Crystal Structure of the Addition Compound $SbI_3 : 3\ S_8$

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The crystal structure of the addition compound containing antimony triiodide and molecular sulphur in the proportion 1:3 has been determined from three-dimensional X-ray data. The primitive rhombohedron contains one formula unit and the space group is *R*3*m*. The edges of the hexagonal unit cell are:

$$a = 24.817 \pm 0.007 \text{ Å}; \quad c = 4.4279 \pm 0.0016 \text{ Å}.$$

These lattice constants correspond to a theoretical density of 2.681 $g.cm^{-3}$. The measured density was 2.65 $g.cm^{-3}$.

The antimony triiodide molecules are situated on trigonal axes, the sulphur molecules in mirror planes and with their chief axes nearly parallel to the chief axis of the crystal. Each iodine atom is attached to a sulphur atom of a particular S_8 molecule with an I—S distance of 3.60 Å and an angle Sb—I—S of 169.4°. Additional short intermolecular distances also occur, however: Each antimony atom has three iodine neighbours at a distance of 3.85 Å, all belonging to the nearest antimony triiodide molecule situated on the same trigonal axis. Further, each iodine atom has two pairs of sulphur neighbours at a distance of 3.78 resp. 3.88 Å. It appears likely that these short distances indicate interactions which may contribute substantially to the remarkable stability of the crystals.

DETERMINATION OF THE STRUCTURE

The first observation which might have led to the suggestion of bonds in solids connecting halogen atoms of halide molecules and atoms possessing lone pair electrons is probably the striking crystallographic resemblance between the (trigonal) 1:3 addition compounds containing iodoform or antimony triiodide and sulphur (S_8), resp. quinoline. A tentative explanation of this similarity as depending on charge transfer bonds formed between the three iodine atoms of a particular iodoform or antimony triiodide molecule and three sulphur or nitrogen atoms belonging to its three partner molecules was, however, put forward in the year 1957 [1]. Since that time the results of crystal structure determinations dealing with the iodoform-quinoline [2] and iodoform-sulphur [3] compounds have been published, investigations which actually proved the existence of the suggested charge transfer bonds .In both cases a nearly linear C—I– – –S (C—I– –N) arrangement was observed, and the I—S (I—N) separations turned out to be about 0.5 Å shorter than those to be expected for regular van der Waals interactions. In the case of the iodoform-sulphur compound the presence of additional, rather short iodine-sulphur separations were also indicated which might be interpreted as resulting from an interaction between iodine and sulphur atoms, stronger than that resulting from regular van der Waals forces.

These findings made us think that a three-dimensional crystal structure determination of the compound formed by antimony triiodide with three molecules of sulphur would be worth while. It would also appear possible to decide whether or not the Sb—I bond distance deviates from the corresponding distance in the free antimony triiodide molecule.

Crystals of the antimony triiodide-sulphur compound, obtained by evaporating the solvent (carbon disulphide) from a solution containing the two molecular species in a proportion considerably smaller than 1:3, turned out to be well suited for X-ray examination.

The melting point of these intensively yellow-coloured crystals was 116—118°C, their density as determined by the flotation method 2.65 g-cm^{-3}. The section of the needle perpendicular to their axes was that of a regular hexagon. Because of the sensitivity of the crystals towards moist air it was found necessary to keep the crystals in sealed thinwalled capillary tubes during the exposures, at least when accurate intensity measurements were desired. Two crystals were selected for this part of the work, both having a length of about 0.40 mm and a diameter of approximately 0.08 mm. One crystal was reserved for Weissenberg diagrams, the other for exposures in the Buerger precession camera.

The (hexagonal) lattice parameter deduced from oscillation and Weissenberg diagrams using filtered Cu$K\alpha$ radiation were:

$$a = 24.79 \text{ Å} \qquad c = 4.44 \text{ Å}$$

These values correspond to a rhombohedral cell with axes equal to 14.39 Å and a rhombohedral angle $\alpha = 119°$.

The space group determined from Weissenberg pictures with rotation about the principal axis — $R3m$ — agrees with that given by West [4]. As a fairly accurate determination of atomic distances was intended, it was felt that an accurate determination of the crystallographic parameters should be carried out. This determination was performed employing a multiple Guinier camera with an asymmetric quartz monochromator, using potassium chloride as a reference substance and Cu$K\alpha$ radiation. The values thus obtained were:

$$a = 24.817 \pm 0.0074; \qquad c = 4.4279 \pm 0.0016.$$

The intensity material collected consisted of integrated zero layer line Weissenberg diagrams (Cu$K\alpha$-radiation and Mo$K\alpha$-radiation) and a set of equi-inclination integrated Weissenberg diagrams also taken with filtered Mo radiation and with rotation about the trigonal axis. The multiple film method was used with four films (Ilford Industrial G) separated by tin-foils. In order to correct intensities of strongly deformed reflections the method described by Phillips [5] was employed and for this purpose non-integrated Weissenberg diagrams had to be produced. In order to bring the measured intensities on a common scale intensity values obtained from zero layer precession diagrams were taken with Mo radiation along three crystallographic directions having

Table 1. Observed (F_o) and calculated (F_c) structure factors and phase angles α (in radians). In order to bring F_o-values on an absolute scale the values given should be multiplied with the factor three. For unobserved reflexions the F_o-value corresponding to the minimum observable value is given. (Indices hexagonal).

