-75
6	0	0	708	612
7	0	0	112	-86
8	0	0	264	-209
9	0	0	358	-326
10	0	0	118	-11
11	0	0	316	308
12	0	0	165	134
14	0	0	90	-126
15	0	0	58	-70
0	0	2	564	626
1	0	2	1082	1124
2	0	2	659	749
3	0	2	510	516
4	0	2	434	-344
5	0	2	572	-528
6	0	2	176	-111
7	0	2	188	62
8	0	2	188	183
9	0	2	193	-132
10	0	2	105	-111
12	0	2	99	51
0	0	4	319	-403
1	0	4	139	-190
2	0	4	148	160
3	0	4	345	377
4	0	4	305	291
5	0	4	204	-183
2	0	6	126	55
3	0	6	85	-86
4	0	6	169	187
5	0	6	207	-203
6	0	6	146	141
7	0	6	99	67
0	0	8	134	-138
1	0	8	109	101
3	0	8	97	107
5	0	8	115	-108
6	0	8	66	-77
-1	0	2	1148	-1310
-2	0	2	1220	-1553
-3	0	2	241	199
-4	0	2	762	799
-5	0	2	379	354
-6	0	2	236	-236
-7	0	2	671	-678
-8	0	2	399	-414
-9	0	2	266	249
-10	0	2	564	617
-11	0	2	202	199
-13	0	2	185	-219
-1	0	4	304	-265
-2	0	4	326	421
-3	0	4	189	261
-5	0	4	426	-583
-6	0	4	387	-526
-8	0	4	313	373
-9	0	4	466	563
-10	0	4	259	231
-11	0	4	325	-384
-12	0	4	289	-316
-1	0	6	146	-98
-2	0	6	248	221
-3	0	6	277	-274
-4	0	6	283	-295
-5	0	6	146	-102
-6	0	6	146	146
-7	0	6	346	475
-8	0	6	146	131
-10	0	6	259	-274
-11	0	6	189	-178
-13	0	6	225	264
-1	0	8	146	-107
-6	0	8	146	160
0	0	10	66	-63
-2	0	10	82	74
-3	0	10	107	86
-4	0	10	50	-69
-5	0	10	90	-45
-8	0	10	50	-6
-9	0	10	107	107
1	1	0	169	231
2	1	0	261	-161
3	1	0	337	264
4	1	0	119	-60
5	1	0	409	-393
7	1	0	140	156
8	1	0	110	87
9	1	0	140	138
12	1	0	132	-123
0	1	1	99	152
1	1	1	518	555
2	1	1	552	-603
3	1	1	348	-343
4	1	1	317	293
5	1	1	354	377
6	1	1	119	-83
7	1	1	98	-64
8	1	1	297	-264
9	1	1	136	-83
10	1	1	148	136
11	1	1	197	188
0	1	2	236	186
1	1	2	134	-142
2	1	2	133	-178
3	1	2	97	69
4	1	2	444	446
5	1	2	152	-56
6	1	2	173	-168
7	1	2	197	-192
8	1	2	182	-144
9	1	2	149	187
10	1	2	134	118
0	1	3	420	429
1	1	3	187	172
2	1	3	175	154
3	1	3	346	-320
4	1	3	73	-139
6	1	3	378	333
7	1	3	235	216
9	1	3	259	-250
10	1	3	190	-180
0	1	4	173	194
1	1	4	235	263
2	1	4	229	-216
3	1	4	258	-257
4	1	4	124	78
5	1	4	253	261
6	1	4	136	97
8	1	4	244	-230
0	1	5	337	-374
1	1	5	128	92
2	1	5	347	381
3	1	5	309	329
4	1	5	333	-326
5	1	5	227	-244
7	1	5	208	198
8	1	5	174	217
1	1	6	223	203
2	1	6	242	261
