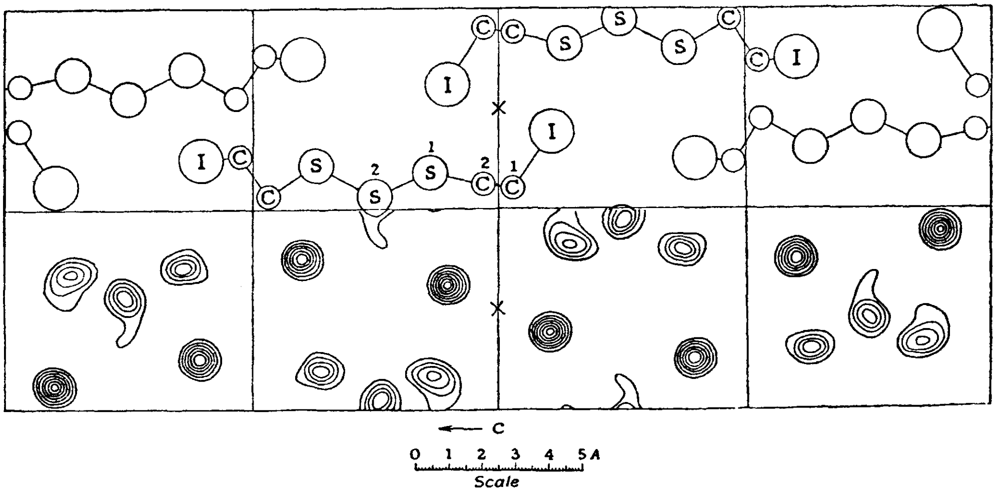
249. *The Structure of Certain Polysulphides and Sulphonyl Sulphides. Part II. The Crystal Structure of 2 : 2′-Di-iododiethyl Trisulphide.*

By I. M. Dawson and J. Monteath Robertson.

The crystal and molecular structure of 2 : 2′-di-iododiethyl trisulphide have been determined by quantitative *X*-ray analysis. There are four molecules in the unit cell and each molecule possesses an exact two-fold axis of symmetry (tetragonal space-group $P4_12_1$). Fourier projections used to refine the trial structure give good definition of the iodine and sulphur positions, but not of the carbon positions. The latter positions may, however, be inferred with reasonable certainty from the known bond lengths and valency angles involved. The molecule is in the form of an extended zigzag, but the planes of the carbon–carbon–iodine zigzags are almost at right angles to the plane of the central sulphur zigzag. The sulphur–sulphur distance is 2·04 ± 0·04 A. and the S–S–S angle is about 113°. The intermolecular distances found are in good agreement with those previously reported for sulphur and iodine, the van der Waals radius for iodine being 2·22 A. and for sulphur 1·58 A. The latter value is considerably less than the sulphur ionic radius (1·85 A.).

It is clear from the preliminary survey given in Part I (Dawson, Mathieson, and Robertson, *J.*, 1948, 322) that the crystal structure of 2 : 2′-di-iododiethyl trisulphide is suitable for detailed *X*-ray analysis, and a full determination is given in the present paper. The tetragonal space group D_4^4–$P4_1/2_1$ with four molecules in the unit cell (a = 6·01, c = 29·4 A.) demands that each molecule should possess a two-fold axis of symmetry, perpendicular to the (110) crystal plane.

Fig. 1.



Projection along b *axis on* (010) *plane showing four molecules of di-iododiethyl trisulphide. Contour lines for iodine atom are drawn at density intervals of* 10 *electrons per* A.², *and for sulphur at intervals of* 4 *electrons per* A.². *Origin of co-ordinates marked by* X.

This fact limits the possible molecular configurations to some extent, and effectively rules out any structure showing co-ordination of the type $\text{—S—}\overset{\overset{\text{S}}{\uparrow}}{\text{S}}\text{—}$.