h k l	F_o	F_c	α
0 3 0	63.46	50.98	0.169
6	129.19	122.55	2.194
9	46.51	37.59	4.113
12	116.67	108.22	4.202
15	47.01	44.57	1.594
18	72.59	75.74	0.140
21	35.71	38.68	0.022
24	41.14	45.78	0.969
27	22.86	15.72	4.936
1 1	93.22	83.18	0.000
4	49.05	45.02	1.179
7	70.48	65.99	1.761
10	42.58	40.81	5.161
13	100.28	91.57	4.858
16	69.83	67.18	0.043
19	58.41	57.70	0.167
22	26.14	26.14	0.967
25	27.04	29.58	2.044
28	<20.71	11.99	5.584
2 2	64.96	54.50	0.000
5	171.22	161.01	1.305
8	36.92	36.39	0.644
11	55.43	51.65	4.716
14	47.45	45.64	5.256
17	71.99	71.96	6.222
20	<16.72	12.34	1.724
23	21.76	22.10	2.354
26	23.65	24.07	6.209
3 3	17.12	12.91	0.000
6	65.39	62.26	0.529
9	109.64	100.20	5.670
12	55.92	50.17	1.688
15	41.32	39.39	0.156
18	57.04	58.62	5.556
21	<14.61	14.22	3.861
24	27.13	30.07	0.790
27	<20.76	10.04	5.496
4 4	20.49	18.88	0.000
7	109.07	101.30	5.906
10	19.77	21.89	0.504
13	69.61	63.84	0.971
16	23.30	28.34	0.730
19	57.43	54.03	4.740
22	<18.44	10.30	0.529
25	28.35	35.64	6.214
5 5	147.40	137.61	0.000
8	47.01	46.94	0.037
11	51.21	47.17	2.120
14	54.49	42.73	1.780
17	<16.17	19.11	4.138
20	21.04	23.90	5.227
23	38.37	43.12	0.023
26	33.95	40.35	6.098
6 6	164.94	157.03	0.000
9	83.73	77.14	0.113
12	34.06	34.07	1.786
15	<15.50	12.76	0.698
18	28.85	31.05	4.652
21	<18.60	12.24	1.233
24	30.12	37.68	6.266
7 7	127.08	116.02	0.000
10	82.06	75.72	2.161
13	48.00	46.25	1.432
16	47.45	48.01	4.646
19	28.64	30.69	4.916
22	39.64	44.53	5.962
25	<21.04	20.54	0.094
8 8	117.07	104.91	0.000
11	22.04	20.26	1.524
14	34.83	35.94	0.750
17	24.20	25.62	5.268
20	26.64	26.62	4.803
23	24.20	29.73	0.691
9 9	29.58	25.66	0.000
12	24.59	27.00	0.208
15	51.11	48.50	4.879
18	<18.22	12.40	0.868
21	<19.71	15.30	0.788
24	26.02	19.57	5.996
10 10	34.94	28.39	0.000
13	65.83	66.23	0.405
16	17.99	18.38	0.292
19	34.83	38.27	1.578
22	22.86	25.23	5.987
11 11	62.63	59.62	0.000
14	49.67	52.54	6.163
17	<18.55	13.83	0.754
20	22.21	22.57	1.300
23	<21.54	8.99	5.052
12 12	63.79	64.65	0.000
15	29.74	31.23	6.200
18	30.17	32.23	1.723
21	<20.93	8.32	6.005

h k l	F_o	F_c	α
13 13	52.17	51.78	0.000
16	27.62	28.40	2.126
19	22.59	24.38	1.526
22	<21.87	8.24	5.057
14 14	<18.44	3.03	0.000
17	<19.82	11.69	2.275
20	<21.32	18.24	5.271
15 15	37.81	37.82	0.000
18	<20.76	15.84	0.923
21	<22.20	17.10	5.766
16 16	<20.26	20.03	0.000
19	24.92	28.71	6.097
17 17	25.19	23.57	0.000
20	26.81	29.50	0.072
18 18	24.53	27.22	0.000
0 2 1	129.78	201.72	0.890
5	204.78	194.12	2.051
8	127.56	117.43	2.729
11	97.29	89.78	4.015
14	27.36	30.13	4.907
17	50.42	42.54	0.616
20	27.36	28.31	1.062
23	32.06	32.81	2.110
26	45.30	47.21	1.346
29	<25.05	22.38	3.531
1 0	33.96	39.64	0.186
3	89.06	84.57	1.653
6	147.19	138.62	1.978
9	47.25	41.26	1.575
12	59.81	59.13	3.035
15	32.69	30.92	0.165
18	33.54	35.04	0.013
21	30.64	30.32	2.142
24	43.46	48.86	2.173
27	<24.13	16.27	2.996
2 1	41.56	31.03	6.025
4	102.52	94.83	2.769
7	97.45	91.34	1.904
10	71.99	64.84	3.773
13	55.11	55.44	3.186
16	56.85	52.42	0.820
19	40.34	43.83	0.125
22	52.74	58.85	2.318
25	<23.21	18.95	1.579
28	33.01	12.12	4.866
3 2	21.25	23.04	2.806
5	91.49	81.57	1.250
8	14.18	10.99	2.680

h k l	F_o	F_c	α
11	33.65	29.04	3.944
14	82.95	79.11	2.091
17	20.88	20.89	2.190
20	<20.44	27.32	2.140
23	<22.23	18.80	1.748
26	<24.20	20.74	0.933
4 0	65.86	66.91	3.627
3	142.44	128.00	2.269
6	68.61	63.69	0.297
9	61.39	55.51	0.230
12	49.63	47.49	2.426
15	61.49	62.09	1.842
18	27.06	27.71	3.570
21	<21.43	18.83	2.887
24	<23.34	21.24	1.076
27	<25.18	10.25	0.853
5 1	148.24	136.31	3.885
4	30.33	24.50	2.606
7	132.57	121.29	0.518
10	87.03	80.16	2.424
13	97.24	94.17	2.133
16	26.53	23.64	0.009
19	38.76	40.63	3.871
22	<22.48	16.24	1.117
25	<24.33	16.30	0.737
6 2	19.78	20.23	2.789
5	75.83	72.81	0.470
8	92.87	81.74	1.231
11	88.91	86.87	1.433
14	44.98	42.57	1.962
17	38.93	42.46	3.568
20	37.70	37.29	3.859
23	<23.47	5.41	0.938
7 0	69.56	64.87	4.442
3	11.67	13.24	5.128
6	63.02	60.73	0.207
9	47.09	40.95	2.434
12	86.50	83.87	2.208
15	29.53	27.69	3.179
18	<20.83	18.53	3.533
21	30.22	29.43	1.177
24	35.70	35.28	0.219
8 1	20.72	18.92	3.646
4	77.20	72.08	0.285
7	17.14	15.78	5.198
10	88.23	85.46	1.844
13	66.34	62.48	2.391
16	24.99	24.29	3.071
19	33.01	34.07	2.595
22	31.17	30.36	0.429
9 2	109.64	100.11	2.315
5	46.15	42.34	1.069