3	1	6	180	-179
4	1	6	115	-74
7	1	6	115	154
0	1	7	299	-307
1	1	7	337	-357
2	1	7	86	76
3	1	7	214	231
4	1	7	102	87
0	1	8	141	-170
1	1	8	115	-110
2	1	8	122	174
1	1	9	102	-120
3	1	9	80	-77
-1	1	1	214	303
-2	1	1	360	-401
-3	1	1	290	-349
-4	1	1	321	343
-5	1	1	270	263
-6	1	1	365	-302
-7	1	1	265	-205
-9	1	1	165	97
-10	1	1	214	188
-12	1	1	145	-144
-1	1	2	283	-150
-2	1	2	430	536
-3	1	2	445	-338
-4	1	2	192	220
-5	1	2	269	-276
-6	1	2	177	-179
-7	1	2	145	-111
-8	1	2	182	151
-9	1	2	114	78
-10	1	2	90	99
-1	1	3	341	-288
-2	1	3	124	-132
-3	1	3	371	-404
-5	1	3	250	228
-8	1	3	180	95
-9	1	3	161	114
-1	1	4	235	224
-2	1	4	150	-156
-3	1	4	390	-412
-4	1	4	219	-133
-5	1	4	224	-170
-6	1	4	305	256
-7	1	4	152	91
-8	1	4	116	73
-1	1	5	283	-288
-2	1	5	248	-278
-3	1	5	289	242
-4	1	5	270	240
-5	1	5	191	169
-7	1	5	226	-195
-8	1	5	148	88
-1	1	6	234	-235
-2	1	6	277	-265
-3	1	6	171	-173
-4	1	6	210	178
-5	1	6	207	164
-6	1	6	146	126
-7	1	6	146	-88
-1	1	7	87	61
-2	1	7	297	286
-3	1	7	262	258
-5	1	7	301	-256
-6	1	7	146	-135
-7	1	7	121	93
-8	1	7	189	182
-1	1	8	121	-170
-3	1	8	121	101
-4	1	8	121	143
-8	1	8	121	130
-1	1	9	174	209
-2	1	9	87	89
-4	1	9	121	-133
-7	1	9	174	214
-9	1	9	115	-173
0	2	0	819	733
1	2	0	457	396
2	2	0	661	-652
3	2	0	564	-544
4	2	0	165	-56
5	2	0	395	308
6	2	0	371	278
7	2	0	135	54
8	2	0	252	-185
0	2	1	463	419
1	2	1	569	-534
2	2	1	925	-906
3	2	1	274	-268
4	2	1	208	-139
5	2	1	444	454
6	2	1	135	117
7	2	1	173	-180
8	2	1	262	-259
9	2	1	128	-47
10	2	1	220	226
11	2	1	139	157
0	2	2	367	-382
1	2	2	266	141
2	2	2	192	137
3	2	2	68	91
4	2	2	260	-165
5	2	2	74	54
7	2	2	185	152
9	2	2	114	-116
0	2	3	788	842
1	2	3	356	377
3	2	3	362	-425
4	2	3	441	-415
5	2	3	149	-81
6	2	3	228	202
7	2	3	128	99
0	2	4	250	-208
1	2	4	90	-108
2	2	4	72	37
4	2	4	227	-166
7	2	4	267	263
0	2	5	145	120
1	2	5	114	104
2	2	5	241	225
3	2	5	173	151
5	2	5	192	-184
0	2	6	137	-116
2	2	6	163	116
3	2	6	97	85
4	2	6	137	-69
5	2	6	125	-103
2	2	7	135	-145
0	2	8	63	-65
3	2	8	136	119
-1	2	1	1453	1696
-2	2	1	206	-189
-3	2	1	223	-177
-4	2	1	141	-111
-5	2	1	128	73
-6	2	1	214	159
-7	2	1	262	291
-8	2	1	188	-161
