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Crystal Structure of the 2:1 Addition Compound Iodoform-1,4-Diselenane, $(CHI_3)_2 \cdot C_4H_8Se_2$

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The crystal structure of the 2:1 addition compound iodoform-diselenane has been determined by X-ray methods. The crystals have a melting point of 98°C and an observed density of 3.50 g cm^{-3}. The space group is $P2_1/c$ and the monoclinic unit cell containing two formula units has the lattice constants $a = 6.73$ Å, $b = 17.27$ Å, $c = 8.31$ Å, $\beta = 104.3°$. The diselenane molecules are situated in centres of symmetry, the iodoform molecules occupy general positions. Two iodine atoms belonging to a particular iodoform molecule form charge transfer bonds with selenium atoms belonging to neighbouring diselenane molecules, and each diselenane molecule is linked to four iodoform molecules, thus forming two-dimensional lattices of alternating diselenane and iodoform molecules. The I—Se bond distances (3.465 Å and 3.514 Å) are about 0.65 Å shorter than anticipated for a van der Waals contact.

In three previous papers,[1] detailed reports have been published on the crystal structures of the (1:1) addition compound CHI_3-1,4-dithiane and the two (1:3) compounds CHI_3-sulphur and CHI_3-quinoline. The structure of these compounds clearly demonstrate the presence of charge transfer bonds between iodine atoms and electron donor atoms belonging to the partner molecules. Iodoform complexes with diselenane as the electron donating molecule might be expected to contain analogous I—Se bonds, and the present report deals with the investigation of the crystal structure of a compound which contains iodoform and diselenane in the ratio 2:1. Crystals of this compound were prepared by evaporating the solvent (carbon disulphide) from a solution containing diselenane and iodoform. The crystals, colourless flat needles, are monoclinic with the lattice constants: $a = 6.73$ Å; $b = 17.27$ Å; $c = 8.31$ Å; $\beta = 104.3°$. The estimated error in these values is ± 0.3 %.

The melting point was found equal to 98°C, and the density measured using the flotation method was 3.50 g·cm^{-3}. From these figures the value $Z = 2$ for the number of molecules in the unit cell results. The density calculated from the lattice constants is 3.53 g cm^{-3}. The space group derived from the X-ray extinctions is $P2_1/c$.

Table 1. Observed and calculated structure factors.

[001] projection

h	k	l	F_o	F_c
0	2	0	137	−144
0	4	0	82	74
0	6	0	45	− 41
0	8	0	142	−129
0	10	0	209	203
0	12	0	140	−149
0	14	0	91	− 97
0	16	0	42	− 41
0	18	0	< 22	− 15
0	20	0	42	46
0	22	0	< 25	6
1	0	0	< 8	9
1	1	0	78	− 84
1	2	0	124	127
1	3	0	161	−175
1	4	0	140	137
1	5	0	158	155
1	6	0	35	35
1	7	0	52	46
1	8	0	< 14	− 16
1	9	0	131	131
1	10	0	123	−117
1	11	0	74	− 69
1	12	0	54	− 49
1	13	0	107	−104
1	14	0	< 19	− 6
1	15	0	78	80
1	16	0	32	− 28
1	17	0	26	− 28
1	18	0	< 22	− 12
1	19	0	35	33
1	20	0	< 24	− 17
1	21	0	35	− 33
1	22	0	< 24	7
1	23	0	< 25	− 25
2	0	0	211	−318
2	1	0	176	232
2	2	0	218	278
2	3	0	57	58
2	4	0	33	30
2	5	0	26	26
2	6	0	25	26
2	7	0	< 14	− 15
2	8	0	73	69
2	9	0	95	− 84
2	10	0	197	−203
2	11	0	101	98
2	12	0	36	32
2	13	0	30	27
2	14	0	< 19	− 5
2	15	0	35	− 34
2	16	0	27	− 27
2	17	0	28	− 27
2	18	0	23	1
2	19	0	27	− 26
2	20	0	27	− 33
2	21	0	< 25	15
2	22	0	< 26	7
3	0	0	179	214
3	1	0	19	− 17
3	2	0	83	78
3	3	0	86	91
3	4	0	87	− 98
3	5	0	45	− 46
3	6	0	< 15	6
3	7	0	44	45
3	8	0	33	− 35
3	9	0	27	− 24
3	10	0	88	90
3	11	0	< 18	9
3	12	0	22	− 19
3	13	0	40	38
3	14	0	107	−112
3	15	0	57	− 61
3	16	0	22	3
3	17	0	27	23
3	18	0	25	− 25
3	19	0	27	− 26
3	20	0	31	33
3	21	0	< 26	7
3	22	0	< 26	1
4	0	0	164	174
4	1	0	179	−208
4	2	0	74	− 81
4	3	0	24	23
4	4	0	99	105
4	5	0	22	20
4	6	0	38	36
4	7	0	29	29
4	8	0	64	− 64
4	9	0	110	116
4	10	0	32	30
4	11	0	100	− 97
4	12	0	79	− 77
4	13	0	27	− 24
4	14	0	< 22	6
4	15	0	< 22	17
4	16	0	< 23	− 15
4	17	0	< 24	2
4	18	0	< 24	− 21
4	19	0	< 25	14
4	20	0	< 26	− 3
5	0	0	50	− 43
5	1	0	73	77
5	2	0	27	25
5	3	0	21	19
5	4	0	90	93
5	5	0	35	33
5	6	0	20	− 15
5	7	0	20	− 18

