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The Crystal Structure of Di-*p*-Tolyl Telluride*

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Di-*p*-tolyl telluride forms orthorhombic crystals, space group $P2_12_12_1$, with four molecules in a unit cell of dimensions $a = 25{\cdot}33$, $b = 8{\cdot}05$ and $c = 6{\cdot}01$ Å. The crystal structure has been determined, the 45 positional parameters being refined by double Fourier series and least-squares methods. There were 299 terms used, derived from visual intensity measurements by two independent observers. The Te–C bond length was measured as 2·05 Å and the C–Te–C bond angle as 101°. The normals to the two aromatic rings are inclined at an angle of 62° to each other. Evidence only for van der Waals forces in the crystals was found.

Introduction

A study of the selenium–tellurium alloys (Grison, 1951), of the crystal structures of the monoclinic modifications of selenium (Burbank, 1951, 1952), of cesium hexasulfide (Abrahams & Grison, 1953) and of barium tetrasulfide monohydrate (Abrahams, 1954) have already been reported by this laboratory, in the course of a program for investigating the crystal chemistry of compounds formed by the group VI_b elements. In this, and the following two papers (Blackmore & Abrahams, 1955*a*, *b*), the distribution of the valency bonds in divalent tellurium, selenium and sulfur linked to two aromatic nuclei, is examined. No determination of the Te–C distance nor the C–Te–C valence angle appears to have been reported previously in the literature.

Crystal data

Di-*p*-tolyl telluride, $(p\text{-}CH_3.C_6H_4)_2Te$: m.p. 69·7° C.; $D_{\text{meas.}} = 1{\cdot}63$ g.cm.$^{-3}$ (measured by flotation in aqueous $ZnCl_2$ solution); $D_{\text{calc.}} = 1{\cdot}677$ g.cm.$^{-3}$; orthorhombic, with

$$a = 25{\cdot}33\pm0{\cdot}02,\ b = 8{\cdot}05\pm0{\cdot}02 \text{ and } c = 6{\cdot}01\pm0{\cdot}02 \text{ Å};$$

absent spectra: $(h00)$ only with $h = 2n+1$, $(0k0)$ only with $k = 2n+1$ and $(00l)$ only with $l = 2n+1$. The space group is uniquely D_2^4–$P2_12_12_1$. There are four molecules per unit cell. No molecular symmetry is required. The absorption coefficient for Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) is 25·7 cm.$^{-1}$, for Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) is 205·8 cm.$^{-1}$. The volume of the unit cell is 1225·3 Å^3. The total number of electrons per unit cell, $F(0, 0, 0)$, is 600.

Analysis of the structure

In the $(hk0)$ layer, reflections of the form $h = 4n+2$ when $k = 2n+1$, and $h = 4n$ when $k = 2n$ (each n may be any integer) are of outstanding intensity (Table 1). Assuming these reflections are largely caused by the tellurium atoms contributing fully to these planes, and by considering the Patterson projection along the c axis, the approximate coordinates of the tellurium atom could readily be established as $\frac{1}{8}$, $\frac{1}{4}$, z, keeping the origin given in the *International Tables* (1952).

The temperature factor B in the expression $\exp\{-B[(\sin\theta)/\lambda]^2\}$ was first found by Wilson's method (1942) to be 6·5 Å^2 and was later changed to 5·0 Å^2. Structure factors calculated for the tellurium atom at $x = \frac{1}{8}$, $y = \frac{1}{4}$, using the atomic scattering factor based on the Thomas field for this atom and the initial value of B, allowed signs to be given to 58 observed reflections. A larger number of phases than this could have been determined, but the initial intensity range used was rather limited. The value of R_1 for these 58 strong planes ($R_1 = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$) was 0·28. Using these signs with the observed structure factors as coefficients, a double Fourier series was computed on XRAC, through the kindness of Prof. R. Pepinsky. Since the strong reflections only were used as coefficients in the series, the projection was artificially symmetrized. Addition of several of the strongest remaining reflections, with various sign permutations, served sufficiently to desymmetrize the series so that a good approximation could be made to the true position of the carbon atoms. Further refinement was then obtained by the iteration process of Fourier-series and structure-factor calculations. Three such cycles produced no more sign changes and resulted in a value of $R_1 = 0{\cdot}19$. The last $(hk0)$ Fourier series is shown in Fig. 1(a).