-9	2	1	425	-455
-10	2	1	217	-269
-11	2	1	104	90
-12	2	1	234	255
-1	2	2	106	150
-2	2	2	1056	-1029
-3	2	2	362	333
-4	2	2	528	542
-5	2	2	506	497
-7	2	2	304	-289
-8	2	2	377	-306
-9	2	2	228	218
-10	2	2	100	90
-1	2	3	347	310
-2	2	3	516	-532
-3	2	3	141	-172
-4	2	3	307	253
-5	2	3	301	303
-6	2	3	223	-167
-7	2	3	233	-232
-8	2	3	427	-475
-9	2	3	197	-206
-10	2	3	255	270
-11	2	3	362	417
-1	2	4	153	196
-2	2	4	98	92
-3	2	4	209	148
-4	2	4	346	251
-5	2	4	213	-218
-6	2	4	158	-138
-7	4	2	241	183
-8	2	4	124	135
-9	2	4	186	153
-11	2	4	126	-162
-1	2	5	276	-268
-2	2	5	138	-87
-3	2	5	149	152
-4	2	5	250	200
-5	2	5	104	-113
-6	2	5	333	-394
-7	2	5	237	-232
-9	2	5	245	262
-10	2	5	259	290
-12	2	5	210	-271
-2	2	6	105	76
-3	2	6	133	98
-4	2	6	73	-75
-8	2	6	73	108
-1	2	7	127	88
-4	2	7	160	-143
-5	2	7	193	-209
-7	2	7	126	114
-8	2	7	163	185
-11	2	7	163	-163
-2	2	8	110	100
-3	2	8	135	83
-4	2	8	105	-109
2	3	0	206	-105
3	3	0	87	-57
4	3	0	128	67
5	3	0	164	-171
6	3	0	219	-188
8	3	0	216	185
9	3	0	174	152
11	3	0	185	-226
12	3	0	157	-147
0	3	1	452	449
1	3	1	246	262
2	3	1	107	-57
3	3	1	93	-125
4	3	1	289	-305
5	3	1	116	-85
6	3	1	149	165
7	3	1	174	219
0	3	2	451	399
1	3	2	290	-341
2	3	2	256	-266
3	3	2	111	-84
4	3	2	334	354
5	3	2	164	170
6	3	2	133	-120
7	3	2	378	-413
9	3	2	84	113
10	3	2	228	311
3	3	3	375	288
5	3	3	348	-319
6	3	3	73	-35
0	3	4	375	407
1	3	4	320	328
2	3	4	359	-355
3	3	4	317	-311
4	3	4	233	-168
5	3	4	409	410
6	3	4	255	215
8	3	4	259	-199
9	3	4	247	-222
0	3	5	118	97
1	3	5	89	-42
2	3	5	99	-68
3	3	5	97	76
4	3	5	119	83
5	3	5	98	-93
0	3	6	69	44
1	3	6	318	360
2	3	6	251	241
3	3	6	117	-119
4	3	6	263	-269
5	3	6	82	-102
1	3	7	60	68
2	3	7	80	65
0	3	8	206	-280
2	3	8	85	131
3	3	8	88	158
-1	3	1	266	-303
-2	3	1	53	-129
-3	3	1	429	-504
-4	3	1	331	347
-5	3	1	323	430
-6	3	1	208	216
-7	3	1	314	-341
-8	3	1	154	-160
-9	3	1	89	-136
-10	3	1	171	154
-1	3	2	198	148
-2	3	2	204	226
-3	3	2	240	164
-4	3	2	333	-337
-7	3	2	191	-132
-9	3	2	124	111
-11	3	2	146	134
-1	3	3	224	-113
-2	3	3	159	132
-3	3	3	362	279
-4	3	3	166	131
-6	3	3	421	-405
-7	3	3	372	-324
-8	3	3	99	46
-9	3	3	265	209