The very long c axis and relatively small cross-section, as well as pronounced cleavage parallel to (100), suggest rod-shaped molecules arranged approximately parallel to the c axis. This is in favour of an extended zigzag chain structure, although alternatives (VII) and (VIII) (Part I) cannot be finally eliminated from space-group and dimensional evidence alone.

In this structure the contribution of the iodine atoms to the *X*-ray intensities far outweighs that of all the other atoms combined. The distribution of scattering power in the molecule $C_4H_8S_3I_2$, obtained by summing the atomic numbers, is 57% for iodine, 26% for sulphur, and only 13% for carbon. The situation is clearly not such a favourable one for the application of the heavy-atom technique as in the case of platinum phthalocyanine (Robertson and Woodward, *J.*, 1940, 36) or cholesteryl iodide (Carlisle and Crowfoot, *Proc. Roy. Soc.*, 1945, *A*, **184**, 64). In the present example there are too many heavy atoms and too few light ones. This is also reflected in the absorption coefficient which, for copper radiation, is about five times higher in the present crystal than in the crystal of platinum phthalocyanine. Because of these factors, the final Fourier projection obtained in this analysis (Fig. 1) fails to give resolution of the carbon atoms, although their positions may be inferred with reasonable certainty from the positions of the other atoms.

The heavy atoms do not occupy any special positions in the structure, and although a Patterson analysis might be feasible, the dimensional evidence mentioned above made it more profitable to proceed by trial and error methods. Certain outstanding features in the ($h0l$) series of reflections help to simplify the problem. Large structure factors were observed for the (008), (106), (1014), (304), and (30, 24) planes, and when traces of these planes are drawn on the *ac* projection it becomes possible to define the probable positions of the iodine atoms. On this basis various trial models were set up and atomic positions were found which gave a satisfactory account of all the stronger reflections.

From this point the work proceeded by the application of double Fourier series methods, utilising the ($h0l$) structure factors. The projection first obtained gave clear resolution of the iodine positions, but the sulphur co-ordinates were rather doubtful. However, the accurate iodine co-ordinates now enabled a more complete Fourier series to be set up, and after several refinements of this kind the diagram shown in Fig. 1 was obtained. This projection, drawn on the (010) plane, covers one complete unit cell, and includes four molecules. The line diagram (upper portion of Fig. 1) indicates the molecular arrangement, and here probable positions for the carbon atoms are shown, although no direct evidence for these positions can be obtained from the electron density contours.

Co-ordinates and Dimensions.

The projection of the structure shown in Fig. 1 allows the co-ordinates of the iodine and sulphur atoms to be determined, the tetragonal symmetry making possible the direct measurement of all three co-ordinates for each atom. Table I lists co-ordinates for the atoms in the asymmetric crystal unit, which is one-half of the chemical molecule, or one-eighth of the total content of the unit cell. The co-ordinates of the remaining atoms follow from the symmetry operations of the space-group, D_4^4 ($P4_12_1$).

In this connection we have found it convenient to employ a different origin of co-ordinates from that adopted in the " International Tables for the Determination of Crystal Structure " (Bell and Son, London, 1935, p. 196). There the origin is taken at the intersection of one of the two-fold rotation axes, perpendicular to (110), with a two-fold screw axis parallel to *c*. For projections along the *c* axis this will give an origin at an apparent centre of symmetry. In the present example, however, the only useful projection of the structure is obtained along the *b* axis, and it is therefore convenient to choose an origin at an apparent centre of symmetry in this projection. Such a point is obtained on a two-fold screw axis parallel to *b* and is conveniently chosen at ($-\ a/4$, $-\ b/4$) with respect to the tetragonal screw axis. This new origin is employed in the present paper, and it is situated at ($a/4$, $3b/4$, $c/8$) with respect to the origin adopted in the International Tables. The co-ordinates of the eight equivalent points then become