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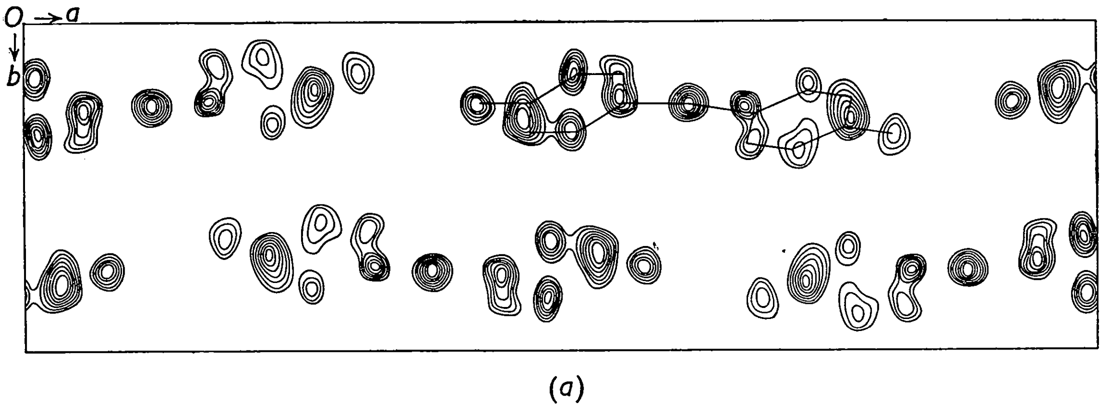
Table 1. *Observed and calculated structure factors for di-p-tolyl telluride*

h0l	F_{obs}	F_{calc}	h0l	F_{obs}	F_{calc}	h0l	F_{obs}	F_{calc}	h0l	F_{obs}	F_{calc}
200	25	-16	25, 0, 2	25	+25	605	28	+22	408	16	-7
400	69	-73	26, 0, 2	< 7	0	705	< 6	-2	508	13	-6
600	23	+29	27, 0, 2	< 7	-4	805	11	-10	608	< 6	+2
800	131	+119	28, 0, 2	< 7	+1	905	< 6	-2	808	15	+6
10, 0, 0	36	-41	29, 0, 2	18	-18	10, 0, 5	54	-39	hk0	F_{obs}	F_{calc}
12, 0, 0	93	-104	30, 0, 2	< 6	0	11, 0, 5	7	+10	020	260	-293
14, 0, 0	47	+48	31, 0, 2	< 6	+3	12, 0, 5	13	+12	040	111	+108
16, 0, 0	75	+73	103	50	-60	13, 0, 5	< 7	+2	060	66	-67
18, 0, 0	40	-42	203	36	+45	14, 0, 5	24	+23	080	32	+50
20, 0, 0	69	-68	303	51	+65	15, 0, 5	24	-19	0, 10, 0	11	-20
22, 0, 0	14	+29	403	< 5	-13	16, 0, 5	16	-16	110	*	+2
24, 0, 0	13	+7	503	63	+66	17, 0, 5	< 7	-2	210	173	-210
26, 0, 0	25	-19	603	53	-64	18, 0, 5	29	-26	310	8	-7
28, 0, 0	14	-15	703	63	-72	19, 0, 5	< 7	+4	410	10	-14
30, 0, 0	18	+15	803	< 5	+8	20, 0, 5	15	+11	510	12	+20
32, 0, 0	13	+5	903	26	-29	21, 0, 5	< 7	+1	610	166	+159
101	97	+90	10, 0, 3	31	+32	22, 0, 5	15	+10	710	< 6	+8
201	102	+108	11, 0, 3	66	+68	23, 0, 5	< 7	-6	810	31	+27
301	131	-128	12, 0, 3	6	-8	24, 0, 5	11	-9	910	< 8	+1
401	16	-27	13, 0, 3	19	+27	25, 0, 5	< 6	0	10, 1, 0	123	-110
501	24	-34	14, 0, 3	26	-29	26, 0, 5	< 6	-4	11, 1, 0	< 9	+4
601	123	-125	15, 0, 3	43	-53	27, 0, 5	< 5	+1	12, 1, 0	50	-45
701	75	+81	16, 0, 3	14	+22	28, 0, 5	9	+6	13, 1, 0	< 10	-1
801	25	+35	17, 0, 3	7	-4	006	22	+15	14, 1, 0	102	+101
901	29	+40	18, 0, 3	13	+13	106	25	-26	15, 1, 0	< 11	-8
10, 0, 1	139	+133	19, 0, 3	37	+28	206	< 7	-2	16, 1, 0	54	+50
11, 0, 1	49	-52	20, 0, 3	7	-9	306	15	-8	17, 1, 0	< 12	-8
12, 0, 1	22	-33	21, 0, 3	< 7	+3	406	13	-13	18, 1, 0	85	-66
13, 0, 1	24	-22	22, 0, 3	17	-13	506	28	+21	19, 1, 0	< 13	+1
14, 0, 1	46	-49	23, 0, 3	29	-24	606	< 7	+5	20, 1, 0	74	-58
15, 0, 1	56	+53	24, 0, 3	12	+12	706	15	+15	21, 1, 0	< 13	-8
16, 0, 1	34	+32	25, 0, 3	< 7	+2	806	19	+19	22, 1, 0	18	+29
17, 0, 1	10	+13	26, 0, 3	< 7	+8	906	28	-22	23, 1, 0	< 14	+8
18, 0, 1	29	+35	27, 0, 3	19	+15	10, 0, 6	< 7	-5	24, 1, 0	< 14	+11