Table 1 (*cont.*)

h	k	l	$\|F_o\|$	F_c
-10	3	3	168	135
-1	3	4	319	309
-2	3	4	327	-353
-3	3	4	176	-178
-4	3	4	380	-351
-5	3	4	273	256
-6	3	4	199	180
-8	3	4	135	-134
-1	3	5	163	118
-2	3	5	193	131
-3	3	5	105	73
-4	3	5	381	-256
-5	3	5	243	-179
-6	3	5	118	-151
-7	3	5	152	97
-8	3	5	115	86
-9	3	5	124	120
-10	3	5	115	-91
-1	3	6	288	-286
-2	3	6	282	-273
-3	3	6	69	-60
-4	3	6	255	220
-5	3	6	270	270
-6	3	6	152	-126
-7	3	6	270	-221
-8	3	6	167	-136
-9	3	6	167	119
-10	3	6	167	178
-11	3	6	69	91
-3	3	7	127	-153
-4	3	7	69	-60
-5	3	7	118	-129
-6	3	7	138	124
-12	3	7	98	112
-1	3	8	118	-128
-2	3	8	118	108
-3	3	8	183	173
-4	3	8	69	63
-6	3	8	222	-285
-8	3	8	167	171
-9	3	8	181	180
-11	3	8	98	-106
-12	3	8	98	-129
0	4	0	500	-563
1	4	0	369	-419
2	4	0	239	213
3	4	0	303	265
4	4	0	168	173
5	4	0	113	91
6	4	0	168	-173
7	4	0	208	-188
8	4	0	249	235
9	4	0	199	202
0	4	1	180	-148
1	4	1	92	-72
2	4	1	211	-196
3	4	1	119	101
4	4	1	412	436
5	4	1	340	355
7	4	1	314	-335
8	4	1	209	-221
10	4	1	160	150
0	4	2	107	-56
1	4	2	601	-703
2	4	2	291	-278
3	4	2	271	-182
4	4	2	274	258
5	4	2	296	264
6	4	2	234	178
7	4	2	252	-227
0	4	3	258	211
1	4	3	181	145
2	4	3	271	-279
3	4	3	378	-365
4	4	3	84	76
5	4	3	354	275
6	4	3	225	181
8	4	3	278	-254
0	4	4	279	285
1	4	4	122	97
3	4	4	346	-329
4	4	4	324	-255
6	4	4	224	182
1	4	5	210	226
2	4	5	112	92
3	4	5	175	-154
6	4	5	133	121
0	4	6	191	-217
2	4	6	183	204
3	4	6	144	122
5	4	6	134	-166
-1	4	1	114	123
-2	4	1	161	-103
-3	4	1	341	-336
-4	4	1	206	-181
-5	4	1	95	97
-6	4	1	305	293
-7	4	1	330	296
-8	4	1	171	-163
-1	4	2	407	396
-2	4	2	305	391
-3	4	2	269	-113
-4	4	2	139	-94
-5	4	2	241	114
-7	4	2	160	183
-8	4	2	162	204
-9	4	2	111	-64
-10	4	2	291	-299
-3	4	3	559	-591
-4	4	3	279	220
-5	4	3	161	146
-6	4	3	285	260
-7	4	3	140	-104
-8	4	3	174	-144
-9	4	3	111	-94
-10	4	3	250	243
-1	4	4	168	141
-3	4	4	432	-456
-4	4	4	309	240
-5	4	4	246	238
-6	4	4	183	152
-8	4	4	214	-153
-9	4	4	276	-299
-11	4	4	168	135
-12	4	4	135	137
-1	4	5	195	-206
-2	4	5	297	-261
-3	4	5	115	-57
-4	4	5	256	213
-5	4	5	305	260
-7	4	5	186	-153
-9	4	5	142	113
-10	4	5	78	82
-11	4	5	78	-40
-1	4	6	89	-96
-3	4	6	119	130
-4	4	6	274	249
-5	4	6	133	98
-6	4	6	279	-284
-7	4	6	203	-159
-8	4	6	142	-87
-10	4	6	203	160
-1	4	7	157	-129
-3	4	7	177	166
-4	4	7	157	115
-7	4	7	133	-105
-8	4	7	78	71
-9	4	7	134	99
-1	4	8	134	158
-2	4	8	153	134
-4	4	8	134	-86
-5	4	8	187	-140
-6	4	8	134	-130
-7	4	8	157	121
-8	4	8	134	107
1	5	0	157	-163
2	5	0	452	-468
3	5	0	164	170
4	5	0	198	240
5	5	0	297	310
6	5	0	165	-156
7	5	0	197	-190
8	5	0	181	-20
9	5	0	232	237
0	5	1	106	-86
1	5	1	129	148
5	5	1	197	-208
7	5	1	231	275
8	5	1	140	118
0	5	2	358	324
2	5	2	231	-227
3	5	2	227	-243
5	5	2	193	184
6	5	2	208	241
7	5	2	126	-139
0	5	3	293	-258
3	5	3	325	256
4	5	3	261	199
6	5	3	308	-264
9	5	3	169	164
0	5	4	173	109
3	5	4	115	-114
4	5	4	185	-159
5	5	4	259	34
0	5	5	173	181
1	5	5	147	-157
2	5	5	265	-267
3	5	5	97	-112
4	5	5	148	82
3	5	7	97	-130
4	5	7	148	-158
-2	5	1	299	-295
-4	5	1	205	190
-5	5	1	140	106
-6	5	1	140	150
-7	5	1	82	81
-8	5	1	115	-131
-1	5	2	200	181
-2	5	2	226	-194
-3	5	2	341	-309