h	k l	F_o	F_c	α
	8	40.87	38.07	3.146
	11	38.66	37.27	1.543
	14	24.47	22.88	0.177
	17	22.57	20.91	4.090
	20	28.16	29.30	1.767
	23	<24.79	8.36	1.191
10	0	109.32	99.94	2.132
	3	34.34	33.51	1.683
	6	48.47	46.15	2.507
	9	27.58	27.63	3.029
	12	44.45	39.85	0.664
	15	28.69	28.98	1.060
	18	23.25	23.51	2.655
	21	<24.06	21.60	2.293
11	1	145.71	137.33	1.944
	4	41.65	39.31	0.965
	7	65.33	61.07	4.118
	10	<18.20	18.73	1.615
	13	48.83	50.86	6.196
	16	22.10	21.58	2.159
	19	38.23	42.63	2.042
	22	<25.12	17.22	2.142
12	2	84.85	82.35	2.515
	5	86.69	81.28	4.247
	8	33.43	33.45	4.017
	11	57.64	57.18	1.241
	14	<20.97	15.59	0.390
	17	37.12	40.06	1.941
	20	<24.46	21.01	1.549
13	0	59.75	60.18	1.594
	3	68.76	65.68	2.756
	6	41.56	41.05	3.385
	9	<18.86	20.17	1.612
	12	28.53	28.52	0.182
	15	43.13	43.64	1.580
	18	32.06	32.53	2.333
14	1	52.95	53.67	1.999
	4	27.22	28.06	3.419
	7	35.33	35.12	3.481
	10	40.03	41.29	0.291
	13	22.94	22.97	0.313
	16	42.18	44.85	2.336
	19	<24.85	21.65	1.477
15	2	31.59	31.70	6.281
	5	37.65	37.41	2.581
	8	38.29	40.37	1.501
	11	24.53	24.44	2.209
	14	23.15	23.84	3.149
	17	<24.26	19.72	1.628

h	k l	F_o	F_c	α
16	0	37.65	39.84	1.445
	3	22.31	19.81	0.453
	6	30.85	32.29	1.306
	9	<20.57	17.74	1.421
	12	<22.09	15.11	4.456
	15	24.79	26.39	3.448
17	1	60.34	56.68	0.584
	4	61.70	59.93	2.131
	7	64.07	64.43	2.074
	10	<21.69	10.42	3.230
	13	<23.21	4.91	4.052
	16	<24.79	14.24	2.708
18	2	30.75	28.95	5.780
	5	46.04	52.73	2.283
	8	60.59	60.75	2.053
	11	<22.75	20.85	3.701
	14	<24.33	21.32	2.826
19	0	53.27	53.53	0.300
	3	20.24	19.92	1.707
	6	62.17	65.28	2.283
	9	23.89	21.34	2.754
	12	<23.87	18.49	3.803
20	1	41.09	45.06	1.290
	4	39.17	42.41	2.149
	7	27.41	30.11	1.632
	10	<23.47	15.85	3.096
	13	<24.92	4.86	2.183
21	2	<20.64	17.14	3.476
	5	27.89	28.80	1.560
	8	29.59	28.44	5.770
	11	<24.53	17.07	3.738
22	0	37.07	29.55	3.330
	3	<21.62	11.82	1.343
	6	<22.88	15.87	1.649
	9	<24.20	16.20	1.604
23	1	39.28	37.23	3.823
	4	<22.68	5.62	1.656
	7	<23.92	13.38	0.169
	10	<25.25	19.72	1.565
24	2	<22.55	5.44	2.231
	5	27.69	25.73	0.794
	8	<24.99	16.20	0.970
25	0	45.30	44.39	5.388
	3	<23.54	7.76	0.417
	6	34.18	36.54	0.429
26	1	<23.47	3.50	3.904
	4	<24.59	9.38	0.290