19, 0, 1	40	-46	28, 0, 3	< 7	-2	11, 0, 6	7	-9	25, 1, 0	< 13	-3
20, 0, 1	15	-13	29, 0, 3	< 7	-2	12, 0, 6	11	-11	26, 1, 0	32	-23
21, 0, 1	< 6	-5	30, 0, 3	< 7	-2	13, 0, 6	16	+16	27, 1, 0	< 12	+1
22, 0, 1	33	-27	31, 0, 3	15	-11	14, 0, 6	< 7	+5	28, 1, 0	24	-21
23, 0, 1	26	+23	004	83	+70	15, 0, 6	< 7	+5	29, 1, 0	< 11	+3
24, 0, 1	27	+30	104	22	-23	16, 0, 6	< 7	+4	30, 1, 0	14	+9
25, 0, 1	< 7	-4	204	< 6	-6	17, 0, 6	14	-11	31, 1, 0	< 8	-1
26, 0, 1	13	+12	304	21	-20	18, 0, 6	6	0	32, 1, 0	18	+13
27, 0, 1	21	-15	404	59	+59	19, 0, 6	< 6	-2	120	43	-37
28, 0, 1	15	-13	504	20	+22	20, 0, 6	6	-7	220	33	-22
29, 0, 1	< 7	+1	604	13	-11	21, 0, 6	16	+12	320	46	+46
30, 0, 1	7	-9	704	< 6	+6	22, 0, 6	6	+4	420	99	+118
31, 0, 1	7	+8	804	70	-70	23, 0, 6	< 5	-1	520	47	+27
002	9	+3	904	7	-14	24, 0, 6	4	+3	620	52	+45
102	113	+108	10, 0, 4	12	+18	25, 0, 6	< 3	-6	720	10	-10
202	< 4	+8	11, 0, 4	< 6	-9	107	19	+13	820	109	-117
302	80	+91	12, 0, 4	52	+51	207	< 7	-2	920	23	+24
402	36	+38	13, 0, 4	9	+9	307	22	-15	10, 2, 0	30	-31
502	82	-95	14, 0, 4	26	-23	407	< 6	-1	11, 2, 0	< 9	+2
602	< 5	-1	15, 0, 4	< 6	+1	507	11	-9	12, 2, 0	96	+94
702	67	-71	16, 0, 4	25	-23	607	< 6	+4	13, 2, 0	11	-9
802	< 5	-23	17, 0, 4	23	-23	707	19	+14	14, 2, 0	59	+45
902	120	+114	18, 0, 4	16	+15	807	< 6	-3	15, 2, 0	< 11	+2
10, 0, 2	< 5	-8	19, 0, 4	< 7	-4	907	11	+8	16, 2, 0	80	-71
11, 0, 2	34	+39	20, 0, 4	30	+21	10, 0, 7	< 6	-1	17, 2, 0	< 12	0
12, 0, 2	21	+20	21, 0, 4	< 7	+8	11, 0, 7	25	-15	18, 2, 0	50	-39
13, 0, 2	80	-84	22, 0, 4	19	-15	12, 0, 7	< 6	+1	19, 2, 0	< 13	+1
14, 0, 2	7	-16	23, 0, 4	< 7	0	13, 0, 7	< 6	-4	20, 2, 0	59	+60
15, 0, 2	16	-20	24, 0, 4	15	-12	14, 0, 7	< 6	+1	21, 2, 0	< 14	+6
16, 0, 2	< 6	-4	25, 0, 4	7	-4	15, 0, 7	14	+8	22, 2, 0	22	+29
17, 0, 2	56	+48	26, 0, 4	20	+11	16, 0, 7	< 6	0	23, 2, 0	< 14	-3
18, 0, 2	6	+10	27, 0, 4	< 6	0	17, 0, 7	< 5	+2	24, 2, 0	24	-15
19, 0, 2	6	+3	28, 0, 4	8	+7	18, 0, 7	< 5	-2	25, 2, 0	< 13	-3
20, 0, 2	< 6	+5	105	8	-7	19, 0, 7	13	-8	26, 2, 0	32	-27
21, 0, 2	46	-47	205	61	-63	008	19	+8	27, 2, 0	< 12	+1
22, 0, 2	< 7	-5	305	20	+19	108	9	+4	28, 2, 0	15	+16
23, 0, 2	< 7	-3	405	< 6	+6	208	< 6	-1	29, 2, 0	7	-4
24, 0, 2	< 7	-7	505	14	+19	308	6	+5	30, 2, 0	21	+13

