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The Structure of Tellurium Di-*p*-toluenethiosulphonate

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In a preceding note¹, the crystal structure of tellurium dibenzenethiosulphonate, $\text{Te}(\text{S}_2\text{O}_2\text{C}_6\text{H}_5)_2$, was described. The crystals are orthorhombic, with a four-molecule unit cell based on the space group $D_{2h}^{14}-Pbcn$, and $a = 14.46 \text{ \AA}$, $b = 11.18 \text{ \AA}$, $c = 10.48 \text{ \AA}$. A twofold axis of symmetry, parallel to the b axis, passes through the tellurium atom at $x = 0$, $z = \frac{1}{2}$. In the projection along the c axis, of symmetry cnm , the tellurium atom lies in an apparent mirror plane.

The six analogous compounds, sulphur² and selenium³ dibenzenethiosulphonate, and sulphur³, selenium and tellurium di-*p*-toluenethiosulphonate and triselenium di-*p*-toluenesulphinat³, crystallize in the tetragonal 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. The crystal structure of tetragonal tellurium di-*p*-toluenethiosulphonate, $\text{Te}(\text{S}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_3)_2$, has been solved by means of reference to the known structure of the benzene analogue, as follows.

In the centered setting, $C4_122_1$, the twofold rotation axes of the tetragonal unit cell of tellurium di-*p*-toluenethiosulphonate become parallel to the a and b axes. The axial lengths then are: $a = 10.93 \text{ \AA}$, $c = 29.88 \text{ \AA}$. These axes, and the centered setting instead of the primitive one, are referred to in the following. It is seen that the tetragonal a axis is of about the same length as the b and c axes of orthorhombic tellurium dibenzenethiosulphonate, *viz.*, 11.18 \AA and 10.48 \AA , respectively, while

the tetragonal c axis is a little longer than twice the orthorhombic a axis, 14.46 \AA .

In the projection of $C4_122_1$ along the b axis, the symmetry corresponds to that of the plane group, pgm , twice along the a axis. Considering the projected area, $a/2 \times c$, the eight general positions may be described as made up of two fourfold sets, both of symmetry pgm , with the coordinates, x, z and $y, \frac{1}{2} + z$, respectively, for the first of the four positions of each set. The corresponding coordinates of the special positions on the twofold rotation axes are, $0,0$ and $y, \frac{1}{2}$. A comparison with the orthorhombic space group, $Pbcn$, shows that a molecule, belonging to the set, x, z , in the b axis projection of $C4_122_1$, corresponds to a molecule in the b axis projection of $Pbcn$, and one belonging to the set, $y, \frac{1}{2} + z$, corresponds to one in the c axis projection of $Pbcn$. The similarities of tetragonal and orthorhombic cell dimensions made it likely that the projected shapes of thus corresponding molecules were the same, or nearly the same, in the two space groups.

The intensities of the $h0l$ reflections of tellurium di-*p*-toluenethiosulphonate were estimated visually from Weissenberg photographs taken with CuK radiation. A Patterson synthesis based on these data gave the y coordinate of tellurium, and a Fourier synthesis was performed, using the strongest reflections and signs obtained from the tellurium contributions alone. Peaks appeared in the Fourier map at or close to the expected sulphur positions, but the oxygen and carbon positions were uncertain, also after a second Fourier synthesis based on signs from the tellurium and the sulphur contributions. Using the tellurium positions as reference points, and corresponding axes of the two crystals coinciding or parallel, the sulphur, oxygen and carbon atoms of the asymmetric units of the two fourfold sets discussed above were then placed exactly as found in the b and c axis projections, respectively, of orthorhombic tellurium dibenzenethiosulphonate, with *p*-methyl carbons added. This was done by placing the tetragonal Fourier map, drawn on transparent paper, on the orthorhombic maps, of the same scale, and marking the positions. The subsequent structure factor calculation, with appropriate temperature and scale factors, lead to a reliability factor of $R = 0.33$. The most notable effect of the inclusion of the oxygen and carbon contributions was to change the sign of the next to strongest