h	*k*	*l*	F_o	F_c
5	8	0	35	34
5	9	0	< 20	−16
5	10	0	83	−84
5	11	0	43	42
5	12	0	< 22	−20
5	13	0	< 22	0
5	14	0	39	38
5	15	0	< 24	7
5	16	0	41	−43
5	17	0	28	−30
5	18	0	< 26	10
5	19	0	< 26	−6
6	0	0	39	36
6	1	0	129	139
6	2	0	58	56
6	3	0	46	−48
6	4	0	41	−41
6	5	0	27	23
6	6	0	< 21	−18
6	7	0	39	36
6	8	0	< 22	18
6	9	0	57	−56
6	10	0	< 23	8
6	11	0	63	66
6	12	0	< 24	9
6	13	0	< 24	−11
6	14	0	41	−44
6	15	0	< 25	−15
6	16	0	< 26	−10
7	0	0	< 22	6
7	1	0	60	−62
7	2	0	29	26
7	3	0	< 23	−2
7	4	0	23	−18
7	5	0	< 23	16
7	6	0	37	38
7	7	0	< 24	14
7	8	0	27	−30
7	9	0	42	44
7	10	0	< 25	6
7	11	0	37	−37
7	12	0	< 25	−1
7	13	0	< 26	−12
7	14	0	29	−31
8	0	0	< 25	−18
8	1	0	57	−56
8	2	0	< 25	−11
8	3	0	52	58
8	4	0	28	25
8	5	0	< 25	−4
8	6	0	< 25	5
8	7	0	< 26	−17
8	8	0	< 26	0
8	9	0	30	31
8	10	0	22	−22
8	11	0	26	−22
9	0	0	34	32
9	1	0	30	29

h	*k*	*l*	F_o	F_c
			[010] projection	
1	0	0	< 14	9
2	0	0	262	−311
3	0	0	210	230
4	0	0	178	178
5	0	0	62	−54
6	0	0	52	46
7	0	0	< 32	18
8	0	0	< 30	−18
$\bar{9}$	0	2	< 24	35
$\bar{8}$	0	2	70	−74
$\bar{7}$	0	2	72	−62
$\bar{6}$	0	2	82	82
$\bar{5}$	0	2	72	−58
$\bar{4}$	0	2	60	−56
$\bar{3}$	0	2	104	94
$\bar{2}$	0	2	168	−204
$\bar{1}$	0	2	262	−324
0	0	2	304	428
1	0	2	70	−68
2	0	2	369	−458
3	0	2	< 27	44
4	0	2	144	152
5	0	2	120	−128
6	0	2	92	−76
7	0	2	< 31	17
8	0	2	< 31	−34
$\bar{9}$	0	4	64	76
$\bar{8}$	0	4	66	−66
$\bar{7}$	0	4	102	−102
$\bar{6}$	0	4	112	122
$\bar{5}$	0	4	74	56
$\bar{4}$	0	4	108	−102
$\bar{3}$	0	4	112	114
$\bar{2}$	0	4	< 23	41
$\bar{1}$	0	4	158	−166
0	0	4	230	252
1	0	4	152	148
2	0	4	210	−226
3	0	4	46	36
4	0	4	196	212
5	0	4	< 32	−34
6	0	4	60	−52
7	0	4	30	38
$\bar{8}$	0	6	30	−26
$\bar{7}$	0	6	116	−112
$\bar{6}$	0	6	94	86
$\bar{5}$	0	6	124	112
$\bar{4}$	0	6	122	−122
$\bar{3}$	0	6	< 29	−13
$\bar{2}$	0	6	98	96
$\bar{1}$	0	6	110	−98
0	0	6	52	44
1	0	6	106	102
2	0	6	136	−144
3	0	6	76	−60
4	0	6	112	106