* Not observable; cut off by layer-line screen.

Table 1 (*cont.*)

hk0	F_{obs}	F_{calc}	hk0	F_{obs}	F_{calc}	hk0	F_{obs}	F_{calc}	hkl	F_{obs}	$\lvert F_{calc}\rvert$
130	< 8	+ 3	15, 5, 0	< 14	+ 3	15, 8, 0	< 10	+ 3	14, 2, 1	55	50
230	135	+132	16, 5, 0	34	+33	16, 8, 0	17	+ 17	15, 2, 1	57	48
330	< 8	- 6	17, 5, 0	13	- 6	17, 8, 0	< 9	0	16, 2, 1	38	32
430	9	+ 12	18, 5, 0	23	-30	18, 8, 0	8	+ 10	17, 2, 1	< 8	12
530	12	- 14	19, 5, 0	< 13	+ 1	19, 8, 0	< 7	- 2	18, 2, 1	47	39
630	144	-141	20, 5, 0	23	-13	20, 8, 0	8	- 12	19, 2, 1	57	49
730	14	- 13	21, 5, 0	< 13	+ 3	190	< 11	- 3	20, 2, 1	8	21
830	20	- 27	22, 5, 0	25	+18	290	20	- 25	21, 2, 1	< 9	10
930	< 10	+ 8	23, 5, 0	< 12	0	390	< 11	- 4	22, 2, 1	47	29
10, 3, 0	79	+ 87	24, 5, 0	21	+20	490	< 11	- 4	23, 2, 1	20	25
11, 3, 0	15	- 11	25, 5, 0	< 10	- 3	590	< 11	+ 7	24, 2, 1	28	25
12, 3, 0	50	+ 39	26, 5, 0	13	-11	690	11	+ 22	25, 2, 1	< 9	5
13, 3, 0	< 11	+ 3	160	< 13	+13	790	< 10	- 6	26, 2, 1	14	14
14, 3, 0	99	- 89	260	< 13	- 3	890	< 10	+ 4	27, 2, 1	22	15
15, 3, 0	< 12	+ 8	360	< 13	- 6	990	< 10	- 3	131	59	63
16, 3, 0	49	- 45	460	73	+69	10, 9, 0	14	- 17	231	< 6	12
17, 3, 0	13	+ 13	560	< 13	- 6	11, 9, 0	< 9	+ 2	331	59	70
18, 3, 0	62	+ 46	660	20	+24	12, 9, 0	< 8	- 6	431	107	109
19, 3, 0	< 13	- 1	760	< 13	-11	13, 9, 0	< 8	+ 2	531	51	57
20, 3, 0	44	+ 27	860	41	-49	14, 9, 0	12	+ 14	631	22	18
21, 3, 0	< 14	9	960	< 13	0	15, 9, 0	< 6	- 1	731	31	33
22, 3, 0	25	- 24	10, 6, 0	14	-14	16, 9, 0	4	+ 7	831	97	81
23, 3, 0	< 13	- 8	11, 6, 0	< 14	+ 6	1, 10, 0	< 7	+ 2	931	70	62
24, 3, 0	26	- 24	12, 6, 0	42	+46	2, 10, 0	< 7	- 6	10, 3, 1	31	30
25, 3, 0	< 13	+ 5	13, 6, 0	< 14	- 4	3, 10, 0	< 7	+ 1	11, 3, 1	29	30
26, 3, 0	28	+ 19	14, 6, 0	21	+14	4, 10, 0	7	+ 12	12, 3, 1	63	63
27, 3, 0	< 11	- 1	15, 6, 0	< 14	- 1	hkl	F_{obs}	$\lvert F_{calc}\rvert$	13, 3, 1	57	50
28, 3, 0	14	+ 18	16, 6, 0	28	-31	011	18	31	14, 3, 1	15	26
29, 3, 0	< 9	- 3	17, 6, 0	< 13	- 5	021	12	10	15, 3, 1	< 8	14
30, 3, 0	7	- 9	18, 6, 0	23	-22	031	83	101	16, 3, 1	62	49
140	< 9	- 1	19, 6, 0	< 12	+ 6	041	< 7	7	17, 3, 1	64	50
240	10	+ 3	20, 6, 0	25	+25	051	65	77	18, 3, 1	18	29
340	10	- 11	21, 6, 0	< 11	- 3	111	79	95	19, 3, 1	< 8	3
440	115	-118	22, 6, 0	18	+16	211	3	5	20, 3, 1	26	27
540	14	- 8	23, 6, 0	< 10	- 2	311	84	94	21, 3, 1	26	25
640	43	- 46	24, 6, 0	18	-15	411	125	179	22, 3, 1	28	26
740	< 10	+ 12	170	< 14	+ 5	511	64	63	141	84	79
840	85	+ 90	270	51	+52	611	23	28	241	110	98
940	12	- 11	370	< 14	0	711	64	46	341	57	55
10, 4, 0	15	+ 18	470	< 14	- 2	811	109	111	441	< 7	7
11, 4, 0	< 12	- 7	570	< 14	- 5	911	84	72	541	< 7	20
12, 4, 0	78	- 70	670	34	-41	10, 1, 1	51	45	641	59	65
13, 4, 0	< 13	+ 10	770	< 14	+ 6	11, 1, 1	25	30	741	24	42
14, 4, 0	34	- 28	870	< 14	-14	12, 1, 1	96	81	841	< 7	19
15, 4, 0	< 13	- 4	970	< 14	+ 8	13, 1, 1	100	69	941	10	20
16, 4, 0	49	+ 51	10, 7, 0	30	+37	14, 1, 1	24	28	10, 4, 1	64	64
17, 4, 0	< 13	+ 7	11, 7, 0	< 13	- 5	15, 1, 1	10	12	11, 4, 1	37	47
18, 4, 0	26	+ 29	12, 7, 0	13	+13	16, 1, 1	65	60	12, 4, 1	15	22
19, 4, 0	< 14	- 7	13, 7, 0	< 13	- 2	17, 1, 1	81	65	13, 4, 1	< 8	19
20, 4, 0	43	- 37	14, 7, 0	31	-33	18, 1, 1	15	28	14, 4, 1	42	38
21, 4, 0	< 14	0	15, 7, 0	< 13	- 4	19, 1, 1	< 7	12	15, 4, 1	39	36
22, 4, 0	28	- 21	16, 7, 0	21	-19	20, 1, 1	30	20	16, 4, 1	24	24
23, 4, 0	< 13	+ 4	17, 7, 0	< 12	+ 1	21, 1, 1	22	21	17, 4, 1	< 8	10
24, 4, 0	24	+ 19	18, 7, 0	20	+20	22, 1, 1	45	27	18, 4, 1	32	34
25, 4, 0	< 12	0	19, 7, 0	< 10	- 2	23, 1, 1	< 9	5	19, 4, 1	26	34
26, 4, 0	25	+ 25	20, 7, 0	10	+13	24, 1, 1	47	29	151	26	33
27, 4, 0	< 10	0	21, 7, 0	< 9	- 5	25, 1, 1	17	20	251	< 7	12
28, 4, 0	9	- 10	22, 7, 0	14	-10	26, 1, 1	25	22	351	26	38
150	< 11	- 6	180	< 13	- 7	27, 1, 1	< 10	0	451	46	62
250	85	- 84	280	< 13	+10	121	85	102	551	31	46
350	11	+ 12	380	< 13	+ 3	221	116	133	651	< 7	12
450	< 11	0	480	28	-32	321	77	96	751	< 7	26
550	< 12	0	580	< 13	+ 3	421	10	16	851	43	53
650	88	+ 84	680	< 13	- 5	521	26	32	951	28	37
750	11	+ 5	780	< 13	+ 9	621	89	103	10, 5, 1	11	17
850	18	+ 25	880	13	+24	721	81	69	11, 5, 1	< 8	19
950	< 12	- 13	980	< 12	- 2	821	29	32	12, 5, 1	35	39
10, 5, 0	60	- 60	10, 8, 0	< 12	+ 9	921	24	33	13, 5, 1	30	33
11, 5, 0	9	+ 10	11, 8, 0	< 12	- 3	10, 2, 1	103	112	14, 5, 1	< 9	20
12, 5, 0	26	- 24	12, 8, 0	21	-25	11, 2, 1	67	59	15, 5, 1	< 9	12
13, 5, 0	13	- 1	13, 8, 0	< 11	+ 1	12, 2, 1	34	31	16, 5, 1	23	32
14, 5, 0	64	+ 61	14, 8, 0	11	- 9	13, 2, 1	25	26	17, 5, 1	19	32



