ACTA CHEMICA SCANDINAVICA **10** (1956) 279—287

The Crystal Structure of Tellurium Dibenzenethiosulphonate

PAUL ØYUM and OLAV FOSS

Institutt for teoretisk kjemi and Institutt for uorganisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The crystal structure of tellurium dibenzenethiosulphonate, $Te(S_2O_2C_6H_5)_2$, has been determined from X-ray data, by two-dimensional Patterson and Fourier methods. The crystals are orthorhombic bipyramidal; space group D_{2h}^{14}—*Pbcn*, with a = 14.46 Å, b = 11.18 Å, c = 10.48 Å, and four molecules per unit cell. A twofold axis of molecular symmetry is present.

The molecule contains an unbranched and non-planar S-S-Te-S-S chain, the three middle atoms of which are divalent, whereas to each of the terminal sulphur atoms are attached two oxygen atoms and a phenyl group. The values, 2.08 Å and 2.41 Å, respectively, were found for the S-S and S-Te bond lengths, and 104° and 97°, respectively, for the S-S-Te and S-Te-S bond angles. The molecule occurs in a *trans* form, with a dihedral angle of 79° between the S-S-Te and S-Te-S planes.

The unit cells and space groups of two pentathionic compounds, *viz.*, sulphur dibenzene- and di-*p*-toluenethiosulphonate, were reported by Dawson, Mathieson and Robertson[1] in 1948. The substances, which are also called *bis*-sulphonyl trisulphides, are derived from pentathionic acid by substitution of aryl groups for the hydroxyl groups. The crystals of the two compounds are isomorphous; space group D_4^4—$P4_12_12$ (or the enantiomorph) with four molecules per unit cell, and a = 7.74 Å, c = 26.29 Å for the benzenethiosulphonate, and a = 7.70 Å, c = 29.50 Å for the *p*-toluenethiosulphonate. Concerning sulphur dibenzenethiosulphonate the authors said[1 p. 327], "Patterson and Harker projections have been made, but the large number of parameters (31) renders the interpretation difficult. Further work is in progress". No further account has, as far as we know, appeared in literature.

Meanwhile, the selenium and tellurium analogues of the above compounds, *viz.*, selenium and tellurium dibenzene- and di-*p*-toluenethiosulphonate, and triselenium dibenzene- and di-*p*-toluenesulphinate, have been prepared by one of us[2,3], and the unit cells and space groups determined[3]. Of the six new compounds, four are isomorphous with sulphur dibenzene- and di-*p*-toluenethiosulphonate; the two benzene compounds, tellurium dibenzenethiosulphonate and triselenium dibenzenesulphinate, being the only ones which do not crystallize in the tetragonal space group referred to above.

The detailed structure of tellurium dibenzenethiosulphonate has now been worked out, and is reported below. The structure of the molecule, which arises from sulphur dibenzenethiosulphonate by substitution of tellurium for the middle, divalent sulphur atom of the latter, is closely analogous to that of tellurium dimethanethiosulphonate[4], and of the telluropentathionate ion in ammonium telluropentathionate[5]. The three telluropentathionic compounds

$$Te(S_2O_2CH_3)_2; \qquad (NH_4)_2Te(S_2O_3)_2; \qquad Te(S_2O_2C_6H_5)_2$$

have thereby been shown to contain unbranched and non-planar S—S—Te—S—S chains.

EXPERIMENTAL

The yellow crystals of tellurium dibenzenethiosulphonate, $Te(S_2O_2C_6H_5)_2$, are orthorhombic bipyramidal, and show the forms {111} and {100}. The latter is frequently the more predominant, thus giving the crystals the appearance of plates. The axial lengths are[3], $a = 14.46 \pm 0.04$ Å, $b = 11.18 \pm 0.02$ Å, $c = 10.48 \pm 0.02$ Å. There are four molecules per unit cell; density, calc. 1.86, found 1.88 g/cm^3. Systematic absences, $hk0$ when $h + k$ is odd, $h0l$ when l is odd, $0kl$ when k is odd. The space group is therefore uniquely determined as D_{2h}^{14}—$Pbcn$.