h	*k*	*l*	F_o	F_c
5	0	6	< 32	8
6	0	6	66	− 66
$\bar{7}$	0	8	100	−100
$\bar{6}$	0	8	< 32	31
$\bar{5}$	0	8	106	104
$\bar{4}$	0	8	108	−106
$\bar{3}$	0	8	94	− 86
$\bar{2}$	0	8	72	72
$\bar{1}$	0	8	34	− 30
0	0	8	44	− 42
1	0	8	56	54
2	0	8	52	− 48
3	0	8	48	− 48
4	0	8	52	50
$\bar{6}$	0	10	< 26	6
$\bar{5}$	0	10	94	48
$\bar{4}$	0	10	< 33	− 29
$\bar{3}$	0	10	54	− 58
$\bar{2}$	0	10	58	72
$\bar{1}$	0	10	40	40
0	0	10	< 32	− 31
1	0	10	32	32
2	0	10	< 26	19

[100] projection

h	*k*	*l*	F_o	F_c
0	2	0	148	−144
0	4	0	81	74
0	6	0	58	− 44
0	8	0	139	−137
0	10	0	209	211
0	12	0	153	−160
0	14	0	112	−111
0	16	0	48	− 47
0	18	0	< 35	− 19
0	20	0	57	58
0	1	1	15	74
0	2	1	47	− 46
0	3	1	85	− 78
0	4	1	20	− 19
0	5	1	168	−178
0	6	1	140	−151
0	7	1	73	− 75
0	8	1	102	−106
0	9	1	213	240
0	10	1	32	− 26
0	11	1	36	− 34
0	12	1	33	− 32
0	13	1	66	70
0	14	1	31	29
0	15	1	92	− 92
0	16	1	< 32	2
0	17	1	< 34	− 4
0	18	1	< 35	12
0	19	1	88	82
0	20	1	42	45
0	0	2	316	406
0	1	2	163	186
0	2	2	255	−311
0	3	2	44	37
0	4	2	61	− 56
0	5	2	< 19	13
0	6	2	71	− 76
0	7	2	48	53
0	8	2	59	− 55
0	9	2	63	− 68
0	10	2	239	255
0	11	2	102	99
0	12	2	37	− 35
0	13	2	33	31
0	14	2	< 30	5
0	15	2	40	− 39
0	16	2	< 33	13
0	17	2	< 34	− 3
0	18	2	< 35	19
0	19	2	37	− 41
0	20	2	46	49
0	1	3	160	170
0	2	3	62	58
0	3	3	< 20	− 10
0	4	3	181	192
0	5	3	42	− 35
0	6	3	58	− 57
0	7	3	86	− 87
0	8	3	< 25	− 13
0	9	3	124	122
0	10	3	88	92
0	11	3	63	− 66
0	12	3	< 29	− 5
0	13	3	< 30	− 13
0	14	3	57	56
0	15	3	94	− 90
0	16	3	62	− 58
0	17	3	< 35	− 21
0	18	3	51	− 55
0	19	3	51	50
0	0	4	231	254
0	1	4	183	190
0	2	4	84	− 87
0	3	4	30	− 31
0	4	4	38	32
0	5	4	82	− 82
0	6	4	39	− 43
0	7	4	47	− 45
0	8	4	< 27	− 15
0	9	4	161	−164
0	10	4	93	98
0	11	4	90	90
0	12	4	66	− 63
0	13	4	33	32
0	14	4	< 33	− 16
0	15	4	36	− 29
0	16	4	43	− 43
0	17	4	< 36	26