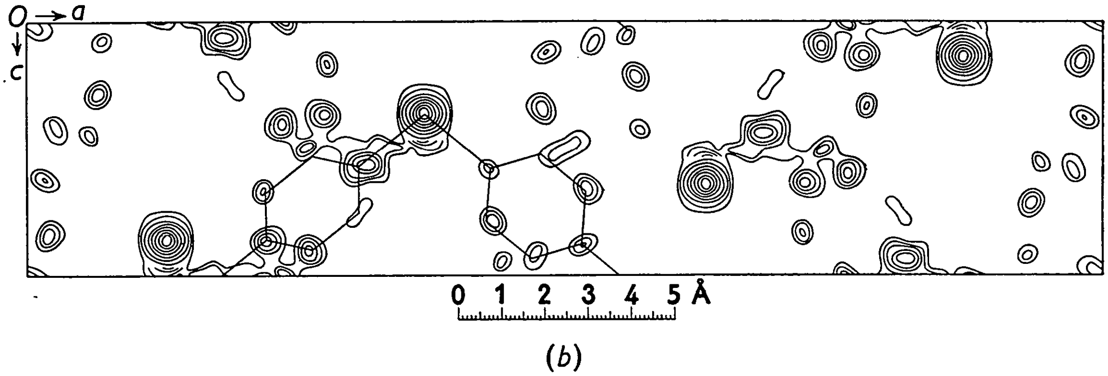


Fig. 1. (*a*) Projection of the unit cell of di-*p*-tolyl telluride along the *c* axis. Each contour for the carbon atoms represents a density increment of 0·8 e.Å^{-2}, and for the tellurium atom of 8·0 e.Å^{-2}. The first contour for the carbon atoms is of 4 e.Å^{-2} and for the tellurium atom is of 16 e.Å^{-2}.

(*b*) Projection of the unit cell along the *b* axis. Each contour for the carbon atoms represents a density increment of 0·95 e.Å^{-2}, and for the tellurium atom of 9·5 e.Å^{-2}. The first contour is of 4·75 e.Å^{-2} for both atoms. The outline of one molecule, based upon the final set of coordinates, is shown.

In the ($h0l$) layer, solution of the Patterson projection gave the z coordinate of the tellurium atom. Structure factors for this atom alone now determined the signs of about 40 of the original set of reflections, and corresponded to an R_1 value of 0·35. A Fourier series, using these signs, was computed on XRAC and the approximate z coordinates of the carbon atoms were thus derived. Four subsequent cycles led to no further sign changes, and R_1 reduced to 0·22. The final electron-density map is shown in Fig. 1(*b*).