h	*k l*	F_o	F_c	α
27	2	33.81	35.80	1.880
28	0	<24.46	22.72	2.641
0	1 2	67.74	84.47	5.882
	4	35.39	34.87	2.869
	7	68.15	66.65	2.613
	10	70.86	98.95	4.189
	13	104.30	99.01	4.497
	16	<18.03	6.66	2.277
	19	51.45	51.39	0.233
	22	41.52	43.32	3.088
	25	<30.22	27.44	2.532
	28	<26.04	2.30	5.617
1	2	25.00	18.47	4.797
	5	127.61	119.69	2.137
	8	32.15	29.21	3.029
	11	101.80	94.72	4.087
	14	55.51	53.94	3.631
	17	51.04	51.99	5.634
	20	<21.03	26.15	4.165
	23	<23.05	20.84	2.496
	26	<25.07	12.51	3.565
2	0	35.74	35.31	5.615
	3	68.62	64.19	3.123
	6	25.86	22.91	4.057
	9	57.47	53.72	4.066
	12	58.78	55.32	4.053
	15	<18.10	6.72	2.827
	18	<20.05	20.36	5.671
	21	<22.07	11.80	3.341
	24	<24.09	26.79	2.281
	27	<26.11	27.90	4.459
3	1	70.97	65.32	4.471
	4	88.44	81.83	3.739
	7	67.34	60.44	1.459
	10	59.45	56.23	3.984
	13	31.70	28.83	3.466
	16	<19.15	18.07	5.686
	19	33.44	37.16	4.381
	22	<23.12	27.30	3.454
	25	<25.14	7.68	4.864
4	2	87.42	82.36	3.827
	5	58.48	53.73	3.040
	8	50.85	48.56	5.551
	11	<16.29	14.85	2.003
	14	<18.24	18.20	2.295
	17	36.36	38.58	3.994
	20	47.36	54.91	4.098
	23	<24.23	0.92	4.573
5	0	78.35	86.14	4.358
	3	89.97	84.28	4.943
	6	75.86	72.31	5.397
	9	35.85	33.20	4.950
	12	76.76	72.07	2.598
	15	47.62	47.59	3.450
	18	<21.31	25.77	3.699
	21	<23.33	12.67	3.614
	24	<25.28	24.12	0.313
6	1	127.65	122.73	4.080
	4	67.55	60.74	0.048
	7	53.81	52.99	5.850
	10	62.07	58.89	3.119
	13	47.82	47.66	2.683
	16	<20.47	37.94	4.295
	19	50.44	57.77	3.867
	22	<24.44	12.38	5.412
7	2	92.12	83.85	4.192
	5	57.05	54.70	5.990
	8	25.29	24.60	5.978
	11	48.94	49.32	2.560
	14	<19.71	22.68	1.724
	17	56.47	61.25	4.408
	20	<23.54	22.03	3.856
	23	<25.49	4.99	1.519
8	0	138.57	129.35	3.158
	3	<13.72	24.01	0.107
	6	32.15	33.64	4.632
	9	17.57	19.80	2.512
	12	39.08	38.17	1.889
	15	53.35	53.68	4.347
	18	49.46	51.42	4.228
	21	<24.65	15.63	5.268
9	1	25.71	25.03	4.353
	4	<14.90	17.99	0.280
	7	35.39	34.02	4.450
	10	43.74	46.34	3.560
	13	<20.12	24.37	0.004
	16	<22.00	17.76	4.342
	19	<23.83	25.11	3.037
	22	<25.83	2.47	2.432
10	2	41.28	35.86	2.708
	5	68.87	65.91	4.503
	8	73.95	72.87	3.850
	11	38.31	36.18	3.521
	14	<21.31	19.28	5.864
	17	<23.12	26.37	3.053
	20	<25.00	11.28	1.761
11	0	75.43	70.24	2.698
	3	50.70	48.95	2.920
	6	59.97	57.65	4.351
	9	<18.94	12.90	4.813
	12	38.15	39.85	5.101
	15	<22.42	12.58	4.245
	18	<24.30	26.82	2.874

h	$k\,l$	F_o	F_c	α
12	1	67.74	64.31	2.781
	4	63.65	62.91	3.792
	7	69.69	66.95	4.214
	10	41.73	38.90	5.806
	13	<21.79	15.42	0.268
	16	<23.61	17.54	3.407
	19	<25.42	25.40	2.434
13	2	43.58	40.27	1.850
	5	91.92	89.11	4.013
	8	40.56	43.59	3.722
	11	37.90	36.61	5.958
	14	<22.98	19.03	4.939
	17	<24.79	23.78	2.608
14	0	30.78	25.89	2.895
	3	49.46	46.28	4.412
	6	26.27	29.68	4.387
	12	<22.42	28.94	5.999
	15	<24.16	20.73	3.748
	18	<25.90	21.81	2.599
15	1	<17.69	15.00	4.783
	4	55.51	57.00	4.028
	7	49.30	46.75	3.141
	10	<21.93	25.82	5.370
	13	35.53	31.69	3.853
	16	<25.28	16.14	3.691
16	2	38.56	36.72	5.408
	5	20.48	21.75	4.999
	8	36.36	36.70	2.451
	11	<23.05	14.77	4.963
	14	<24.72	38.73	3.769
17	0	44.24	41.73	5.930
	3	<19.85	17.20	3.753
	6	55.21	53.84	2.832
	9	<22.63	25.88	3.379
	12	38.31	38.34	4.191
	15	<25.90	7.28	6.086
18	1	28.22	22.12	0.666
	4	<20.89	18.20	2.286
	7	<22.28	18.32	2.357
	10	<23.81	25.11	4.062
	13	<25.42	38.21	4.032
19	2	<20.75	14.74	5.734
	5	31.49	33.45	2.173
	8	<23.40	10.88	4.212
	11	<24.93	34.89	4.365
20	0	59.75	56.78	5.186
	3	<21.79	28.15	2.953
	6	36.57	36.71	2.780
	9	<24.51	24.02	3.773
	12	<26.04	31.03	3.941
21	1	32.10	31.41	4.092
	4	<22.91	20.45	3.542
	7	<24.23	14.98	4.914
	10	<25.69	1.21	5.384
22	2	47.27	48.88	3.712
	5	<23.95	7.69	1.274
	8	<25.35	18.12	4.871
23	0	32.46	30.14	4.660
	3	<23.81	22.44	4.351
	6	<25.07	21.46	0.412
24	1	35.02	37.52	4.173
	4	<24.86	16.19	5.227
25	2	<24.79	35.05	3.803
	5	<25.97	17.15	5.871
26	0	<24.72	23.87	4.617
	3	<25.83	6.01	3.827
27	1	<25.76	10.39	3.332
0	0 3	141.24	170.11	6.157
	3	33.72	30.80	0.367
	6	35.76	34.17	1.405
	9	22.63	20.96	4.451
	12	52.50	49.96	4.268
	15	31.38	31.06	0.404
	18	28.92	27.61	6.200
	21	31.80	33.29	0.413
1	1	65.85	69.55	6.179
	4	< 9.18	14.73	2.760
	7	76.62	73.19	2.124
	10	45.13	39.61	5.205
	13	58.56	53.50	4.679
	16	54.27	55.15	6.238
	19	48.79	51.83	6.027
	22	<22.13	4.27	0.800
2	2	32.05	30.56	6.127
	5	42.30	40.65	1.248
	8	44.61	42.71	6.061
	11	29.29	28.05	5.069
	14	27.60	26.00	5.088
	17	32.31	31.74	6.270
	20	<21.25	18.69	4.793
3	0	51.46	45.86	5.915
	3	< 9.78	7.45	1.353
	6	64.48	60.17	6.047
	9	51.61	48.64	5.471
	12	29.79	26.96	3.396
	15	32.05	27.85	6.264
	18	32.36	34.24	5.504
	21	<22.27	9.24	1.747