$h\ k\ l$	F_o	F_c
0 18 4	< 37	2
0 1 5	25	15
0 2 5	31	31
0 3 5	103	−106
0 4 5	92	96
0 5 5	27	22
0 6 5	117	−113
0 7 5	74	− 72
0 8 5	86	− 81
0 9 5	86	81
0 10 5	44	44
0 11 5	< 31	20
0 12 5	< 32	− 12
0 13 5	< 33	16
0 14 5	56	54
0 15 5	< 35	10
0 16 5	40	− 42
0 17 5	< 37	10
0 0 6	39	34
0 1 6	156	155
0 2 6	48	− 47
0 3 6	49	43
0 4 6	< 39	16
0 5 6	33	26
0 6 6	39	− 40
0 7 6	39	29
0 8 6	< 31	22
0 9 6	57	− 62
0 10 6	< 33	23
0 11 6	105	101
0 12 6	< 34	− 23
0 13 6	< 35	14
0 14 6	< 36	35
0 15 6	< 37	− 37
0 1 7	67	60
0 2 7	38	39
0 3 7	< 31	− 32
0 4 7	44	46
0 5 7	82	89
0 6 7	48	− 51
0 7 7	50	− 55
0 8 7	52	− 50
0 9 7	< 34	0
0 10 7	35	34
0 11 7	< 36	− 28
0 12 7	< 36	− 1
0 13 7	< 37	− 43
0 14 7	< 38	37
0 0 8	34	− 25
0 1 8	67	65
0 2 8	< 34	− 6
0 3 8	< 34	− 4
0 4 8	< 34	23
0 5 8	< 35	− 23
0 6 8	< 35	− 18
0 7 8	39	− 42
0 8 8	< 36	24
0 9 8	63	− 62
0 10 8	< 37	− 19
0 1 9	< 37	− 23
0 2 9	37	37
0 3 9	45	− 54
0 4 9	< 37	13
0 5 9	48	52
0 6 9	< 38	0

The X-ray material on which the structure determination was based consisted of integrated Weissenberg diagrams for the *hk*0- and 0*kl*-zones and precession diagrams for the *h*0*l*-zone. Mo$K\alpha$-radiation was employed and the sections of the crystals selected for the X-ray examination were approximately 0.08 × 0.08 mm^2. During the exposure the crystals were kept in sealed thin-walled capillaries of boronlithium glass in order to avoid evaporation of the substance. The intensities of the reflections were measured photometrically. No corrections for absorption or secondary extinction were applied. The number of observed reflections in the 0*kl*-, *h*0*l*- and *hk*0-zones are 107, 63 and 118, respectively. The number of reflections compatible with the actual experimental conditions are 153, 79 and 168.

Approximate coordinates of the iodine and selenium atoms could be found from Patterson projections along the *c*- and *a*-axes. The coordinates were refined in the usual way by the Fourier method until no further change in the structure factor signs occurred. In the resulting Fourier maps, peaks giving the positions of the carbon atoms were present in addition to the higher peaks due to the iodine and selenium atoms. The final atomic parameters based on the *hk*0- and 0*kl*-reflections were calculated using a two-dimensional least squares program worked out by Curtis[2] for the Ferranti Mercury computer. Three reflections (200), (002), and (202), were suspected to suffer from extinction errors and were omitted in the least squares refinements. No attempt was made to introduce the contribution from the hydrogen atoms. Anisotropic temperature factors were introduced for the iodine and selenium atoms. The R-factors including only observed reflections thereby dropped from 0.154 to 0.081 for $hk0$-reflections and from 0.091 to 0.072 for $0kl$-reflections. In the case of the $h0l$-zone, least squares refinements were performed directly, starting with the coordinates obtained from the two other projections. The final R-factor for this zone was 0.115 assuming isotropic vibrations of all atoms and 0.105 assuming anisotropic vibrations of the iodine and selenium atoms. The calculated structure factors based on anisotropic temperature factors for the iodine and selenium atoms are listed in Table 1, together with the observed values. In the final two-dimensional refinements the same mean values for

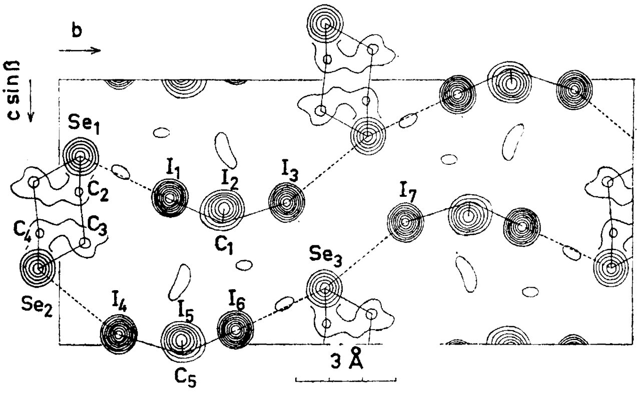

Fig. 1. Electron density projection along the a-axis. Contour intervals: 10 e·Å^{-2} from 10 e·Å^{-2} upwards for iodine and selenium, 5 e·Å^{-2} from 5 e·Å^{-2} upwards for other peaks.