Further refinement of the atomic coordinates, beyond that obtainable from the Fourier series alone, was then sought by applying the method of least squares. A weight of unity was assigned each observation except for $F(020)$ and $F(210)$, which apparently suffered from extinction and were given a weight of zero. Because there were 30 unknowns in each projection, exact solution of the resulting 30 normal equations was not attempted. Instead, the off-diagonal terms were omitted, for it was assumed that, in general, these would be small since the number of observational equations in each zone was large. A complete solution of a similar determinant (Blackmore & Abrahams, 1955*b*) showed this assumption not to be completely valid, but, nevertheless, in successive least-squares iterations, the value of R_1 did become smaller than that obtained from the Fourier-series method alone. In applying the least-squares method, no constraints were placed on any of the atomic coordinates.

Five cycles of least-squares applications and structure factor calculations reduced $R_1(hk0)$ to 0·117 (in evaluating this $R_1(hk0)$, $F(020)$ and $F(210)$ were omitted). A similar number of least-squares cycles with the ($h0l$) structure factors reduced $R_1(h0l)$ to 0·138. In both layers, it was found that the algebraic sign of many of the $\Delta\xi_j$'s to be added to the ξ_j's (the atomic coordinate of the jth atom) changed between successive least-squares applications. The stationary value of R_1, together with the large proportion of $\Delta\xi_j$'s with oscillating signs resulting from the last several iterations in the two layers, was assumed to be an indication of convergence in the method. In this refinement procedure, 299 observations were used for the determination of 45 parameters.

Atomic coordinates

In selecting the final atomic coordinates, each of the ξ_j's resulting from the least-squares cycles with stationary R_1 was circumscribed by a circle with radius the root of the sum of the mean variance of Δx and Δy in ($hk0$) and of Δx and Δz in ($h0l$). The lines Te–C_1–C_4–C_7 and Te–C_1'–C_4'–C_7' were assumed straight, and were required to pass as closely as possible through the sets of points around each atomic position, and always through the circumscribed circles. Upon each of these lines, a regular planar hexagon of side 1·40 Å was constructed to fit the remaining four sets of points. The methyl-carbon–aromatic-carbon distance was assumed to be 1·51 Å.

The final combined coordinates derived from the ($h0l$) and ($hk0$) intensities are given in Table 2. As an independent check of these coordinates, the ($hk1$) intensities were recorded and reduced to structure factors. The final values of R_1, using all the structure factors as listed in Table 1, are 0·134 for ($hk0$), 0·154 for ($h0l$) and 0·198 for ($hk1$).

Table 2. *Atomic coordinates in* (p-$CH_3.C_6H_4)_2Te$

The origin is half way between three pairs of non-intersecting screw axes

	Atom	x	y	z
	Te	0·1304	0·2529	0·1106
Ring *A*	C_1	0·0690	0·2195	0·3267
	C_2	0·0759	0·1303	0·5239
	C_3	0·0343	0·1103	0·6708
	C_4	0·9846	0·1798	0·6250
	C_5	0·9776	0·2681	0·4266
	C_6	0·0196	0·2882	0·2797
	C_7	0·9391	0·1575	0·7839
Ring *B*	C_1'	0·1941	0·2529	0·3234
	C_2'	0·1941	0·3576	0·5066
	C_3'	0·2378	0·3576	0·6534
	C_4'	0·2807	0·2529	0·6122
	C_5'	0·2807	0·1508	0·4307
	C_6'	0·2378	0·1508	0·2838
	C_7'	0·3279	0·2529	0·7689

Dimensions in the di-*p*-tolyl telluride molecule

The only distance not assumed in deriving the final coordinates is the Te–C bond length. This distance occurs twice, with no crystallographic relation between the two bonds, and was found to be 2·05 Å for both bonds. The angle C_1'–Te–C_1 is 101°. The angles made by the normals of the unprimed ring (*A* in Fig. 2) with the *a*, *b* and *c* axes are 74°, 33° and 62°, respectively. The corresponding angles for the normal to ring *B* are 116°, 136° and 57°. The two normals form an angle of 62° with each other.

Intermolecular distances

No distance less than 3·40 Å between non-bonded atoms was found, except for a single approach of 3·23 Å between $C(B)_5$ and $C(BI)_6$ (Fig. 2). This short distance is very sensitive to small changes in the orientation of the benzene ring *B*, and hence, in view of the standard deviation in the coordinates of the carbon atoms (see next section), this close approach is not thought to be very significant. It hence appears that only van der Waals forces are present between molecules in this crystal, accounting for the low m.p.