The intensities of the $h0l$ and $hk0$ reflections were read visually from Weissenberg photographs about the b and c axes. Unfiltered CuK radiation (a wave-length, 1.54 Å) was used, and crystals having cross-sections of 0.04 × 0.08 mm and 0.07 × 0.08 mm, respectively, in the case of the b and c axis photographs. There are 101 $h0l$ and 114 $hk0$ reflections accessible with Cu$K\alpha$ radiation; of these, 76 and 94, respectively, were recorded on the films with measurable intensities, with values ranging from about thousand to one. The intensities were corrected for the Lorentz and polarization factors, and were converted to relative structure amplitudes, which were eventually put to an approximately absolute scale by comparison with the calculated structure factors. No corrections for absorption were made.

The crystals used for the X-ray photographs had been prepared two years earlier[3], and were still unchanged. On exposure to X-rays, a slight liberation of tellurium took place, which, however, did not appear to affect the intensities of the reflections to any observable degree.

The Patterson and Fourier summations were made at 6° intervals by means of Beevers-Lipson strips.

ANALYSIS OF THE STRUCTURE

The space group, D_{2h}^{14}-$Pbcn$, has eightfold general positions, and the four molecules in the unit cell must accordingly lie in special positions, of which there are three fourfold sets, two having a centre and one a twofold axis of symmetry. Since the molecule cannot reasonably have a centre of symmetry, it must possess a twofold axis, which passes through the tellurium atoms in the positions:

$$0,\ y,\ \tfrac{1}{4};\quad 0,\ \bar{y},\ \tfrac{3}{4};\quad \tfrac{1}{2},\ \tfrac{1}{2}+y,\ \tfrac{1}{4};\quad \tfrac{1}{2},\ \tfrac{1}{2}-y,\ \tfrac{3}{4}.$$

Although the x and z coordinates of tellurium are thus fixed, at $x = 0$, $z = \frac{1}{4}$, a direct solution of the projection along the b axis is not possible, since the tellurium atom does not contribute to $h0l$ reflections having odd h indices.

As the first steps, Patterson and Fourier maps, based on $h0l$ data with even values of h only, and Fourier signs corresponding to the tellurium contributions alone, were prepared. Both maps have mirror planes normal to the

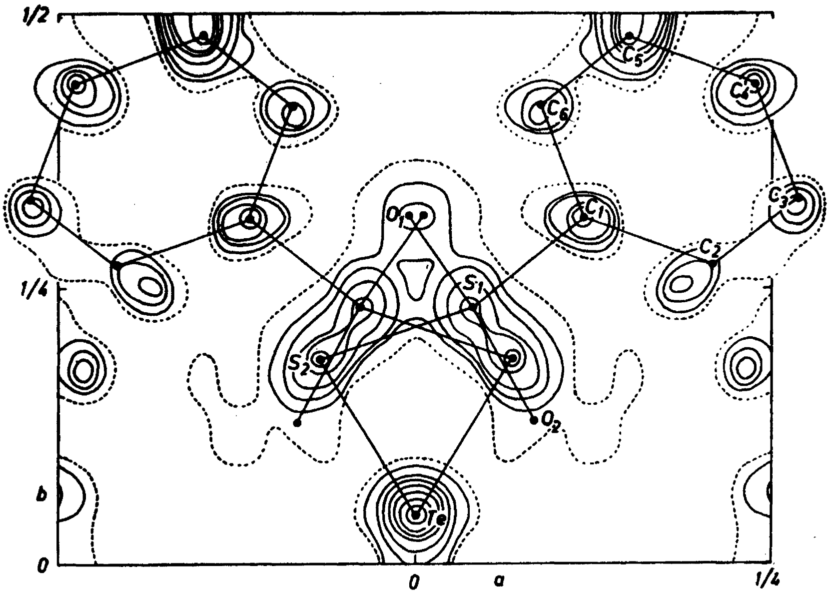

Fig. 1. Electron density projection of $Te(S_2O_2C_6H_5)_2$ *along the* c *axis, showing two asymmetric units. Contour lines are at intervals of 1* $e \cdot Å^{-2}$ *for carbon atoms, 5* $e \cdot Å^{-2}$ *for sulphur and oxygen atoms and 15* $e \cdot Å^{-2}$ *for the tellurium atom, starting with 6, 10 and 15* $e \cdot Å^{-2}$*, respectively. The 5-electron line is dashed.*