-4	5	2	231	-241
-5	5	2	297	286
-6	5	2	348	374
-7	5	2	125	109
-8	5	2	205	-224
-9	5	2	193	-187
-2	5	3	123	89
-3	5	3	379	360
-4	5	3	130	73
-5	5	3	76	-95
-6	5	3	130	-60
-7	5	3	108	-28
-1	5	4	132	-87
-2	5	4	354	-314
-4	5	4	404	360
-5	5	4	288	273
-7	5	4	279	-260
-8	5	4	288	-298
-1	5	5	239	239
-2	5	5	158	99
-4	5	5	288	-204
-3	5	6	97	100
-4	5	6	305	313
-2	5	7	122	-130
0	6	0	185	-180
2	6	0	159	175
3	6	0	293	300
4	6	0	90	63
5	6	0	214	-245
6	6	0	305	-310
8	6	0	181	152
0	6	1	366	-351
2	6	1	253	265
3	6	1	194	182
4	6	1	306	284
6	6	1	289	-302
7	6	1	165	-155
8	6	1	165	156
1	6	2	128	-138
2	6	2	201	-172
3	6	2	149	149
4	6	2	183	171
5	6	2	104	84
6	6	2	163	-173
1	6	3	165	-174
2	6	3	340	-343
3	6	3	184	-145
4	6	3	238	217
5	6	3	428	355
7	6	3	153	-109
8	6	3	169	-172
0	6	4	152	141
1	6	4	133	92
0	6	5	181	180
1	6	5	171	291
2	6	5	66	-91
3	6	5	200	-218
4	6	5	165	-146
2	6	7	115	99
4	6	7	116	-104
-1	6	1	255	-221
-2	6	1	157	-155
-3	6	1	271	210
-4	6	1	78	45
-5	6	1	115	124
-7	6	1	115	-134
-8	6	1	140	-165
-9	6	1	140	134
-1	6	2	338	298
-2	6	2	223	226
-3	6	2	112	-42
-4	6	2	305	-302
-5	6	2	311	-336
-7	6	2	193	194
-8	6	2	163	178
-10	6	2	104	-106
-1	6	3	249	192
-2	6	3	282	263
-3	6	3	165	-125
-4	6	3	242	-218
-8	6	3	184	186
-1	6	4	222	154
-2	6	4	222	-175
-3	6	4	321	-226
-4	6	4	260	-232
-5	6	4	203	116
-6	6	4	258	202
-2	6	5	202	-210
-3	6	5	255	-154
-4	6	5	140	-127
-2	6	6	122	-90
-1	6	7	146	-200
-3	6	7	144	145
-4	6	7	206	146
1	7	0	157	-196
2	7	0	162	-178
3	7	0	106	120
4	7	0	193	184
5	7	0	140	142
7	7	0	140	-149
8	7	0	140	-176
0	7	1	132	-120
1	7	1	239	-229
2	7	1	80	101
3	7	1	255	236
4	7	1	214	195
5	7	1	82	-125
6	7	1	181	-190
7	7	1	165	-200
8	7	1	165	183
0	7	2	251	278
3	7	2	97	-89
6	7	2	163	192
1	7	3	224	-187
2	7	3	167	-142
4	7	3	217	184
5	7	3	152	142
7	7	3	168	-155
2	7	4	157	108
3	7	4	181	147
-2	7	1	248	229
-3	7	1	182	163
-4	7	1	210	-198
-5	7	1	231	-235
-6	7	1	181	-150
-7	7	1	165	185
-8	7	1	181	225
-2	7	2	267	-256
-3	7	2	255	-258
-4	7	2	103	-83
-5	7	2	191	180
-6	7	2	163	163
-7	7	2	103	96
-1	7	3	203	148
-2	7	3	197	165
-3	7	3	270	-240
-4	7	3	262	-231
-6	7	3	199	169
-7	7	3	231	252
-9	7	3	169	-183
-1	7	4	164	-141
-2	7	4	277	-248
-3	7	4	145	114
-4	7	4	261	218
-3	7	5	263	-259
-3	7	6	104	76
7	8	0	140	135
0	8	1	84	-158
3	8	1	97	78
3	8	2	173	159
5	8	2	148	-73
2	8	3	57	-63
3	8	3	107	-50
4	8	3	115	78
2	8	7	86	16
1	8	4	109	-162
2	8	4	122	-136
4	8	4	189	222
-3	8	1	109	122
-4	8	1	185	194
-6	8	1	140	-122
-1	8	3	108	122
-2	8	3	150	168
-5	8	3	184	-146
-2	8	4	122	74
-4	8	4	206	-194
1	9	0	136	128
2	9	0	86	78
4	9	0	115	-112
0	9	1	177	-180
1	9	1	176	-183
3	9	1	182	170
4	9	1	140	131
6	9	1	115	-177
7	9	1	82	-146
-1	9	1	136	136
-2	9	1	236	225
-3	9	1	144	105
-4	9	1	144	-145
-5	9	1	197	-223
-1	9	2	109	-111
-2	9	2	122	109
-3	9	2	200	159
-1	9	3	297	295
-2	9	3	57	-19
-3	9	3	191	-173
-4	9	3	194	-172
-6	9	3	129	142
-7	9	3	107	113
-4	9	4	165	-143
-2	9	5	81	-117
-3	9	5	97	-124
3	10	1	97	-75
3	10	5	128	167
4	10	3	99	-102
1	11	0	132	212
2	11	0	107	123
3	11	2	112	110
4	11	0	140	-156
-2	10	3	115	-97
-2	11	2	201	142
-3	11	2	169	200
-2	11	5	79	65