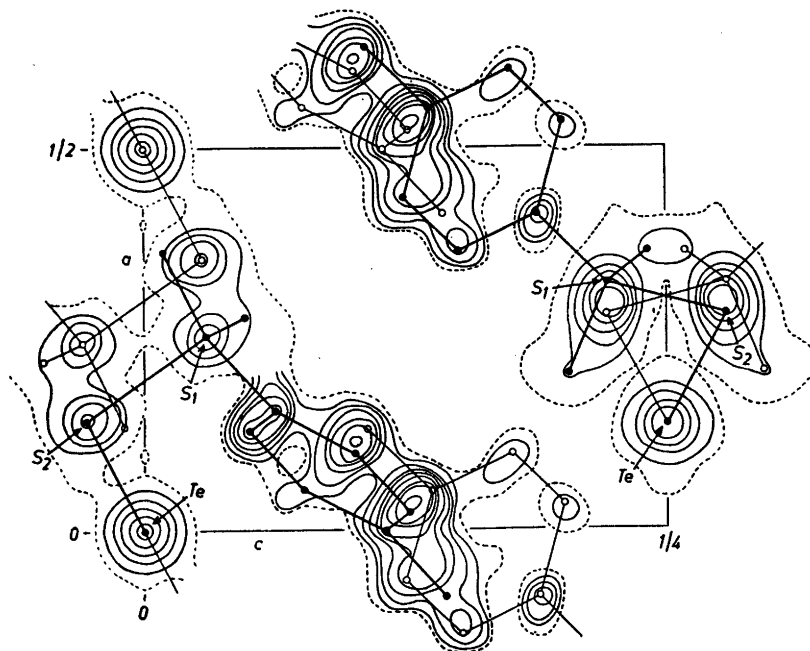


Fig. 1. Electron density projection of tellurium di-*p*-toluenethiosulphonate along the *b* axis. The summations were made at 6° intervals along the *a* axis and 3° intervals along the *c* axis. The first contour line is at $6 \text{ e} \cdot \text{Å}^{-2}$ for the carbon atoms, $10 \text{ e} \cdot \text{Å}^{-2}$ for the sulphur and oxygen atoms and $15 \text{ e} \cdot \text{Å}^{-2}$ for the tellurium atom, with subsequent intervals of 1, 5, and $15 \text{ e} \cdot \text{Å}^{-2}$, respectively. The 5-electron line is dashed.

reflection, 204; this change brought about a marked improvement of the Fourier map with respect to oxygen and carbon atoms. The new map indicated some small adjustments, chiefly a slight rotation of the molecule as a whole about the twofold axis, and of the *p*-tolyl groups about the S—C bonds, so as to give the following atomic coordinates, in fractions of cell edges and referring to an origin at the intersection of a twofold rotation axis [010] and a twofold screw axis.

These coordinates, with a temperature factor of $B = 5.0 \text{ Å}^2$, give a reliability factor of $R = 0.21$ for the $h0l$ reflections.

The $h0l$ Fourier map is shown in Fig. 1. The positions corresponding to the given coordinates are marked with dots (equivalent positions with rings) and lines are drawn to show the outline of the molecules. The bond lengths and angles of the S—S—Te—S—S chain are, Te—S₂ = $2.41 \pm 0.04 \text{ Å}$, S₂—S₁ = $2.11 \pm 0.04 \text{ Å}$,

	<i>x</i>	<i>y</i>	<i>z</i>
Te	0	0.136	0
S ₂	0.145	0.283	-0.028
S ₁	0.253	0.322	0.029
O ₁	0.365	0.361	0.009
O ₂	0.278	0.203	0.047
C ₁	0.154	0.413	0.062
C ₂	0.130	0.533	0.050
C ₃	0.052	0.604	0.075
C ₄	-0.003	0.555	0.113
C ₅	0.021	0.435	0.126
C ₆	0.099	0.363	0.100
C ₇	-0.089	0.634	0.105

$\angle \text{S}_2\text{TeS}_2' = 96 \pm 3^\circ$, $\angle \text{TeS}_2\text{S}_1 = 103 \pm 3^\circ$, and the dihedral angle, $\text{S}_2\text{S}_1\text{Te}/\text{S}_2\text{TeS}_2' = 86^\circ$. These data agree well with those found for tellurium dibenzenethiosulphonate.

The structure will not be refined further, but employed as a reference in the determination of the detailed structure of the

isomorphous crystals of triselenium di-*p*-toluenesulphinate. Work on the latter structure is in progress.