a axis at $x = \frac{1}{4}$, due to the omission of the odd *h* data. The signs used in the Fourier summation were later found to be correct, but for a single reflection, 202. Peaks due to the two sulphur atoms of the asymmetric unit appeared in both maps, and allowed approximate coordinates to be determined for these atoms. The *z* coordinate of S_1 turned out to be equal to or close to $\frac{1}{2}$. With this *z* value, S_1 does not contribute, or contributes very little, to *h0l* reflections with *h* odd. Signs of most of the latter reflections were then calculated on the basis of the S_2 contributions alone, and these data when included in the Fourier summation served to remove the false symmetry elements and show S_1 a little displaced from $z = \frac{1}{2}$. The oxygen and carbon positions were uncertain, however, and further work on this projection was not made until the *c* axis projection had been worked out.

In the Patterson projection along the *c* axis, the Te-Te vector at $u = 0$, $v = 2y$ was found to lie close to $v = 0$, and the centre was located through graphical removal of the origin peak, its curvature along $u = 0$ being taken to be the same as along $v = 0$. The *y* coordinate of tellurium, 0.043, found in this way is the same as the final value. In the first Fourier synthesis of the *hk*0 data, signs were calculated from the tellurium contributions alone, and 79 out of the 94 observed terms were included; of these, only one sign was later found to be wrong. Although considerable overlapping of sulphur and oxygen atoms occurs, the resulting map allowed trial coordinates for these atoms to

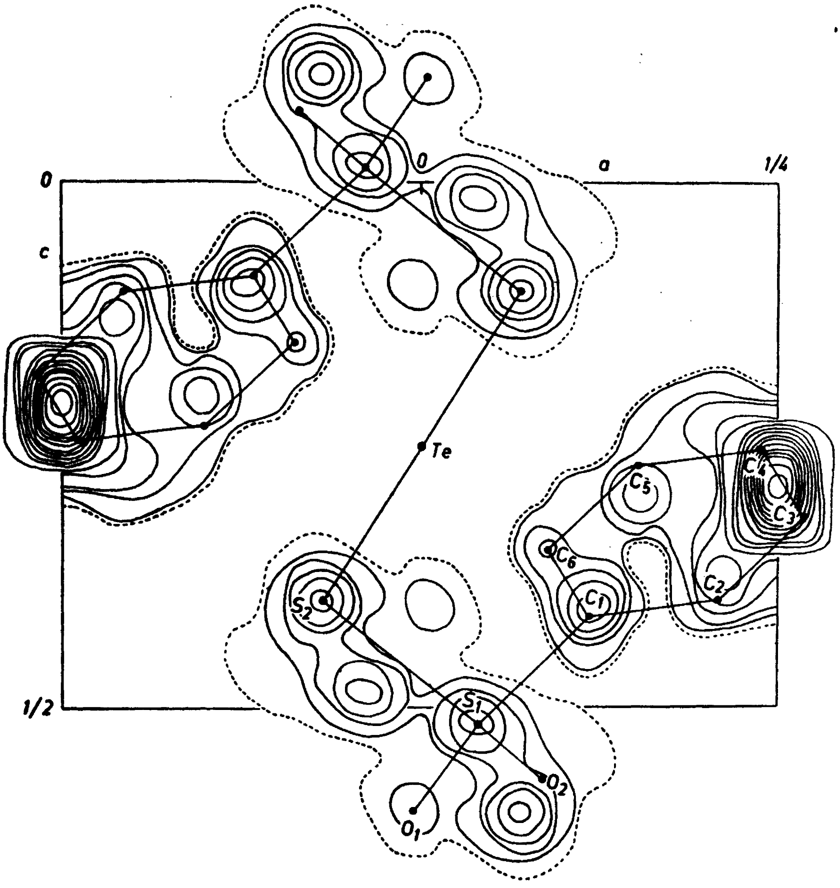

Fig. 2. Electron density projection of $Te(S_2O_2C_6H_5)_2$ *along the* b *axis, with the tellurium atom removed. Two asymmetric units are shown. Contour lines as in Fig. 1.*

be determined and used to calculate signs of the remaining *hk*0 reflections. In the next Fourier map, the benzene ring was recognizable, and the projection was then refined through successive approximations in the usual way.