h	$k\,l$	F_o	F_c	α
4	1	55.63	51.59	4.688
	4	31.33	30.83	0.582
	7	58.09	54.95	5.552
	10	21.45	20.28	5.788
	13	35.14	36.19	1.233
	16	27.19	26.99	0.513
	19	40.95	39.09	4.657
5	2	79.02	72.00	4.095
	5	67.92	65.88	0.144
	8	40.31	40.23	0.013
	11	<16.76	20.08	1.043
	14	38.65	37.63	1.683
	17	34.40	32.86	5.051
	20	<22.40	16.45	4.607
6	0	110.97	103.91	3.995
	3	29.79	28.88	4.737
	6	98.77	91.35	0.057
	9	44.38	43.85	0.452
	12	25.78	24.91	1.609
	15	26.25	25.60	5.479
	18	37.65	35.97	4.903
7	1	56.22	52.95	5.561
	4	68.07	63.86	6.095
	7	69.70	66.29	6.109
	10	32.78	30.19	2.183
	13	<18.96	18.11	1.079
	16	<20.78	14.33	3.264
	19	<22.67	22.21	4.889
8	2	24.16	24.47	4.103
	5	59.30	55.14	6.068
	8	60.71	57.10	5.358
	11	<18.22	7.57	2.075
	14	<20.04	23.49	0.748
	17	27.60	26.13	4.811
9	0	16.32	13.86	4.924
	3	47.06	46.26	0.466
	6	44.71	42.60	0.040
	9	<17.61	16.27	1.168
	12	22.28	23.52	5.886
	15	26.32	28.01	5.307
	18	<23.01	4.86	5.268
10	1	25.83	26.19	1.144
	4	28.59	25.35	5.428
	7	37.49	37.68	4.478
	10	24.01	22.29	0.346
	13	39.78	45.09	5.977
	16	<22.27	16.22	5.511
11	2	39.02	37.51	1.793
	5	35.34	33.65	4.291
	8	29.79	29.24	4.813
	11	44.65	47.24	0.368
	14	43.45	47.12	5.935
	17	<23.41	0.28	4.096
12	0	43.91	44.83	1.658
	3	45.44	43.94	4.937
	6	25.99	30.39	4.580
	9	23.01	23.11	5.012
	12	43.67	46.14	0.162
	15	<22.74	8.49	5.341
13	1	35.87	32.28	1.197
	4	35.14	35.04	5.110
	7	48.58	45.69	4.518
	10	43.67	45.89	5.863
	13	30.54	32.85	5.826
	16	<23.82	13.58	1.935
14	2	19.82	17.54	0.464
	5	25.36	26.64	5.054
	8	<20.04	11.38	5.905
	11	<21.59	23.38	0.385
	14	<23.28	11.21	5.563
15	0	<17.21	29.09	1.608
	3	39.26	37.19	5.543
	6	24.85	23.32	4.184
	9	22.06	19.66	0.867
	12	33.58	33.90	6.033
16	1	35.14	37.26	0.012
	4	19.82	16.11	0.447
	7	39.11	37.88	0.891
	10	<22.27	7.36	5.528
	13	<23.82	23.94	4.946
17	2	52.65	53.29	6.064
	5	<20.44	16.90	2.753
	8	<21.86	23.73	0.240
	11	<23.33	21.88	4.799
18	0	75.34	73.16	6.041
	3	22.49	25.64	0.644
	6	<21.52	24.04	2.821
	9	<22.94	2.54	5.659
19	1	32.16	29.55	5.724
	4	<21.32	15.73	1.596
	7	<22.67	22.42	1.098
	10	<24.09	16.91	4.941
20	2	21.64	21.83	5.531
	5	<22.40	16.13	1.563
	8	<23.75	18.56	0.012
21	0	36.91	34.27	0.513
	3	<22.20	8.99	0.049
	6	<23.41	9.86	0.465