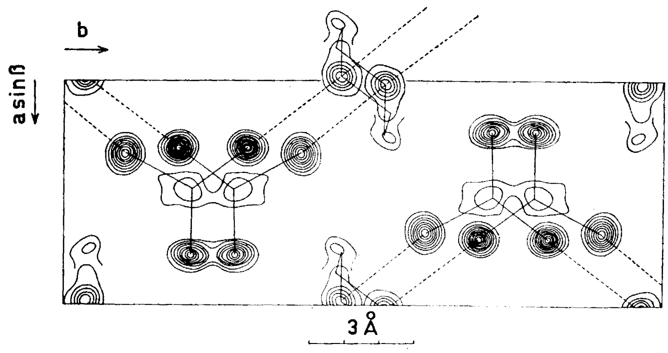

Fig. 2. Electron density projection along the c-axis. Contour intervals: 10 e·Å^{-2} from 10 e·Å^{-2} upwards for iodine and selenium, 5 e·Å^{-2} from 5 e·Å^{-2} upwards for carbon atoms.

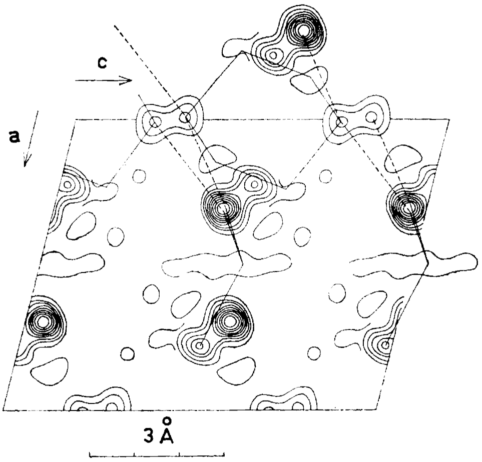

Fig. 3. Electron density projection along the *b*-axis. Contour intervals: 20 e·Å^{-2} from 20 e·Å^{-2} upwards for iodine and selenium, 10 e·Å^{-2} from 10 e·Å^{-2} upwards for other peaks.

the carbon temperature factors were used for all projections. The analytical approximations to the atomic scattering factors computed by Forsyth and Wells were employed.[3]

Fourier maps, based on the structure factor signs finally arrived at, are reproduced in Figs. 1, 2, and 3. The diselenane molecules are situated in centres of symmetry, but the iodoform molecules occupy general positions. Each particular selenium atom forms charge transfer bonds to *two* iodine atoms belonging to different iodoform molecules. A two-dimensional lattice of

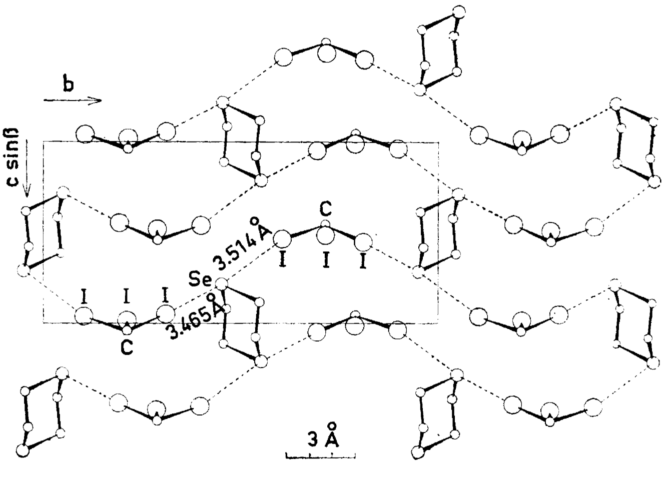

Fig. 4. Structure of the iodoform-diselenane lattice as seen along the *a*-axis.

Table 2. Positional and temperature parameters (Standard deviations in parentheses).