With the *x* coordinates of the oxygen and carbon atoms thus known, work on the *h*0*l* data was resumed, and refinement of the *b* axis projection successfully carried out. In this projection, where the tellurium coordinates are known exactly, the heavy atom diffraction effects were studied through removal of the tellurium peak, by subtracting the calculated, temperature-corrected tellurium contributions from the scaled, observed *h*0*l* structure factors. This procedure needs to be carried out for reflections with even *h* indices only. The resulting difference map showed better resolved C_6 and O_1 peaks, and lead to an adjustment of the O_1 coordinates which changed the S_1—O_1 distance from 1.39 Å to 1.44 Å and gave a more reasonable value for the $S_2S_1O_1$ angle.

The *hk*0 Fourier map, and the *h*0*l* Fourier map with the tellurium peak removed as described above, are reproduced in Figs. 1 and 2, respectively. The atomic positions are marked with dots, and lines are drawn to show the outline of the molecule.

In both projections, the coordinates of the carbon atoms were adjusted so as to give the best fit with the observed structure factors on the basis of positions defining the corners of a regular hexagon with edges of 1.39 Å, and a linear arrangement of the S_1, C_1 and C_4 atoms.

The position of the tellurium peak in the *c* axis projection corresponds to a tellurium y coordinate of 0.046. This coordinate gives a Te-S_2 distance of 2.39 Å and a S_2TeS_2' angle of 99°. It was found, however, that the value, $y = 0.043$, derived from the Patterson map gave a better agreement between observed and calculated *hk*0 structure factors. The displacement of the tellurium peak may be due to diffraction effects, produced by the equivalent atom on the other side of the glide plane *c* at $y = 0$.

Table 1. Atomic coordinates for tellurium dibenzenethiosulphonate, in fractions of cell edges. Origin at a centre of symmetry.

	x	y	z		x	y	z
Te	0	0.043	0.250	C_1	0.117	0.312	0.413
S_2	−0.068	0.186	0.395	C_2	0.207	0.271	0.396
S_1	0.041	0.233	0.514	C_3	0.268	0.316	0.316
O_1	−0.006	0.316	0.598	C_4	0.238	0.435	0.253
O_2	0.083	0.139	0.566	C_5	0.148	0.476	0.270
				C_6	0.087	0.414	0.349

The final atomic coordinates are listed in Table 1. In Table 4, observed and calculated values of structure factors are compared for all *h*0*l* and *hk*0 reflections within the range of Cu$K\alpha$ radiation. The calculated values are based on the coordinates of Table 1, and the atomic scattering curves of the *International Tables*, with a temperature factor of $B = 2.38$ Å^2 for both zones. The hydrogen atoms of the phenyl group have been ignored. The reliability factor, $R = \Sigma||F_{\text{obs}}| - |F_{\text{calc}}||/\Sigma|F_{\text{obs}}|$, with non-observed reflections included in the difference only when $|F_{\text{calc}}|$ in greater than the lowest observable value of $|F_{\text{obs}}|$, is 0.157 and 0.172, respectively, for the *h*0*l* and *hk*0 reflections. The largest discrepancy occurs for F_{200}, the observed and calculated values of which are 237 and 352, respectively. This reflection is the strongest one, and is probably subject to extinction. If F_{200} is not included, the R values drop to 0.142 and 0.160, respectively, for the two zones.