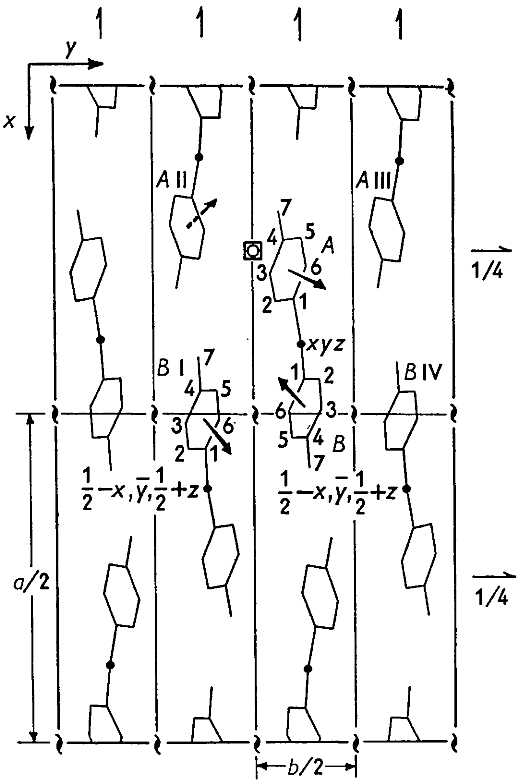


Fig. 2. Schematic representation of the molecular environment in di-*p*-tolyl telluride (also selenide and sulfide, Blackmore & Abrahams (1955*a*, *b*)). The benzene ring normals are indicated by tapered arrows.

Accuracy of the coordinates

In the present study, since the final atomic coordinates were based upon least-squares methods, the uncertainties in these coordinates were determined by the same method. The normal procedure (Whittaker & Robinson, 1944) of placing

$$\sigma(\Delta\xi_j) = \left\{\frac{\Sigma v^2}{(m-s)}\cdot\frac{A_{11}}{D}\right\}^{\frac{1}{2}} \doteqdot \left\{\frac{\Sigma[\Delta F(hkl)]^2}{(m-s)\Sigma\left[\frac{\partial F(hkl)}{\partial\xi_j}\right]^2}\right\}^{\frac{1}{2}}, \quad (1)$$

where $\sigma(\Delta\xi_j)$ is the standard deviation (Plummer, 1940), v is the residual, D the determinant formed from the coefficients of the normal equations, A_{11} the minor determinant of the coefficient of the unknown $\Delta\xi_j$, m the number of observational equations and s the number of unknowns, could not be used here because of the non-diagonality of D. Now, in the case where D is diagonal (for practical purposes, when the ratio of an off-diagonal to the diagonal element in any normal equation is less than, e.g. 0·03),

$$\frac{\sigma(\Delta\xi_i)}{\sigma(\Delta\xi_j)}=\left\{\frac{\Sigma\left[\frac{\partial F(hkl)}{\partial \xi_j}\right]^2}{\Sigma\left[\frac{\partial F(hkl)}{\partial \xi_i}\right]^2}\right\}^{\frac{1}{2}}=\left\{\frac{\Sigma h^2 f_j^2 t_j^2}{\Sigma h^2 f_i^2 t_i^2}\right\}^{\frac{1}{2}}, \qquad (2)$$

where h is the index, f_j the atomic scattering factor, and t a trigonometric function. As an approximation, the right-hand side of equation (2) is not very different from $\bar{f}_j/\bar{f}_i$. In the case of $BaS_4.H_2O$ (Abrahams, 1954), this relationship held to within 10% for the three heavier atoms. This relationship was assumed to hold for D non-diagonal.

On examining the normal equations, it was found that the diagonal elements for Δx_{Te} entirely dominated the remaining coefficients in its equation (and indeed, the other diagonal coefficients as well). The standard deviation in Δx_{Te} could thus be found by means of the diagonal approximation, and then from (2) estimates could be made of all the remaining $\sigma(\Delta\xi_j)$'s. Hence, $\sigma(\Delta x_{Te}) = 0{\cdot}005$ Å, and since there is no evidence of strong anisotropy in the temperature factor of the tellurium atom, $\sigma(r_{Te}) = 0{\cdot}005$ Å also. The ratio $\bar{f}_{Te}/\bar{f}_C$ was computed to be 14·0 and therefore $\sigma(r_C) = 0{\cdot}070$ Å.

The standard deviation σ(Te–C) in the Te–C bond length was found by the use of Cruickshank & Robertson's (1953) relation $\sigma^2(\text{Te–C}) = \sigma^2(\text{Te})+\sigma^2(\text{C})$, where σ^2(Te) and σ^2(C) are the variances in the direction of the bond. The standard deviation in this bond length is thus 0·07 Å; and since this length has been independently measured twice, the standard error in the averaged bond length is $0{\cdot}07/\sqrt{2} = 0{\cdot}05$ Å. Similarly, the standard deviation $\sigma(\beta)$ in the bond angle C–Te–C is 2·7°, using their relation

$$\sigma^2(\beta)=\frac{2\sigma^2(C_1)}{(\text{Te–C}_1)^2}+\frac{2\sigma^2(\text{Te})}{(\text{Te–C}_1)^2}\cdot(1-\cos\beta)\doteqdot\frac{2\sigma^2(C_1)}{(\text{Te–C}_1)^2},$$

since σ^2(Te) is so small.