h	$k\ l$	F_o	F_c	α
22	1	22.58	25.15	4.898
	4	<23.21	11.63	5.184
23	2	<23.14	16.86	4.899
	5	<24.29	29.99	6.614
24	0	36.80	37.52	4.805
	3	<24.16	13.33	5.864
25	1	<24.02	15.48	4.536
0	2 4	87.99	85.28	0.834
	5	94.59	91.07	1.872
	8	30.88	27.62	1.724
	11	35.06	34.91	3.915
	14	21.31	19.97	4.921
	17	<19.76	24.36	1.454
	20	<21.85	7.56	4.328
1	0	32.53	26.29	0.656
	3	18.43	22.86	1.675
	6	50.63	48.42	1.835
	9	24.11	20.91	1.990
	12	<16.62	22.20	4.060
	15	<18.78	23.04	0.921
	18	36.29	35.00	0.364
	21	<22.83	18.91	2.061
2	1	< 7.40	7.82	5.729
	4	51.62	52.81	2.162
	7	31.46	29.47	1.526
	10	26.95	24.31	5.455
	13	41.13	37.20	2.396
	16	23.52	24.64	0.644
	19	<21.85	16.47	0.159
3	2	20.17	17.32	0.994
	5	40.53	39.27	2.162
	8	22.59	21.89	1.135
	11	<16.76	3.12	3.512
	14	36.82	38.39	1.970
	17	<20.95	17.78	0.785
	20	<22.90	4.52	1.989
4	0	29.10	26.86	3.681
	3	21.24	20.95	2.375
	6	42.09	42.65	1.103
	9	28.29	26.35	0.263
	12	23.29	21.68	1.931
	15	31.08	26.44	1.587
	18	<21.99	2.42	3.694
5	1	27.65	24.91	3.435
	4	28.88	27.90	0.478
	7	60.29	57.87	0.440
	10	32.80	31.12	2.978
	13	35.33	38.93	1.888
	16	<21.15	10.91	3.486
	19	<23.11	10.03	3.210
6	2	28.13	24.94	4.021
	5	33.93	32.05	0.018
	8	46.12	43.73	0.794
	11	45.37	46.46	1.592
	14	36.46	26.28	2.023
	17	<22.27	14.33	4.980
7	0	16.76	16.55	4.346
	3	30.23	30.28	1.150
	6	23.57	22.38	0.485
	9	30.92	27.28	1.986
	12	36.72	39.27	2.090
	15	<21.43	3.59	5.727
	18	<23.39	18.74	3.198
8	1	19.26	19.11	2.475
	4	31.08	30.22	0.341
	7	<16.90	22.20	0.901
	10	37.74	37.21	1.530
	13	30.54	30.00	1.576
	16	<22.62	5.13	5.866
9	2	44.24	41.77	1.967
	5	16.76	14.38	1.109
	8	21.91	20.39	2.609
	11	31.90	30.94	1.740
	14	<21.85	10.14	0.333
10	0	26.68	25.98	2.264
	3	24.86	22.97	0.825
	6	<17.66	3.22	0.077
	9	<19.34	9.14	3.442
	12	22.11	21.99	1.438
	15	<22.97	11.57	0.223
11	1	65.60	64.72	1.848
	4	25.18	25.79	1.313
	7	34.36	33.82	4.090
	10	<20.60	24.12	0.481
	13	<22.34	22.55	0.341
12	2	43.28	42.17	2.241
	5	29.36	30.79	4.520
	8	<20.04	18.47	2.555
	11	<21.71	23.74	0.906
	14	<23.46	11.79	1.087
13	0	31.78	32.81	2.385
	3	29.69	28.89	2.336
	6	<19.62	13.78	3.902
	9	<21.22	17.43	1.395
	12	33.88	32.53	0.438
14	1	30.65	28.06	1.326
	4	27.91	24.35	2.947
	7	<20.81	20.25	2.269
	10	<22.41	19.31	0.642

h	$k\ l$	F_o	F_c	α
15	2	23.41	18.18	0.157
	5	<20.46	13.05	4.742
	8	<21.92	24.09	1.448
16	0	30.39	28.15	0.878
	3	<20.18	19.92	1.764
	6	<21.57	17.72	2.229
	9	<23.11	21.79	1.956
17	1	26.36	26.12	0.537
	4	<21.29	26.67	2.028
	7	31.78	34.21	2.184
18	2	21.63	20.52	0.345
	5	40.86	41.02	1.918
19	0	37.22	36.29	0.764
	3	<22.20	9.86	2.358
	6	29.69	30.01	1.868
20	1	<22.13	14.34	0.520
	4	<23.32	10.83	2.155
21	2	<23.18	17.05	2.759
22	0	<23.11	13.61	0.124
0	1 5	34.66	36.72	5.487
	4	21.45	22.25	2.980
	7	40.23	40.85	2.648
	10	36.15	34.50	4.170
	13	49.80	46.88	3.970
	16	<24.84	15.06	0.543
1	2	< 9.72	8.46	2.593
	5	29.44	30.17	2.353
	8	26.32	22.27	2.917
	11	29.39	28.21	3.865
	14	26.08	22.23	3.409
2	0	<21.83	16.34	1.919
	3	29.26	31.60	3.118
	6	<16.18	15.00	2.722
	9	<19.36	21.41	4.580
	12	26.46	23.10	4.126
	15	<24.93	19.70	3.320
3	1	31.40	26.68	4.588
	4	<15.12	18.96	2.762
	7	<18.03	12.46	2.023
	10	30.68	28.00	4.010
	13	<23.78	15.15	3.170
4	2	36.15	39.13	3.986
	5	<16.88	6.79	3.358
	8	<19.80	6.61	3.567
	11	<22.34	17.62	2.808
	14	<25.19	19.69	2.768
5	0	<22.98	21.61	4.206
	3	27.18	26.83	4.126
	6	20.80	19.51	5.243
	9	<21.48	7.52	3.506
	12	31.67	28.95	2.974
6	1	43.23	44.72	3.868
	4	<17.86	14.47	5.892
	7	<20.51	10.29	6.141
	10	23.60	23.68	2.588
	13	32.70	23.82	2.474
7	2	27.57	25.71	3.906
	5	<19.62	9.49	0.556
	8	<22.10	31.38	4.515
	11	31.47	26.49	2.723
8	0	33.36	29.08	3.368
	3	<19.09	8.87	5.391
	6	<21.30	2.71	0.191
	9	<23.78	10.54	3.058
9	1	21.45	19.26	3.213
	4	<20.77	6.31	2.191
	7	26.32	23.92	4.445
	10	<25.28	18.65	3.169
10	2	<20.33	16.94	3.313
	5	<22.37	13.52	4.714
	8	28.21	26.45	3.359
11	0	33.41	31.22	3.036
	3	32.70	29.22	3.135
	6	27.49	23.11	3.618
	9	<26.08	11.67	3.694
12	1	27.77	26.78	2.273
	4	35.04	34.11	3.753
	7	26.59	25.20	4.276
13	2	<23.16	4.46	2.735
	5	32.83	31.10	4.077
14	0	<23.07	18.03	3.122
	3	<24.66	15.64	4.372
15	1	<24.49	11.54	2.642
	4	<26.08	22.45	3.634
16	2	<25.81	9.05	5.534
17	0	<25.72	9.52	0.613

the rhombohedral indices [100], [110], and [1$\bar{1}$0]. In the case of precession diagrams intensities were measured using a recording Speedomax photometer, a Hilger photometer being employed in the case of integrated Weissenberg diagrams. The intensity of the weakest reflections had, however, to be estimated visually, using a standard blackening scale for comparison. On each film all observable reflections were measured or estimated, most of them on several films. In all, intensities of about 5000 individual reflections were measured or estimated.