THE TELLURIUM DIBENZENETHIOSULPHONATE MOLECULE

The present structure is the third to be reported for a telluropentathionic compound, the two earlier ones being those of the methane analogue, tellurium dimethanethiosulphonate[4], and of ammonium telluropentathionate[5]. The compounds are built up of S—S—Te—S—S chains, with the three middle atoms in the divalent state, whereas to each of the terminal sulphur atoms are attached three oxygen atoms, or in the case of the thiosulphonates, two oxygen

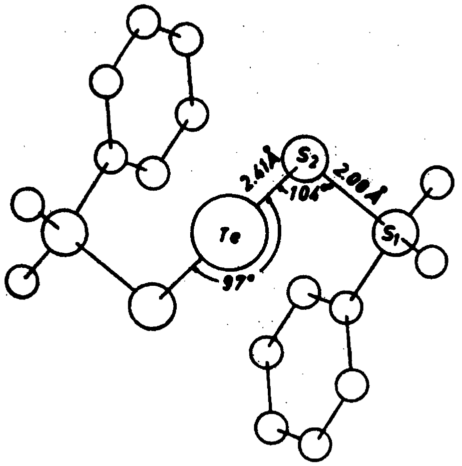

Fig. 3. The tellurium dibenzenethiosulphonate molecule as seen along the twofold axis, showing some bond lengths and angles.

atoms and a methyl or a phenyl group. The chains are non-planar, the terminal sulphur atoms being rotated out of the plane of the three middle atoms, to opposite sides of the plane. This is the *trans* configuration [6] of pentathionic compounds; the *cis* configuration [6], where the terminal atoms are located on the same side of the plane of the three middle atoms, has been found in the crystals of barium pentathionate [7] and selenopentathionate [8] dihydrate.

The shape of the tellurium dibenzenethiosulphonate molecule will appear from the electron density maps of Figs. 1 and 2, which also show the numbering of atoms, and from the line drawing of one isolated molecule in Fig. 3. The principal bond lengths and angles, calculated on the basis of the coordinates of Table 1, are given in Table 2, together with non-bonded Te—S and S—S distances within the molecule. The molecule possesses an exact twofold axis of symmetry, and a prime is used, when relevant, to denote the equivalent of an atom produced by the operation of the twofold axis. In Table 2, data for

Table 2. Dimensions of S-S-Te-S-S chains.

Bond lengths (in Å units) and angles.

Bond or angle	$Te(S_2O_2C_6H_5)_2$	$Te(S_2O_2CH_3)_2$	$(NH_4)_2Te(S_2O_3)_2$
S_1-S_2	2.08	2.13; 2.16	2.11; 2.12
S_2-Te	2.41	2.36; 2.35	2.36; 2.35
$\angle S_1S_2Te$	104°	106°; 104°	105°; 104°
$\angle S_2TeS_2'$	97°	100°	103°
Dihedral angle S_1S_2Te/S_2TeS_2'	79°	81°; 81°	86°; 95°

Non-bonded distances (in Å units).

Distance	$Te(S_2O_2C_6H_5)_2$	$Te(S_2O_2CH_3)_2$	$(NH_4)_2Te(S_2O_3)_2$
S_1-Te	3.54	3.57; 3.55	3.57; 3.52
S_1-S_2'	4.28	4.38; 4.36	4.52; 4.69
S_2-S_2'	3.62	3.60	3.68
S_1-S_1'	5.74	5.74	6.11

Table 4. *Observed and calculated values of structure factors for tellurium dibenzenethiosulphonate.*