atoms. Refinement was therefore continued with all the atoms other than hydrogen. All the vibration parameters, except U_{33} for O(4), eventually reached maxima, *i.e.* the shifts became negative; U_{33} for O(4) continued to increase but by the final cycle the shift was 0·2 times the corresponding standard deviation. When the largest shift in a coordinate was 0·45 of the corresponding standard deviation, the value of R had reached 0·15.

The hydrogen atoms of the phenyl group were then included, their positions being calculated so as to make the carbon–hydrogen bond length 1·0 Å and maintain a trigonal arrangement for the bonds round the carbon atoms. Each hydrogen atom was designated by the number of the carbon atom to which it was attached. For the subsequent refinement, all the hydrogen atoms were given an isotropic temperature factor, $U = 0{\cdot}08$ Å^2, and the temperature factor was refined while the coordinates were kept constant. Two cycles of refinement reduced R to 0·14 and all the U values for hydrogen were less than 0·08 Å^2 (see Table 3); thus indicating that the hydrogen atoms were correctly placed.

Comparison of the final coördinates for the other atoms before and after the inclusion of hydrogen atoms showed, surprisingly, that the largest total change was in an oxygen atom; x for O(3) had moved by 0·047 Å, 1·6 times its standard deviation, while the largest effect on a carbon atom of a phenyl group was 0·019 Å in y for C(2), 0·8 times the standard deviation.

The final list of observed and calculated structure factors is given in Table 1.

For each ion an analysis of the molecular vibration was made on the assumption that it could be treated as a rigid body. Internal consistency indicated that, except for O(3), this assumption was justified and the results were used to calculate the correction for the systematic error caused by rotational oscillation. The corrected coordinates were used for calculation of bond lengths and angles and of all interionic contacts of less than 3·5 Å.

Results

The atomic coordinates are shown in Table 2 as fractions of the unit cell edges with the corresponding standard deviations in Å. Table 3 shows the thermal parameters and standard deviations.

The results of the molecular vibration analysis (Cruickshank, 1956, 1961) are presented in Table 4. For the perchlorate ion the translatory vibration is, as expected, the same as the vibration of the chlorine atom and the average is similar to that in other perchlorates (*e.g.* hydroxonium perchlorate). As usual for ions or molecules with small moments of inertia, the rotational oscillation of the perchlorate ion is large and this leads to average corrections in the atomic coordinates for oxygen of 0·025 Å and consequent increases in the chlorine–oxygen bond lengths of 0·04 Å.

For the sulphonium ion the translatory motion is the major contributor to the observed anisotropic vibration so that rotational oscillation is comparatively small. The maximum correction to any coordinate is only 0·01 Å and the average for the carbon atoms other than C(1) (which being 0·2 Å from the mass centre has no correction) is 0·006 Å.

Table 5 shows the atomic coordinates in the system of orthogonal axes, parallel to the crystallographic a, b, and c^* axes after correction for rotational oscillation. The bond lengths and angles with their standard deviations are shown in Table 6; the dimensions are calculated from the atomic coordinates given by the computer to four decimal places, not from the rounded-off values in Table 5. A program by Mr

Table 2. *Final fractional coordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cl	0·1873	0·0669	−0·0848	0·005 Å	0·006 Å	0·006 Å
S	0·1641	−0·3831	−0·1539	0·005	0·005	0·005
O(1)	0·1522	−0·0414	−0·1980	0·02	0·03	0·03
O(2)	0·0903	0·1369	−0·0761	0·02	0·02	0·02
O(3)	0·2386	−0·0151	0·0631	0·03	0·04	0·03
O(4)	0·2688	0·1497	−0·0859	0·03	0·03	0·05
C(1)	0·3089	−0·3767	−0·0259	0·02	0·02	0·02
C(2)	0·3494	−0·4565	0·1030	0·02	0·02	0·02
C(3)	0·4680	−0·4483	0·1949	0·02	0·03	0·02
C(4)	0·5305	−0·3542	0·1609	0·02	0·03	0·02
C(5)	0·4797	−0·2780	0·0281	0·02	0·03	0·02
C(6)	0·3726	−0·2883	−0·0656	0·02	0·02	0·02
C(7)	0·0886	−0·3311	−0·0342	0·02	0·02	0·02
C(8)	0·1301	−0·5588	−0·1808	0·03	0·02	0·03
Calculated values						
H(2)	0·3022	−0·5252	0·1318			
H(3)	0·5004	−0·5051	0·2902			
H(4)	0·6111	−0·3467	0·2355			
H(5)	0·5271	−0·2098	−0·0005			
H(6)	0·3396	−0·2319	−0·1606			

Table 3. *Vibration parameters*

(Units 10^{-3} Å^2)

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	σ
Cl	34	3	50	3	56	3	−8	3	−8	3	10	2
S	29	3	39	3	38	2	−3	3	8	3	7	2
O(1)	113	18	145	23	137	19	−4	16	−95	18	31	15
O(2)	74	11	75	13	85	12	11	10	−21	11	43	10
O(3)	118	21	271	39	108	18	79	24	−14	23	−23	16
O(4)	110	20	125	21	386	51	−24	17	41	28	122	27
C(1)	52	13	42	12	28	10	16	11	14	10	14	9
C(2)	53	14	49	15	63	14	−11	12	−6	13	26	12
C(3)	72	16	62	17	37	11	17	13	5	12	−2	11
C(4)	59	16	72	18	49	13	18	14	−12	13	13	12
C(5)	41	13	71	18	59	13	−6	13	−9	14	9	11
C(6)	36	12	69	15	46	11	3	11	9	12	5	10
C(7)	60	15	59	15	53	13	13	13	−13	12	33	12
C(8)	74	18	35	14	111	20	−8	13	−32	15	3	16

	U_{iso}	
H(2)	0·04 Å^2	All ±0·08 Å^2
H(3)	0·07	
H(4)	0·07	
H(5)	0·01	
H(6)	0·07	

J. G. F. Smith was used to calculate the standard deviations. The equation of the plane through the carbon atoms of the phenyl group is

$$0{\cdot}468X' - 0{\cdot}689Y' - 0{\cdot}553Z' - 4{\cdot}631 = 0$$

the largest deviation of an atom from this is 0·04 Å for C(3); the sulphur atom, which was not included in the calculation, lies in this plane (the deviation is 0·007 Å). Interionic contacts between atoms other than hydrogen atoms are shown in Figs. 1 and 2.