(1) $x, \quad y, \quad z$
(2) $\frac{1}{2} - y, x, \quad \frac{1}{4} + z$
(3) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$
(4) $y, \quad \frac{1}{2} - x, \frac{3}{4} + z$
(5) $-y, \quad -x, \quad \frac{1}{4} - z$
(6) $\frac{1}{2} + x, -y, \quad \frac{1}{2} - z$
(7) $\frac{1}{2} + y, \frac{1}{2} + x, \frac{3}{4} - z$
(8) $-x, \quad \frac{1}{2} + y, -z$

with four special positions at

(1) $x, \quad x, \frac{1}{8}$
(2) $\frac{1}{2} + x, x, \frac{3}{8}$
(3) $\frac{1}{2} - x, \frac{1}{2} + x, \frac{5}{8}$
(4) $-x, \quad \frac{1}{2} - x, \frac{7}{8}$

This treatment yields a simplified expression for the geometrical structure factor for the ($h0l$) reflections. In the usual notation this becomes

$$A = 4\left[\cos 2\pi\left(hx - \frac{h+l}{4}\right) . \cos 2\pi\left(lz + \frac{h+l}{4}\right) + \cos 2\pi\left(hy - \frac{h-l}{4}\right) . \cos 2\pi\left(lz + \frac{h+2l}{4}\right)\right]$$

$$B = 0$$

The expression may be simplified further for special values of the indices h and l.

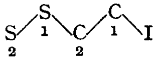
TABLE I.

Co-ordinates with respect to tetragonal crystal axes.

[Origin on 2_1 axis parallel to b, at ($-a/4$, $-b/4$) from 4_1 axis.]

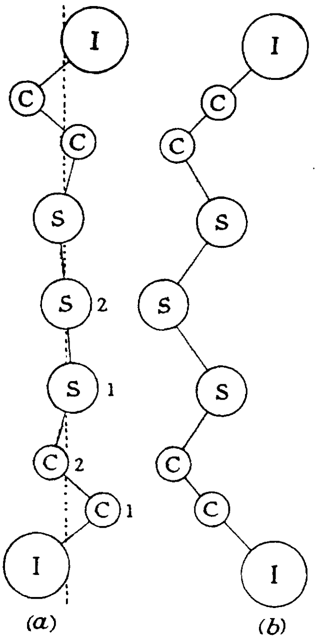
Atom (cf. Fig. 1).	x, A.	$\frac{2\pi x}{a}$.	y, A.	$\frac{2\pi y}{b}$.	z, A.	$\frac{2\pi z}{c}$.
I	−0·694	− 41·7°	1·500	90°	−1·531	−18·7°
C_1	−2·4	−144	1·4	84	−0·4	− 4·9
C_2	−2·3	−138	2·68	161	0·45	5·5
S_1	−1·96	−117·5	1·81	108·5	1·98	24·2
S_2	−2·68	−160·7	2·68	160·7	3·675	45

No clearly-defined carbon peaks occur in the Fourier projection and the carbon co-ordinates listed above are probable values only, based on the requirements of accepted single-bond lengths and angles for the atoms in question. In particular, the measured distance between the sulphur atom S_1 and the iodine atom in the chain is only 3·74 A. Assuming normal single-bond values, a *trans*-planar configuration for the group



would require a sulphur–iodine distance of 4·65 A. The difference is too great to be attributed to any minor bond-length or bond-angle variations, and the *trans*-planar configuration is therefore unlikely. The iodine atoms are also found to lie somewhat out of the plane of the S–S–S zigzag.

FIG. 2.



(*a*) (*b*)

(a) *Projection of the molecule along the axis of symmetry.*
(b) *A projection at right angles to* (a).

The positions which we have assigned to the carbon atoms give reasonable values for all the bond lengths and bond angles in which they are involved, and also provide a maximum clearance between the carbon atom C_2 and the iodine atom on the neighbouring molecule at equivalent position (8), $-x$, $\frac{1}{2}+y$, $-z$. The van der Waals approach distance between carbon and iodine is not likely to be less than the value of 3·68 A. which is given by the co-ordinates now assigned to these atoms.

On this basis, the principal dimensions of the molecule are summarised in Table II.

TABLE II.