hkl	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}
200	237	+352	8	92	− 93	15	69	+ 61
4	196	+231	9	< 23	− 8	17	37	+ 44
6	51	+ 39	10	86	− 85	020	75	− 75
8	96	+ 75	11	47	− 30	2	37	+ 5
10	77	+ 63	12	78	− 92	4	61	+ 59
12	97	+ 84	13	< 22	− 14	6	125	+144
14	74	+ 83	14	62	− 88	8	148	+155
16	52	+ 51	15	< 17	+ 3	10	103	+ 97
18	24	+ 34	16	42	− 58	12	102	+104
002	114	− 72	008	134	+137	14	56	+ 55
1	58	+ 42	1	< 22	− 8	16	33	+ 32
2	51	+ 11	2	135	+120	18	27	+ 19
3	127	−120	3	< 22	+ 22	130	19	+ 24
4	154	−145	4	114	+105	3	132	+122
5	86	− 73	5	< 19	+ 17	5	155	+166
6	132	−146	6	67	+ 74	7	149	+190
7	41	− 30	7	< 24	− 24	9	141	+143
8	156	−177	8	47	+ 41	11	87	+ 88
9	48	+ 41	9	42	− 46	13	< 28	+ 8
10	105	−102	10	47	+ 25	15	30	+ 32
11	67	+ 65	11	30	− 40	17	22	+ 27
12	116	−114	12	35	+ 30	040	125	+131
13	27	+ 22	13	< 17	+ 1	2	95	+ 86
14	73	− 77	14	36	+ 35	4	118	+124
15	< 22	+ 4	15	< 8	+ 10	6	120	+108
16	44	− 49	00, 10	< 24	− 9	8	44	+ 37
17	< 17	− 14	1	< 24	− 7	10	< 27	− 3
18	27	− 33	2	30	− 22	12	< 29	− 24
004	123	+111	3	33	− 17	14	< 27	+ 8
1	69	− 58	4	46	− 40	16	< 21	+ 8
2	116	+116	5	32	− 33	18	< 14	+ 24
3	74	− 75	6	54	− 55	150	76	+ 79
4	174	+168	7	25	− 16	3	79	+ 66
5	83	− 77	8	55	− 69	5	< 21	− 7
6	167	+160	9	< 17	− 13	7	76	− 67
7	< 18	− 1	10	50	− 50	9	38	− 37
8	123	+124	11	< 15	− 6	11	< 28	− 11
9	< 21	+ 20	12	31	− 56	13	28	+ 28
10	50	+ 20	00, 12	48	+ 73	15	23	+ 5
11	42	+ 48	1	< 19	− 7	17	< 15	+ 15
12	38	+ 25	2	47	+ 52	060	< 21	+ 24
13	< 23	+ 3	3	33	− 40	2	< 21	+ 12
14	< 22	0	4	44	+ 55	4	48	− 34
15	< 20	− 11	5	30	− 23	6	34	− 16
16	20	+ 13	6	37	+ 32	8	< 27	+ 7
17	< 14	− 1	7	19	− 19	10	< 28	+ 12
006	167	−177	8	30	+ 40	12	28	+ 37
1	< 18	+ 5	110	142	+179	14	28	+ 37
2	112	−110	3	191	+215	16	17	+ 24
3	< 19	− 6	5	128	+120	170	71	− 46
4	96	− 82	7	79	+ 68	3	87	− 62
5	< 16	− 7	9	93	+ 70	5	66	− 96
6	81	− 77	11	103	+ 85	7	41	− 35
7	25	− 16	13	78	+ 63	9	< 28	+ 23

hkl	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}
11	< 28	+ 16	9	50	− 43	11	28	− 38
13	< 25	+ 3	11	47	− 50	0, 12, 0	39	− 35
15	< 19	− 8	13	43	− 50	2	51	− 41
080	103	−101	0, 10, 0	57	− 50	4	42	− 41
2	81	− 52	2	63	− 55	6	48	− 50
4	57	− 56	4	82	− 71	8	34	− 41
6	< 28	− 7	6	77	− 63	10	24	− 35
8	49	− 51	8	48	− 46	1, 13, 0	30	− 30
10	36	− 37	10	42	− 32	3	29	− 23
12	50	− 68	12	23	− 21	5	21	− 28
14	35	− 43	1, 11, 0	84	− 86	7	< 15	− 27
190	50	− 38	3	79	− 81	0, 14, 0	38	− 49
3	51	− 25	5	60	− 53	2	29	− 41
5	57	− 38	7	64	− 74	4	< 11	− 29
7	49	− 26	9	45	− 46			

tellurium dimethanethiosulphonate[4] and ammonium telluropentathionate[5] are included for comparison; the latter compounds possess no exact molecular symmetry element in the crystals studied, and the two figures listed for these where one only occurs for the benzenethiosulphonate, refer to the two, here not quite identical halves.

The three structure determinations are probably about equally accurate, with probable errors of about 0.03—0.04 Å for Te—S and S—S distances, and 2—3° for bond angles involving these atoms. It appears that the only differences in dimensions which can be considered significant, are the larger dihedral angles in ammonium telluropentathionate, and the correspondingly larger S_1—S_2' and S_1—S_1' non-bonded distances. These distances, and the dihedral angles, are dependent on rotations about the Te—S bonds, and may vary without change of Te—S and S—S bond lengths and angles.