Table 4. *Molecular vibration analysis*

Sulphonium ion	Direction cosines with respect to orthogonal axes parallel to *a*, *b*, *c**		
Axes of inertia, I_{min}	−0·852	−0·139	−0·515
II_{max}	0·487	−0·566	−0·665
III	−0·194	−0·812	0·550
Mean square amplitudes of translation	Principal directions		
0·042 ± 0·008 Å^2	−0·994	−0·108	0·024
0·034 ± 0·006	0·058	−0·700	−0·1714
0·029 ± 0·004	0·094	−0·708	0·700
Root mean square angular oscillation	Principal directions		
8 ± 1°	−0·889	0·067	−0·453
4 ± 1	0·289	−0·686	−0·668
3 ± 1	−0·355	−0·724	0·591
Perchlorate ion			
Axes of inertia, I	0·215	−0·973	−0·082
II	−0·777	−0·120	−0·618
III	−0·591	−0·197	0·782
Mean square amplitudes of translation	Principal directions		
0·067 ± 0·016 Å^2	−0·183	−0·655	0·733
0·055	0·588	−0·670	−0·453
0·032	−0·788	−0·348	−0·508
Root mean square angular oscillation	Principal directions		
20 ± 2°	−0·780	0·623	0·059
11 ± 4	0·613	0·779	−0·131
9 ± 4	0·128	0·066	0·990

Table 5. *Atomic coordinates corrected for rotational oscillation*

Values refer to orthogonal axes with *a′* and *c′* parallel to the crystallographic *a* and *c** directions respectively

	X'	Y	Z'
Cl	2·681 Å	0·677 Å	−0·745 Å
S	2·608	−3·855	−1·349
O(1)	2·59	−0·45	−1·77
O(2)	1·38	1·39	−0·67
O(3)	2·85	−0·17	0·60
O(4)	3·76	1·54	−0·75
C(1)	4·04	−3·79	−0·23
C(2)	4·13	−4·60	0·91
C(3)	5·35	−4·52	1·71
C(4)	6·27	−3·56	1·41
C(5)	6·06	−2·79	0·24
C(6)	5·00	−2·89	−0·58
C(7)	1·24	−3·33	−0·29
C(8)	2·26	−5·64	−1·58
H(2)	3·44	−5·28	1·15
H(3)	5·46	−5·08	2·53
H(4)	7·05	−3·49	2·06
H(5)	6·75	−2·11	0·00
H(6)	4·88	−2·33	−1·40

Discussion

The structure consists of perchlorate anions and sulphonium cations, each ion being surrounded by six of the opposite charge. The shortest interionic O · · · C distances (Figs. 1 and 2) are no shorter than van der Waals O · · · C separations as found in, for example, 4,4′-dichlorodiphenylsulphone (Sime & Abrahams, 1960).

Table 6. *Bond lengths and angles with corresponding standard deviations*

Perchlorate ion

Cl–O(1)	1·52 ± 0·03 Å	O(1)–Cl–O(2)	110°	±1°
Cl–O(2)	1·49 ± 0·02	O(3)–Cl–O(2)	108	
Cl–O(3)	1·60 ± 0·03	O(4)–Cl–O(2)	113	
Cl–O(4)	1·38 ± 0·03	O(1)–Cl–O(3)	100	±2°
		O(1)–Cl–O(4)	120	
		O(3)–Cl–O(4)	105	

Sulphonium ion

S–C(7)	1·81 Å	±0·02 mean 1·82 Å	C(7)–S–C(1)	103°	±1°
S–C(8)	1·83		C(8)–S–C(1)	105	
S–C(1)	1·82		C(7)–S–C(8)	102	
C(1)–C(2)	1·40	±0·03 mean 1·39 Å	C(6)–C(1)–S	115	±1·5°
C(2)–C(3)	1·46		C(2)–C(1)–S	122	
C(3)–C(4)	1·36		C(2)–C(1)–C(6)	123	±2°
C(4)–C(5)	1·42		C(1)–C(2)–C(3)	118	
C(5)–C(6)	1·35		C(2)–C(3)–C(4)	119	
C(6)–C(1)	1·36		C(3)–C(4)–C(5)	118	
			C(4)–C(5)–C(6)	125	
			C(5)–C(6)–C(1)	117	