Discussion

Considerable caution is required in any discussion of the Te–C bond distance measured in this crystal as 2·05 Å, because of the rather large value of the standard deviation. No previous measurement of a Te–C distance has apparently been reported in the literature. The Te–Te distance in hexagonal tellurium has been determined as 2·82 Å (Grison, 1951). If now, half this distance is taken as the single covalent bond radius for tellurium, and 0·75 Å as the corresponding carbon radius, the single covalent Te–C bond length will be 2·12 Å on correcting for the difference in electronegativity between the two atoms (Schomaker & Stevenson, 1941). The observed bond length is short of this value by 0·07 Å, while the standard deviation in the length is 0·05 Å. If this apparent decrease in the Te–C bond is real, it could be interpreted as involving a partial conjugation between the tellurium atom and the aromatic group. It has previously been suggested by Schomaker & Pauling (1939), Longuet-Higgins (1949) and Price & Zomlefer (1950) that sulfur can participate in such pro-conjugation when in a similar molecular environment.

The C–Te–C bond angle of 101° compares very closely with the Te–Te–Te angle of 102° in the hexagonal element (Grison, 1951).

Experimental

The colorless needles of di-p-tolyl telluride were prepared by the method of Lyons & Bush (1908) and recrystallized from aqueous alcohol. Decomposition of the crystals during X-ray exposures was prevented by mounting them in very thin-walled, glass capillaries. The nature of the decomposition products was not investigated. The largest of the four crystals examined was 0·5 × 0·4 × 3·5 mm.^{3} and the smallest was 0·05 × 0·09 × 0·7 mm.^{3}.

Weissenberg and precession cameras were used in this study, employing Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation only in the final determination of the atomic coordinates. The cell constants were all measured from precession photographs, correcting for film shrinkage as suggested by Barnes, Przybylska & Shore (1951). Both multiple-exposure and multiple-film-pack methods were used, and in the latter, 1 mil nickel foil was interleaved between films. The ratio of the intensity of a Mo $K\alpha$ X-ray beam before passing through a thickness of foil and film (Ilford 'Industrial-G'), to that of the emergent beam was determined to be 3·4:1. The intensities, which were estimated visually by two independent observers, agreed within 10% on reduction to structure factors and were then averaged. Absorption corrections were not made since the smallest crystals were so small. The larger crystals were used only for the recording of the weakest intensities. The ratio of the strongest intensity to the weakest in each zone was 1665:1 in ($hk0$), 1458:1 in ($h0l$) and 2500:1 in ($hk1$).

The magnetic anisotropy of these crystals was measured through the courtesy of Prof. K. Lonsdale (Toor, 1952). The values of the gram-molecular susceptibilities, in units of c.g.s.e.m.u. per mole, were found to be:

$$\chi_a=-146\times10^{-6},\quad \chi_b=-206\times10^{-6},\quad \chi_c=-154\times10^{-6}.$$

From these anisotropy measurements the angles made by the normals to the aromatic rings with the a, b and c axes were calculated to lie within the following ranges:

$60° \leqslant \alpha \leqslant 120°$; $0° \leqslant \beta \leqslant 54°$ or $136° \leqslant \beta \leqslant 180°$; $51° \leqslant \gamma \leqslant 129°$;

$120° \geqslant \alpha' \geqslant 60°$; $180° \geqslant \beta' \geqslant 136°$ or $54° \geqslant \beta' \geqslant 0°$; $129° \geqslant \gamma' \geqslant 51°$.

These ranges may be compared with the angles found of 74°, 33°, 62°, and 116°, 136°, 57°, respectively.

The values for the measured structure factors were derived from the intensities in the usual way, applying Waser's (1951) Lorentz and polarization correction in the zero layer measured with the precession camera, and the Tunell (1939) rotation factor for the upper-layer equi-inclination Weissenberg intensities. The calculated structure factors are based on the atomic coordinates given in Table 2. The least-squares and structure-factor calculations were carried out on International Business Machines. A Patterson series was computed on Whirlwind* (the Massachusetts Institute of Technology high-speed digital computer) and the Fourier series were summed, with the aid of Beevers–Lipson strips, at intervals of $a/60$, $b/30$ and $c/30$. The positions of the contour lines were obtained from the summation totals by careful interpolation on a scale of 5 cm. and 6 cm. to 1 Å, in directions parallel with each axis.

We would like to thank J. Kalnajs for preparing the crystals and Prof. A. von Hippel for his interest and support.

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The Crystal Structure of Di-*p*-Tolyl Selenide*

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Di-*p*-tolyl selenide forms orthorhombic crystals, space group $P2_12_12_1$, with a unit cell of constants $a = 25{\cdot}12$, $b = 7{\cdot}99$ and $c = 5{\cdot}88$ Å, containing four molecules. The crystal structure has been determined, and the 45 positional parameters refined by double-Fourier-series and least-squares methods, employing 401 terms. The intensities were measured visually by two observers. The Se–C distance is 1·93 Å and the C–Se–C valence angle is 106°. The normals to the two aromatic rings form an angle of 55° with each other.

Introduction

A series of investigations on the crystal structures of organo-selenium compounds have been reported by McCullough and his co-workers, and their results are summarized in Table 1. The present crystal has been

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