Atom	*x*	*y*	*z*	*B*
I_1	0.2959(0.0007)	0.1923(0.0003)	0.4498(0.0006)	2.7
I_2	0.7757(0.0007)	0.2864(0.0004)	0.4840(0.0007)	3.7
I_3	0.3220(0.0008)	0.3966(0.0003)	0.4618(0.0005)	3.3
Se_1	−0.0159(0.0013)	0.0370(0.0004)	0.2886(0.0009)	3.2
C_1	0.484 (0.009)	0.284 (0.030)	0.540 (0.004)	2.0
C_2	−0.234 (0.010)	0.035 (0.026)	0.403 (0.004)	2.0
C_3	−0.141 (0.012)	0.049 (0.026)	0.612 (0.004)	2.0

alternating diselenane and iodoform molecules is formed as indicated in Fig. 4 in the form of a projection along [100]. Only two of the iodine atoms of each iodoform molecule take part in charge transfer bonds with selenium atoms.

The atomic coordinates finally arrived at are listed in Table 2. In this table the mean of the two values available for each coordinate are given. The temperature factors (Table 2) are mean values derived from computations in which the vibrations were assumed to be isotropic. The results obtained in refinements allowing for anisotropic vibrations clearly show, however, that the iodine atoms are vibrating more freely in directions perpendicular to the C—I bond direction than along the bond. The more important interatomic distances and bond angles are listed in Table 3. Mean isotropic values have been used for the standard deviations of the positional atomic parameters, in order to simplify the calculations. These values are 0.0049 Å, 0.0075 Å, and 0.048 Å, respectively, for iodine, selenium, and carbon atoms. The Se—I bond distances (3.465 Å and 3.514 Å) are about 0.65 Å shorter than the van der Waals' radii sum (4.15 Å). This clearly indicates the presence of charge transfer bonds between iodine and selenium atoms. Apart from these short distances all other intermolecular distances are equal to or longer than those

Table 3. Distances and angles in $(CHI_3)_2 \cdot C_4H_8Se_2$ (Standard deviations in parentheses).

(a) Distances in Å

C_1-I_1	2.05 (0.05)
C_1-I_2	2.13 (0.05)
C_1-I_3	2.24 (0.05)
I_1-I_2	3.563(0.007)
I_2-I_3	3.564(0.007)
I_3-I_1	3.533(0.007)
Se_1-C_2	1.94 (0.05)
Se_2-C_3	1.89 (0.05)
C_2-C_3	1.71 (0.07)
Se_3-I_6	3.465(0.009)
Se_3-I_7	3.514(0.009)
I_1-I_4	4.487(0.007)
I_5-C_1	3.92 (0.05)
I_4-C_4	3.79 (0.05)
I_4-C_3	3.82 (0.05)
I_5-I_2	4.343(0.007)
I_6-C_1	3.93 (0.05)
Se_3-I_3	4.120(0.009)
Se_1-Se_2	3.696(0.015)

(b) Angles in degrees

$I_1-C_1-I_2$	116.8(2.3)
$I_2-C_1-I_3$	109.2(2.1)
$I_3-C_1-I_1$	110.7(2.1)
$Se_1-C_2-C_3$	111.4(3.0)
$C_2-C_3-Se_2$	111.2(3.0)
$C_3-Se_2-C_4$	100.4(2.1)
$Se_2-Se_1-I_1$	90.7(0.3)
$Se_1-Se_2-I_4$	102.3(0.4)
$I_6-Se_3-I_7$	177.0(0.3)
$Se_2-I_4-C_5$	160.3(1.3)
$Se_1-I_1-C_1$	178.6(1.4)

expected for a normal van der Waals' contact. The observed difference in the I—Se distances for different types of iodine atoms is probably significant (the difference being 3.0 times the relevant standard deviation).

The arrangements C—I—Se do not appear to be far from linear, the angles C—I—Se being 178° and 160°, respectively. The I—Se—I bond angle is 177° with one of the iodine atoms in the axial direction of the ring. The diselenane molecule together with its four nearest iodine neighbours does not, within the accuracy obtained in the present study, deviate from an arrangement involving a mirror plane. The presence of a mirror plane is not required by the symmetry of the space group, however.

The main difference between the structure of the 1:1 iodoform complex of dithiane and the present 2:1 complex is the number of iodine atoms linked to the ring system. In the dithiane complex, the iodine atoms are linked to the ring only in equatorial positions, while in the diselenane complex iodine occupys positions corresponding to both axial and (roughly) equatorial directions. It is interesting to note that iodine forms a 2:1 complex with diselenane in which the Se—I bonds are all of the axial type.[4] The S—I bonds in the 2:1 iodinedithiane compound are, however, all equatorial.[5] The interatomic distances and angles in iodoform and diselenane are, within the standard deviations of the present investigation, identical with those found for the free iodoform and diselenane molecules.[6,7]

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