Dimensions of the 2 : 2′-*di-iododiethyl trisulphide molecule.*

Bond lengths, A.	Bond angles.
S–S = 2·04 ± 0·04	S–S–S = 113° ± 2°
C–S = 1·79	S–S–C = 120°
C–C = 1·54 (assumed)	S–C–C = 96°
C–I = 2·05	C–C–I = 100°

The shape of the molecule is interesting. It does, of course, possess an exact two-fold axis of symmetry in accordance with the space-group requirements. This axis is perpendicular to the (110) crystal plane and it passes through the central sulphur atom, S_2. Two views of the molecule are shown in Fig. 2, representing projections along the symmetry axis, and at right angles to that axis. The chain is almost fully extended but the atoms do not all lie in one plane. In fact, the plane of the central sulphur zigzag is nearly at right angles to the plane of the carbon–carbon–iodine zigzag. Starting from an original *trans*-planar configuration, the present model may be derived by making a very small rotation about the S_1S_2 bond, a larger rotation about the C_2S_1 bond, and finally a rotation of about 90° about the C_1C_2 bond.

Intermolecular Distances.—The measured intermolecular distances are shown in Fig. 3. The molecules are so packed that the iodine–iodine approach is never less than 4·4 A. The shortest iodine–sulphur intermolecular distance is 3·80 A., this being the distance from an iodine atom to the terminal sulphur atom of the S–S–S chain in the adjacent molecule. The distance from iodine to the central sulphur atom in the chain is 3·85 A.

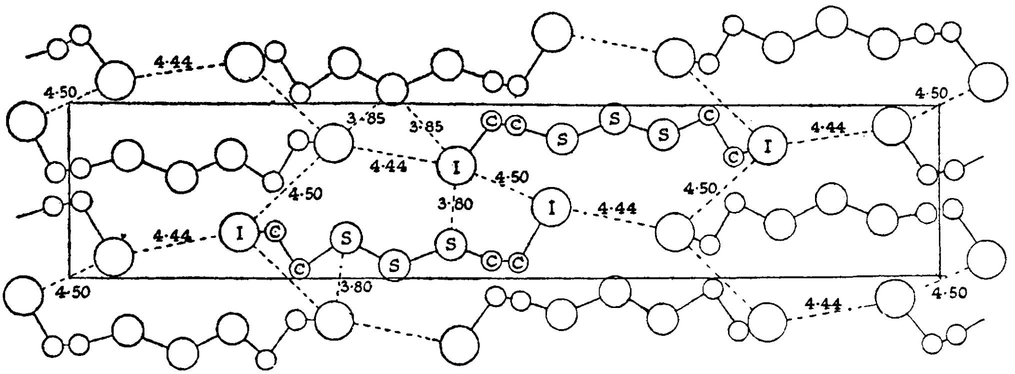
DISCUSSION.

The sulphur–sulphur bond length found is shorter than that reported for orthorhombic sulphur (Warren and Burwell, *J. Chem. Physics*, 1935, **3**, 6) or by electron-diffraction study of sulphur vapour (Maxwell, Hendricks, and Moseley, *Physical Rev.*, 1936, **49**, 199; Lu and Donohue, *J. Amer. Chem. Soc.*, 1944, **66**, 818). These investigations favour the higher value of 2·12 A. The value of 2·04 A. has, however, been reported for dimethyl disulphide, studied by the electron-diffraction method by Stevenson and Beach (*ibid.*, 1938, **60**, 2872). We thus have both *X*-ray and electron-diffraction evidence confirming a decrease in bond length of about 0·08 A. in the polysulphides as compared with sulphur itself.

In the present structure the S–S–S bond angle of about 113° is somewhat larger than the values previously reported, which vary from 100° to about 106°.

The intermolecular distances found are in good agreement with those previously reported for sulphur and iodine. The observed iodine van der Waals radius of 2·22 A., when subtracted from the sulphur–iodine approach, gives a van der Waals radius for sulphur of 1·58 A. Warren and Burwell in their investigation of orthorhombic sulphur (*loc. cit.*) found a value of 1·65 A.