From a Patterson synthesis along the trigonal axis preliminary values of the iodine coordinates and the projection of the Sb—I distance, and the sulphur coordinates had then to be determined. As found also in the case of the iodoform compound [3] the S_8 rings must be situated in mirror planes, and the short identity period along the trigonal axis (4.43 Å) indicates that even in the antimony triiodide compound the chief axis must be assumed to be nearly parallel to the trigonal axis. Trial and error computations based on this assumption led to an agreement between observed and calculated intensities for the c-axis zone which was thought to be good enough to start two-dimensional least squares calculations for the projection along the trigonal axis using the intensity material obtained with Mo radiation. The final coordinate values thus arrived at led to an R factor of 0.05 with isotropic B values for the S, I, and Sb atoms all lying within the limits 2.21—2.83. A Fourier synthesis based on structure factors computed from these coordinates is reproduced in Fig. 1.

In order to determine atomic coordinates along the trigonal axis a Fourier projection was next computed choosing the edge of the primitive rhombohedron as axis of projection. It was hoped that the z-coordinates derived from this projection might be accurate enough to make possible a direct computation of a three-dimensional least squares refinement. The number of reflections the intensities of which could be estimated in this projection was 81 (out of 84 theoretically possible). Even when we assume that the Sb—I—S angle is close to 180° and that the chief axis of the S_8 ring is nearly parallel to the trigonal axis, some ambiguity regarding the general arrangement along the latter direction still remains. In view of the close agreement so far observed between the present structure and that of the previously examined iodoform sulphur compound it was thought, however, that the arrangement along the trigonal axis would be very similar in both cases. The correctness of this assumption could soon be confirmed. Although the z-coordinates with which the least squares refinement started corresponded to an R factor as high as 0.30 the least squares refinement finally brought it down to $R = 0.082$. The damping factor B was found equal to 2.22 for the antimony atom and the mean values 2.81 and 2.93 were obtained for iodine and sulphur, respectively.

Using the coordinates and B-values derived from the two projections discussed above the R-factor calculated from the complete intensity material was found equal to 0.15. Although a rather high accuracy of initial coordinate values is generally needed for a structure lacking symmetry centres, it was believed that the values obtained by the two-dimensional analyses would prove to be sufficiently accurate to make a three-dimensional least squares refinement successful. The computations were carried out on a Ferranti Mercury computer using a programme worked out by Rollett [6].

Table 2. a) Final atomic coordinates and b) some interatomic distances and angles and their σ values.

a

	x	y	z
Sb	0.0000	0.0000	0.3146
I_1	−0.0551	0.0551	0.0000
S_1	−0.1339	0.1339	−0.2770
S_2	−0.0836	0.2165	−0.0523
S_3	−0.0926	0.2825	−0.2876
S_4	−0.1595	0.2937	−0.0796
S_5	−0.2420	0.2420	−0.3065

b

	distances	σ		angles	σ
Sb−I	2.747 Å	0.002 Å	I−Sb−I	96.56°	0.04°
I−I	4.101 Å	0.002 Å	Sb−I_1−S_1	169.44°	0.10°
I_1−S_1	3.602 Å	0.006 Å	I_1−S_1−S_2	98.79°	0.17°
S_1−S_2	2.047 Å	0.007 Å	S_1−S_2−S_3	107.31°	0.33°
S_2−S_3	2.047 Å	0.008 Å	S_2−S_3−S_4	107.66°	0.35°
S_3−S_4	2.037 Å	0.008 Å	S_3−S_4−S_5	108.57°	0.33°
S_4−S_5	2.054 Å	0.007 Å	S_4−S_5−S_6	108.36°	0.35°
			S_8−S_1−S_2	107.34°	0.35°
$\overline{S-S}$	2.046 Å	0.003 Å	$\overline{S-S-S}$	107.85°	0.23°

In all 49 atomic parameters had to be refined and the number of independent intensity values available was 505. The final coordinate values and interatomic distances, the latter with their standard deviation (σ) values are listed in Table 2. The resulting R factor is 0.068. Standard deviation values for the coordinates were calculated using Cruickshank's formula [7]. As a three-dimensional Fourier synthesis was not performed, it was necessary to use projections of the electron density distribution for this purpose. The $\sigma(z)$ value was found equal to 0.0015 Å for the antimony atom, the same value was obtained for $\sigma(x)$ $\sigma(y)$ and $\sigma(z)$ for iodine, whereas the corresponding values obtained for sulphur were all close to 0.006 Å.

From the B values obtained for the individual atoms it follows that lattice vibrations are rather pronounced. It may safely be concluded, however, that although the vibrations of the Sb atoms are nearly isotropic with an amplitude almost identical with that of the iodine atoms along the direction of the I−S bond, the iodine amplitudes are greater in directions perpendicular to this bond and nearly independent of the direction.

DISCUSSION OF THE STRUCTURE

The correctness of our assumption that the middle plane of the sulphur ring is approximately perpendicular to the trigonal axis has been verified, the angle was found equal to 91°51′.

