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The Crystal Structure of the Molecular Complex of Iodine with Tetrahydroselenophene, $C_4H_8Se.I_2$

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Crystals of $C_4H_8Se.I_2$ display orthorhombic symmetry with $a = 12{\cdot}804$, $b = 7{\cdot}625$ and $c = 9{\cdot}256$ Å, each with an e.s.d. of 0·003 Å. There are four molecules in the unit cell and the space group is either *Pnma* or $Pn2_1a$. The trial structure was refined by three-dimensional, full-matrix least-squares procedures in both space groups. The preferred structure is in *Pnma* and involves a twofold disorder of carbon atoms C(5) and C(6) opposite selenium in the five-membered ring. The observed distances and bond angles, with e.s.d.'s in parenthesis, are:

Se(3)–I(2)	2·762(0·005) Å	I(1)–I(2)–Se(3)	179·4(0·3)°
I(1)–I(2)	2·914(0·004)	I(2)–Se(3)–C(4)	100·5(1·0)
Se(3)–C(4)	1·960(0·025)	C(4)–Se(3)–C(4′)	93·2(1·8)
C(4)–C(5)	1·55(0·05)	Se(3)–C(4)–C(5)	102·1(2·2)
C(5)–C(6)	1·59(0·07)	C(4)–C(5)–C(6)	107·8(3·0)
C(6)–C(4′)	1·52(0·05)	C(5)–C(6)–C(4′)	105·8(3·0)
C(4′)–Se(3)	1·960(0·025)	C(6)–C(4′)–Se(3)	104·6(2·2)

Although $C_4H_8Se.I_2$ is a molecular complex, the Se–I bond distance of 2·762 Å is only 0·26 Å longer than the sum of the single, covalent bond radii, 2·50 Å. A short intermolecular Se–I contact of 3·638 Å (sum of van der Waals radii = 4·15 Å) is of interest because it makes a bond angle I(2)–Se(3)–I(1′) of 167° and suggests a tendency toward the X–Se–X bonding found in compounds of the type R_2SeCl_2 and R_2SeBr_2.

Introduction

The preparation and properties of tetrahydroselenophene and a number of its halogen addition compounds have been described by Morgan & Burstall (1929). Spectrophotometric studies of the iodine complexes of a series of sulfur compounds (McCullough & Mulvey, 1959) indicate maximum stability of the complex of tetrahydrothiophene (thiacyclopentane). By analogy, one might expect the iodine complex of tetrahydroselenophene to be among the most stable of the compounds of this type, and therefore to have a short Se–I bond. For this reason the present study of the structure of $C_4H_8Se.I_2$ was undertaken.

Experimental

Crystals of $C_4H_8Se.I_2$ suitable for the X-ray study were obtained by permitting a hot, saturated solution of the substance in ethanol to cool to laboratory temperature. Since the crystals are somewhat volatile, the specimens selected for study were sealed in thin-walled glass capillaries. Weissenberg and precession photographs show orthorhombic diffraction symmetry. The unit-cell dimensions were determined by means of zero-level *h*0*l* and *hk*0 Weissenberg photographs prepared with unfiltered Cu radiation. The *hk*0 reflections of a small quartz crystal were superimposed on these films for calibration purposes (Pabst, 1957). The 2θ values (based on $a = 4{\cdot}9131$ Å for quartz) for a total of fifty *h*0*l* and *hk*0 reflections were used in a least-squares refinement of the lattice parameters (Sparks, 1963). With the wavelengths for Cu *K* radiation taken as $\alpha_1 = 1{\cdot}54050$, $\alpha_2 = 1{\cdot}54434$, $\alpha = 1{\cdot}5418$ and $\beta = 1{\cdot}39217$ Å, the following results were obtained:

$$a = 12{\cdot}804, \quad b = 7{\cdot}625, \quad c = 9{\cdot}256 \text{ Å}$$
$$\text{e.s.d.} = 0{\cdot}003 \text{ Å}.$$

The density observed by flotation was 2·85 $g.cm^{-3}$, while that calculated for $Z = 4$ is 2.857 $g.cm^{-3}$. The photographs showed the following systematic extinctions: *hkl*, none; 0*kl* with $k+l$ odd; *h*0*l*, none; *hk*0 with *h* odd. The space group is accordingly indicated to be *Pnma* or $Pn2_1a$.