FIG. 3.



Intermolecular distances in the 2 : 2′-*di-iododiethyl trisulphide structure.*

Both these values are less than the sulphur ionic radius of 1·85 A., but the analogy between ionic and van der Waals radii is not likely to be so good for bivalent as for univalent ions (see also Pauling, " Nature of the Chemical Bond ", Cornell, 1939, p. 174).

EXPERIMENTAL.

Crystallisation.—Specimens of 2 : 2′-di-iododiethyl trisulphide were obtained from C.D.E.S., Porton. These were recrystallised from alcohol–benzene solution and yielded flat rectangular plates, m. p. 110°.

Intensity Measurements.—On account of high absorption (μ = 551 per cm. for Cu-$K\alpha$ radiation) special precautions were necessary. It was found that the crystal specimens could readily be cut to uniform cross-sectional area. That used for intensity measurements was in the form of a lath, 0·13 mm. by 0·13 mm., and of length 0·65 mm., so that the necessity for absorption corrections was reduced for the ($h0l$) zone. The effect of the high absorption was further decreased by taking several series of films from crystals of slightly varying cross-sectional area and making a comparison of the intensities measured. Crystals were completely immersed in a beam of filtered copper radiation, and the reflections recorded photographically by means of a moving-film camera, using the multiple-film technique (Robertson, *J. Sci. Instr.*, 1943, **20**, 175). The absolute scale of the F values was not determined directly but was obtained by correlation with the calculated F values. The atomic scattering factor adopted for iodine was taken as a mean of the Thomas–Fermi scattering factors (" International Tables for the Determination of Crystal Structure ", p. 572) and the Pauling–Sherman scattering factors (*Z. Krist.*, 1932, **81**, 1). An arbitrary temperature correction was applied by means of the Debye–Waller temperature factor (" International Tables ", p. 570), using for the value of Θ the characteristic temperature given for crystalline iodine. The sulphur contribution was then weighted $\frac{2}{7}$ on this scale, and the carbon contribution was ignored in the evaluation of calculated structure factors. This rather empirical treatment was found to be sufficiently accurate for the determination of the trial structure, and in the final comparison of experimentally observed with calculated structure factors (Table III), the agreement is reasonably good.

Fourier Analysis.—The electron density on the *ac* plane (010) was computed at 900 points on the asymmetric unit. The *a* axis was subdivided into 30 parts and the *c* axis into 120 parts, the intervals along *a* being 0·200 A., and along *c* 0·245 A. The usual formula for ρ (x, z) was employed, the summation being carried out by means of 3-figure strips of cosine factors and a mechanical sorting device (Robertson, *J. Sci. Instr.*, 1948, **25**, 216). This method is designed to give full 3-figure accuracy with