In the sulphonium ion the three S–C bonds are pyramidally arranged about the sulphur atom suggesting that the sulphur is in a state of sp^3 hybridization with a lone pair of electrons in the fourth orbital and no electrons in the *d* orbitals. Greater atom–lone pair than atom–atom repulsion would account for the observation that all the C–S–C angles are less than the tetrahedral angle. The three bonds are apparently equal in length, *viz.* 1·82 Å, which is the usual value for S(II) to C(sp^3) and so is as expected for the methyl–sulphur bonds. As the single-bond radius for carbon is about 0·03 Å less for sp^2 than for sp^3 hybridization and any double bond character should produce a further reduction, the S–C(phenyl) bond might be expected to be shorter than 1·82 Å and the apparent equality may be chance result. Some conjugation between phenyl groups and the sulphur atom in sulphonium salts was postulated by Bordwell & Boutan (1956) on the basis of studies of the ultraviolet spectra and acidity constants. The orientation of the phenyl group with respect to the methyl groups is consistent with overlap between the *p* orbitals on C(7) and a *d* orbital on the sulphur, but it is also the one in which the atoms of the phenyl groups are as far as possible from those of the methyl groups. In di-*p*-tolyl sulphide, Blackmore & Abrahams (1955) found the phenyl groups to be in a sterically unfavourable configuration which suggested that there was some restriction on the rotation about the C–S bond which may not be a pure single bond; the S–C bond length found was 1·75 ± 0·03 Å, which is not significantly different from ours ($\Delta/\sigma = 1{\cdot}9$).

For the phenyl group the mean C–C bond length is the same as in benzene (Cox, Cruickshank & Smith, 1958) and the variations are not significant but confirm the calculated standard deviations. However, there is an important illustration of the care required in interpreting the significance of differences in bond lengths; the bonds C(2)–C(3) and C(6)–C(5) are parallel, so that a difference between them is unlikely to result from systematic errors, yet they differ by 0·11 Å and application of the usual significance tests gives $\Delta/\sigma = 2{\cdot}6$, corresponding to only one chance in a hundred that the difference results from random error (a level sometimes taken as 'significant').

Several structures containing perchlorate ions have been studied. In some, the Cl–O bond lengths are equal, *e.g.* nitronium perchlorate (Truter, Cruickshank & Jeffrey, 1960) with mean Cl–O 1·46 Å, while in others there appear to be differences, *e.g.* in hydronium perchlorate at −80 °C (Nordman, 1962) with lengths of 1·445 ± 0·006 and 1·478 ± 0·005 Å ($\Delta/\sigma = 4{\cdot}2$). We have found that three bonds Cl–O(1), Cl–O(2) and Cl–O(4) have an average value of 1·46 Å and do not differ significantly from this mean. For Cl–O(3), however, the length, 1·60 Å, is greater than any previously reported; it is subject to considerable uncertainty, for not only are the vibration parameters of O(3) large (corresponding to a r.m.s. amplitude of vibration of 0·4 Å), but they are in poor agreement with those calculated on the assumption that the perchlorate ion undergoes a rigid-body motion. There is no real evidence for supposing that this atom is more strongly bound to the cation.

We are grateful to Mr G. H. W. Milburn for preparing the crystals, Mr J. G. F. Smith and other colleagues (Cruickshank *et al.*, 1961) for the use of their programs and the Director and operators of the Leeds University Computing Laboratory for their help. One of us (A. L.-C.) thanks the Physics Department (Sevilla) of the Consejo Superior de Investigationes Cientificas for leave to hold a Brotherton Research Fellowship. Some of the equipment used was provided by the Royal Society and Imperial Chemical Industries Limited.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Blackmore, W. R. & Abrahams, S. C. (1955). *Acta Cryst.* **8**, 329.

Bordwell, F. G. & Boutan, P. J. 1956). *J. Amer. Chem. Soc.* **78**, 87.

Cox, E. G., Cruickshank, D. W. J. & Smith, J. A. S. (1958). *Proc. Roy. Soc.* **247**, 1.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757.

Cruickshank, D. W. J. (1961). *Acta Cryst.* **14**, 896.

Cruickshank, D. W. J., Pilling, D. E., and (in part) Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. p. 32. Oxford: Pergamon Press.

Nordman, C. E. (1962). *Acta Cryst.*, **15**, 18.

Sime, J. G. & Abrahams, S. C. (1960). *Acta Cryst.* **13**, 1.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Truter, M. R., Cruickshank, D. W. J. & Jeffrey, G. A. (1960). *Acta Cryst.* **13**, 855.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.