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The Structure of Triclinic Barium Pentathionate Dihydrate

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The isolation of two crystalline modifications of barium pentathionate dihydrate, *viz.*, one orthorhombic, space group D_{2h}^{16} -*Prma* with $Z = 4$, and one triclinic, was reported two years ago¹. The structure of the orthorhombic crystals has later been published in detail², and a preliminary account of the structure of the triclinic dimorph is given below.

The unit cell dimensions of triclinic barium pentathionate dihydrate, $\text{BaS}(\text{S}_2\text{O}_5)_2 \cdot 2\text{H}_2\text{O}$, are: $a = 5.00 \text{ \AA}$, $b = 10.36 \text{ \AA}$, $c = 11.53 \text{ \AA}$, $\alpha = 109^\circ$, $\beta = 98^\circ$, $\gamma = 90^\circ$. There are two molecules per unit cell, and the space group is C_2^1 -*P* $\bar{1}$. The intensi-

ties of the $0kl$ and $h0l$ reflections were estimated visually from zero layer Weissenberg photographs taken with CuK radiation, and the structure was solved through Patterson and Fourier projections along the a and b axes, using in the initial stages the heavy atom technique. The $0kl$ Fourier map is shown in Fig. 1. The atomic coordinates, in fractions of corresponding cell edges and referring to the triclinic axes, are:

	x	y	z
Ba	0.749	0.211	-0.104
S ₁	0.755	0.077	0.186
S ₂	0.808	0.225	0.366
S ₃	0.564	0.381	0.359
S ₄	0.808	0.542	0.366
S ₅	0.755	0.554	0.186
O ₁	0.462	0.070	0.158
O ₂	0.920	-0.031	0.210
O ₃	0.874	0.140	0.108
O ₄	0.462	0.551	0.158
O ₅	0.920	0.676	0.210
O ₆	0.874	0.432	0.108
(H ₂ O) ₁	0.253	0.250	0.007
(H ₂ O) ₂	0.603	0.131	-0.363

With a temperature factor of $B = 2.2 \text{ \AA}^2$, the reliability factor, $R = 0.18$ and 0.19 , respectively, for the $0kl$ and $h0l$ reflections. The coordinates give the following dimensions of the sulphur chain, $\text{S}_1 - \text{S}_2 = 2.12 \text{ \AA}$, $\text{S}_2 - \text{S}_3 = 2.04 \text{ \AA}$, $\text{S}_3 - \text{S}_4 = 2.04 \text{ \AA}$, $\text{S}_4 - \text{S}_5 = 2.10 \text{ \AA}$ (all $\pm 0.04 \text{ \AA}$), $\angle \text{S}_1\text{S}_2\text{S}_3 = 107^\circ$, $\angle \text{S}_2\text{S}_3\text{S}_4 = 107^\circ$, $\angle \text{S}_3\text{S}_4\text{S}_5 = 106^\circ$ (all $\pm 3^\circ$), and the dihedral angles, $\text{S}_1\text{S}_2\text{S}_3/$

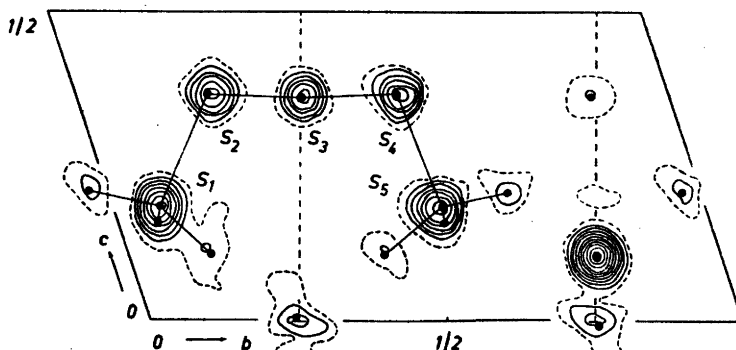


Fig. 1. Electron density projection of triclinic $\text{BaS}(\text{S}_2\text{O}_5)_2 \cdot 2\text{H}_2\text{O}$ along the a axis. The atomic positions are marked with dots, and lines are drawn to show the outline of the pentathionate ion. The 5-electron line is dashed. Contour intervals: $10 e \cdot \text{Å}^{-3}$ for the barium ion, and $4 e \cdot \text{Å}^{-3}$ for sulphur and oxygen atoms and water molecules.