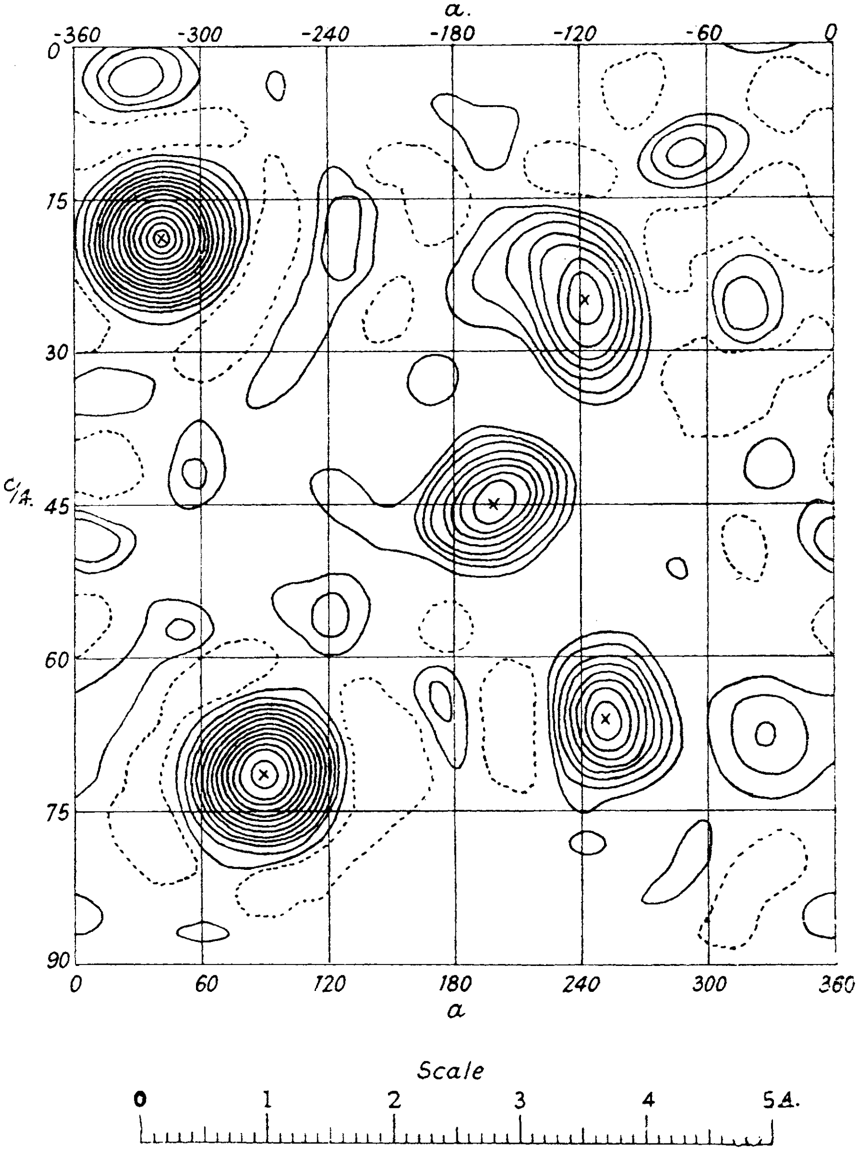
TABLE III.

Measured and calculated values of the structure factor.