The benzenesulphonyl groups, data for which are given in Table 3, have dimensions very like those found for the same group in sulphur dibenzenesulphinate[9] and selenium dibenzenesulphinate[10].

Table 3. Dimensions of the benzenesulphonyl groups.

Bond lengths and bond angles.

$S_1-O_1 = 1.44$ Å
$S_1-O_2 = 1.43$ Å
$S_1-C_1 = 1.77$ Å

$\angle S_2S_1O_1 = 100°$
$\angle S_2S_1O_2 = 110°$
$\angle S_2S_1C_1 = 104°$

$\angle O_1S_1O_2 = 120°$
$\angle O_1S_1C_1 = 106°$
$\angle O_2S_1C_1 = 111°$

Non-bonded distances (in Å units).

$O_1-O_2 = 2.49$
$O_1-C_1 = 2.57$
$O_2-C_1 = 2.65$

$S_2-O_1 = 2.73$
$S_2-O_2 = 2.90$
$S_2-C_1 = 3.03$

As mentioned above, the benzene ring has been assumed to be a regular hexagon with C—C bond lengths of 1.39 Å, and with a linear arrangement of the S_1, C_1 and C_4 atoms. Within the benzenesulphonyl group, the shortest oxygen-carbon approaches are O_2—C_2 = 2.99 Å and O_1—C_6 = 3.13 Å. The plane of the benzene ring and S_1 makes angles of 5°, 121° and 251°, respectively, with the $O_2S_1C_1$, $S_2S_1C_1$ and $O_1S_1C_1$ planes.

There are no particularly short intermolecular approaches in the crystals; *e. g.*, the shortest Te—S distance of this kind is 4.00 Å and occurs between Te and S_1 atoms.

THE TETRAGONAL ANALOGUES

In the tetragonal crystals of sulphur [1] and selenium [3] dibenzenethiosulphonate, and sulphur [1], selenium and tellurium di-*p*-toluenethiosulphonate and triselenium di-*p*-toluenesulphinate [3], of space group D_4^4—$P4_12_12$ (or the enantiomorph) with four molecules per unit cell, a twofold axis of molecular symmetry is required, as in orthorhombic tellurium dibenzenethiosulphonate. As shown in a note [11] following the preliminary report on the present structure [12], the similarities extend further, there being a close correspondence between the *b* and *c* axis projections of the orthorhombic structure and the *b* axis projection of the tetragonal structure in the centered setting, $C4_122_1$. In fact, the structure of tetragonal tellurium di-*p*-toluenethiosulphonate was solved by means of direct reference to the *b* and *c* axis projections of the orthorhombic benzene analogue. The dimensions found for the S-S-Te-S-S chain of the *p*-toluenethiosulphonate [11] agree well with those reported here for the benzenethiosulphonate.

REFERENCES

1. Dawson, I. M., Mathieson, A. McL. and Robertson, J. M. *J. Chem. Soc.* **1948** 322.
2. Foss, O. *Acta Chem. Scand.* **6** (1952) 508.
3. Foss, O. *Acta Chem. Scand.* **6** (1952) 521.
4. Foss, O. and Vihovde, E. H. *Acta Chem. Scand.* **8** (1954) 1032.
5. Foss, O. and Larssen, P. A. *Acta Chem. Scand.* **8** (1954) 1042.
6. Foss, O. *Acta Chem. Scand.* **7** (1953) 1221.
7. Foss, O. and Zachariasen, H. *Acta Chem. Scand.* **8** (1954) 473.
8. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **8** (1954) 1701.
9. Mathieson, A. McL. and Robertson, J. M. *J. Chem. Soc.* **1949** 724.
10. Furberg, S. and Øyum, P. *Acta Chem. Scand.* **8** (1954) 42.
11. Foss, O. and Øyum, P. *Acta Chem. Scand.* **9** (1955) 1014.
12. Øyum, P. and Foss, O. *Acta Chem. Scand.* **9** (1955) 1012.

Received October 31, 1955.