A set of interatomic distances and valence angles has been listed in Table 2. The sulphur ring is, within the probable limits of error, identical with that found in the orthorhombic modification of sulphur [8], the mean S−S bond distance being 2.046 Å (in sulphur 2.048 Å) the S−S−S angle 107°51′ (in sulphur 107°55′). The S−I bond distance is about 0.4 Å shorter than the van der Waals radius sum, the angle Sb−I−S (169.4°) is smaller than the corre-

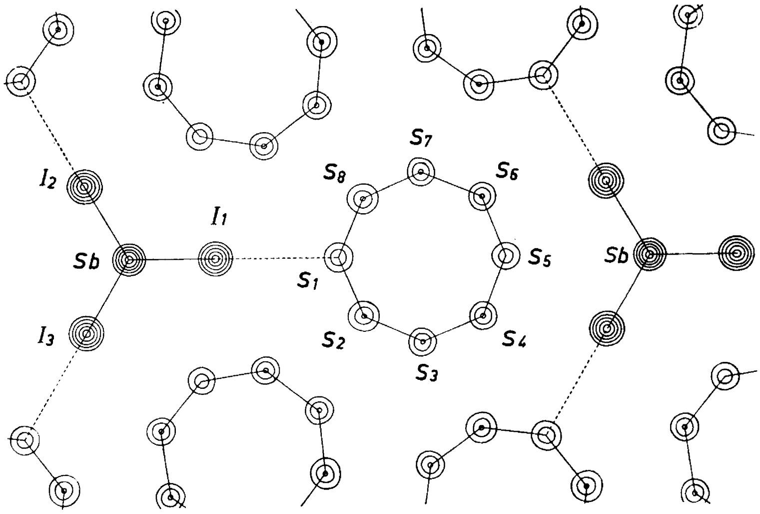

Fig. 1. Electron density projection along the trigonal axis.

sponding angles in the iodoform complexes in which angles equal to 175° or greater have been reported [3,9]. In the iodoform compounds the shortening of the S—I distance relative to the van der Waals value is also more pronounced. In the case of the antimony triiodide compound it appeared possible that the Sb—I distance is a few hundredths of an Ångström greater than in the free antimony triiodide molecule as found in electron diffraction investigations of the vapour. From early investigations a value a little greater than 2.70 Å appeared to be the most probable and an angle I—Sb—I close to 99°. A new investigation carried out by A. Almenningen and one of us (T. Bjorvatten) using the new Oslo E.D. apparatus confirmed this view. The Sb—I bond length was found equal to 2.719 Å and the I—Sb—I angle equal to 99.1°. There is therefore a significant change in the antimony triiodide molecule due to the formation of the addition complex. Similar changes in the iodoform molecule probably also take place when it forms addition compounds with sulphur (S_8) or sulphur compounds, but in these cases a sufficiently accurate X-ray determination is made more difficult because of the dominating influence of the iodine atoms on the X-ray intensities.

A closer inspection of the intermolecular atomic distances reveals, besides the short I—S bond distance, the presence of intermolecular antimony-iodine separations which are shorter than those expected for a regular van der Waals contact. Each antimony atom has three iodine neighbours belonging to the antimony triiodide molecule situated directly above it on the trigonal axis. The Sb-I distance in question (3.85 Å) is certainly shorter than the van der Waals radius sum and indicates a comparatively strong interaction between the atoms. It would actually appear possible that the antimony atom in the triiodide molecule may have acceptor properties sufficiently strong to result in the formation of addition compounds depending on charge transfer bonds between antimony atoms and donor atoms belonging to partner molecules.

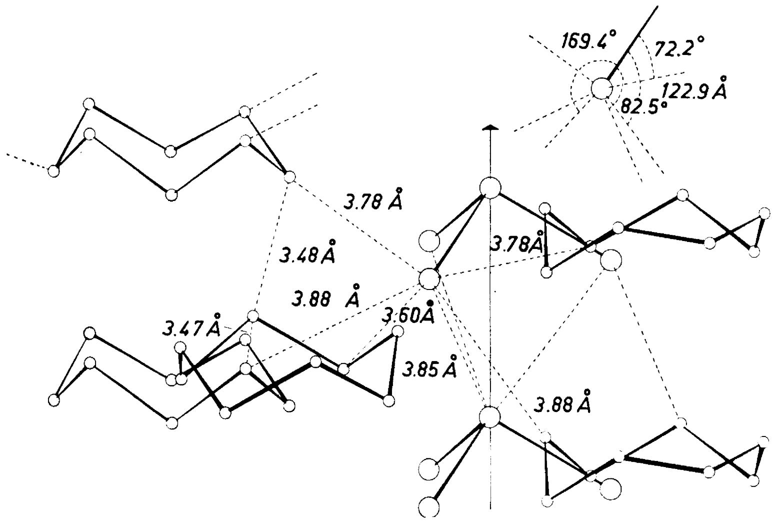

Fig. 2. Schematical drawing indicating the shortest intermolecular separations.

Rather short iodine-sulphur distances are also observed in the present structure. Each iodine atom has in addition to the sulphur atom mentioned above (at a distance of 3.60 Å) four sulphur neighbours all belonging to different sulphur rings with I—S separations of 3.78 resp. 3.88 Å. Here, however, contrary to the finding in the former case, the angles Sb—I—S (72.2° and 122.9°) are far from approaching 180°.

In Fig. 2 a schematical drawing is reproduced indicating the nearest surroundings of the iodine and sulphur atoms in the structure. It appears very probable that the great stability of the crystalline compound depends not only on the shortest I—S charge transfer bond but also to some extent on the interactions just mentioned between antimony and iodine and between iodine and sulphur atoms. In this connection the fact should perhaps not be forgotten that there is rather strong evidence of 1:3 complexes between iodoform and quinoline being present even in dilute solution of the analogous addition compound [10].

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