hkl.	sin θ (λ = 1·54).	F, meas.	F, calc.
004	0·105	33	+29
008	0·211	427	−424
0012	0·316	270	−275
0016	0·421	294	+282
0020	0·525	184	+172
0024	0·632	< 56	−6
0028	0·738	139	−134
101	0·130	81	+77
102	0·138	147	−124
103	0·150	81	+145
104	0·166	33	+64
105	0·184	81	+34
106	0·203	270	−275
107	0·224	107	−110
108	0·246	< 33	+32
109	0·269	147	−150
1010	0·293	41	−28
1011	0·317	74	−96
1012	0·341	41	−36
1013	0·365	57	−24
1014	0·390	229	+223
1015	0·415	< 44	−30
1016	0·440	< 45	−30
1017	0·466	< 46	+36
1018	0·491	179	+156
1019	0·516	115	+132
1020	0·542	< 48	+9
1021	0·568	117	+97
1022	0·594	156	−144
1023	0·620	< 55	+12
1024	0·645	< 56	+34
1025	0·671	< 56	−32
1026	0·697	148	−149
1027	0·723	< 57	−45
1028	0·749	< 57	+10
1029	0·775	< 56	−43
1030	0·800	< 56	+39
200	0·256	205	−199
201	0·258	131	−89
202	0·261	197	+197
203	0·268	222	−165
204	0·277	82	−82
205	0·287	222	−181
206	0·301	82	−97
207	0·315	156	−141
208	0·331	220	+245
209	0·349	< 41	−52
2010	0·367	196	−200
2011	0·386	90	+97
2012	0·407	57	+33
2013	0·427	155	+112
2014	0·449	< 44	+1
2015	0·471	164	+167
2016	0·493	< 45	−67
2017	0·516	70	+82
2018	0·539	131	+134
2019	0·562	< 49	−41
2020	0·586	107	−97
2021	0·610	73	−23
2022	0·634	82	+56
2023	0·658	90	−89
2024	0·682	< 55	+1
2025	0·707	91	−92
2026	0·731	91	−67
2027	0·756	82	−20
2028	0·781	< 56	+24
301	0·385	57	−46
302	0·387	41	+24
303	0·392	82	−63
304	0·398	270	−257
305	0·406	< 44	+31
306	0·415	< 44	−23
307	0·426	< 45	−16
308	0·438	156	−137
309	0·451	< 46	0
3010	0·465	46	+46
3011	0·481	123	+121
3012	0·497	171	+152
3013	0·514	74	+46
3014	0·532	74	−34
3015	0·551	< 50	0
3016	0·570	196	+191
3017	0·588	< 52	−25
3018	0·610	< 53	−3
3019	0·631	62	−67
3020	0·652	< 54	−39
3021	0·672	< 55	−35
3022	0·695	< 56	−42
3023	0·717	< 56	−41
3024	0·739	163	−145
3025	0·762	< 56	−17
3026	0·785	< 55	−47
400	0·512	< 47	+22
401	0·512	< 47	−24
402	0·514	246	−224
403	0·518	66	−30
404	0·523	< 48	−19
405	0·530	< 49	−59
406	0·536	115	+119
407	0·544	< 50	−26
408	0·551	< 50	+19
409	0·564	106	−26
4010	0·575	270	+230
4011	0·588	< 52	−34
4012	0·601	< 53	−21
4013	0·616	57	+85
4014	0·631	< 53	0
4015	0·647	< 54	+19
4016	0·663	< 54	+13
4017	0·680	< 55	−5
4018	0·698	180	−156
4019	0·716	< 56	+13
4020	0·734	< 56	−8
4021	0·753	< 56	−17
4022	0·773	< 56	−90
4023	0·793	< 55	−27
501	0·640	115	−117
502	0·642	< 53	−25
503	0·645	< 54	−11
504	0·649	98	+104
505	0·653	< 54	−12
506	0·659	82	−60
507	0·666	82	+74
508	0·673	82	+69
509	0·682	107	+98
5010	0·692	58	+49
5011	0·702	82	−47
5012	0·714	56	−64
5013	0·725	< 56	+50
5014	0·738	< 56	+33
5015	0·752	57	−40
5016	0·766	90	−96
5017	0·781	74	−74
5018	0·799	< 56	+19

cell-side subdivision into 120 parts (3° intervals). The positions of the contour lines were obtained by graphical interpolation from the summation totals by making sections of the rows and columns. The resulting contour map is shown in Fig. 1, and an enlargement of a portion of it is given in Fig. 4.

FIG. 4.



One quarter of the unit cell, showing co-ordinates assigned to atoms. The zero-electron line is dotted. Each contour line represents an increase of 2 *electrons per* A.^{2}, *except for the iodine atoms where the increment is* 5 *electrons per* A.^{2}. *The* 2-*electron line is omitted throughout.*

Diffraction Effects.—It is clear from Fig. 4 that diffraction effects in the Fourier projection are of an order sufficient to preclude any observation of the carbon positions. The method of removing these effects adopted in the study of platinum phthalocyanine (Robertson and Woodward, *loc. cit.*) has not been attempted here because of the uncertain state of the sulphur and carbon scattering curves in compounds of this type, and the less accurate intensity estimations due to high absorption in the crystal. Spurious density maxima, rising to eight electrons per A.^{2}, are present near the iodine and the sulphur atom, but these effects are small compared with the iodine and sulphur peak values of about 70 and 20 electrons per A.^{2}, respectively.

Structure Factor Tables.—The co-ordinates of Table I and Fig. 4 were used for a final calculation of the structure factors of all the planes. The results are collected in Table III under " F, calc." The agreement between the observed and calculated values of F, expressed in the usual way as a sum of all the discrepancies divided by the total of the measured structure factors, is 14·8% for the (*h*0*l*) reflections actually observed. If the absent reflections are included in the count, at their limiting, or " $<$" values, this figure is improved to 11·4%.

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