The intensity data were taken mainly from multiple-film equi-inclination Weissenberg photographs prepared by use of filtered Mo radiation with 0·025 mm brass foil interleaves between films. Six levels, *h*0*l* through *h*5*l*, were photographed in this manner. For interlayer scaling, sets of timed *hk*0 and 0*kl* precession photographs were prepared. The crystal used for the intensity data was 0.10 mm by 0.20 mm by 0·06 mm along the *a*, *b* and *c* axes respectively. All intensities were estimated visually and the preces-

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sion photographs were also measured on a densitometer. The calculated linear absorption coefficient for molybdenum radiation is 117 cm^{-1} and the corresponding values for μr are between 0·35 and 0·6. No corrections for absorption in the specimen were applied. Some 400 independent reflections were observed. Within the geometric range covered by these reflections an additional 200 reflections were below observational limits.

Determination of the structure

It was noted that the intensity distribution on the *h0l* films was repeated closely on the films for layers with *k* even. In like manner, the intensity distribution on the *h1l* films was repeated on the other films with *k* odd. This situation suggested that the heavy atoms are located in the mirror planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$ in *Pnma* and this was assumed to be the case in obtaining a trial structure. However, the possibility that the heavy atoms are in positions approximating these in $Pn2_1a$ was considered in the refinement of the structure.

Approximate *x* and *z* parameters for selenium and the two iodine atoms were obtained by means of an *h0l* Patterson synthesis. Two-dimensional Fourier refinement improved the heavy atom parameters and served to locate the carbon atoms, C(4) and C(4′) which are bonded to selenium, but the positions of the other two carbon atoms remained obscure. The selenium and iodine atoms were then used to determine the phases for a three-dimensional Fourier synthesis. This yielded improved heavy atom parameters, a well defined peak for C(4) and an elongated maximum in the region expected for C(5). Fourier refinement which included C(4) in the phasing did little to improve the situation with regard to C(5).

The positional parameters from the Fourier refinement were then refined by three-dimensional least-squares procedures. Isotropic temperature factors were initially assigned to all atoms and were refined with the positional parameters in six cycles. Unobserved reflections were not included at this stage. In these cycles, the temperature factors for all atoms except C(5) behaved normally but the *B* for this atom increased to 8 Å^2. Before proceeding to further refinement, the interlayer scaling was adjusted by use of the ratios $\Sigma|F_o|/\Sigma|F_c|$ for the various layers. The original scale factors were multiplied by the following coefficients in all further refinement: *h0l*, 0·948; *h1l*, 0·975; *h2l*, 1·002; *h3l*, 0·987; *h4l*, 1·018; *h5l*, 1·028. Three more cycles of least-squares refinement were then carried out after introducing anisotropic temperature factors on all atoms. In these cycles the *b* values behaved normally except for b_{33} for C(5) which rose to a value correspomding to 21 Å^2, implying an r.m.s. displacement of approximately 0·5 Å. This behavior suggested a disordered structure in *Pnma* or the possibility that the true space group is $Pn2_1a$. At this stage a three-dimensional difference synthesis was computed with F_c based on I(1), I(2), Se(3) and C(4). The atom C(5) again appeared as a maximum elongated in the direction of the *c* axis. On the assumption that

Table 1. *Final positional parameters from least-squares refinement in two possible space groups*

		Pnma refinement			$Pn2_1a$ refinement		
		Parameter	e.s.d.	Ratio of last shift to e.s.d.	Parameter	e.s.d.	Ratio of last shift to e.s.d.
I(1)	*x*	0·2889	0·0002	0·000	0·2889	0·0002	0·120
	y	0·2500	—	—	0·2500	—	—
	z	0·1100	0·0002	0·000	0·1100	0·0002	0·043
I(2)	*x*	0·3104	0·0001	0·007	0·3103	0·0002	0·067
	y	0·2500	—	—	0·2506	0·0014	0·017
	z	0·4234	0·0002	0·005	0·4233	0·0002	0·030
Se(3)	*x*	0·3285	0·0002	0·005	0·3284	0·0002	0·004
	y	0·2500	—	—	0·2465	0·0028	0·097
	z	0·7208	0·0003	0·013	0·7210	0·0003	0·006
C(4)	*x*	0·4319	0·0018	0·001	0·4357	0·0026	0·026
	y	0·0633	0·0041	0·002	0·0642	0·0067	0·046
	z	0·7475	0·0023	0·001	0·7327	0·0034	0·029
*C(4′)	*x*	(0·4319)			0·4234	0·0050	0·022
	y	(0·4367)			0·4336	0·0110	0·025
	z	(0·7475)			0·7771	0·0064	0·061
*C(5)	*x*	0·5245	0·0038	0·004	0·5218	0·0038	0·093
	y	0·1638	0·0072	0·003	0·1562	0·0081	0·006
	z	0·8173	0·0056	0·001	0·8170	0·0054	0·034
*C(6)	*x*	0·5371	0·0030	0·009	0·5379	0·0030	0·068
	y	0·3446	0·0067	0·000	0·3458	0·0068	0·011
	z	0·7345	0·0042	0·004	0·7359	0·0040	0·018
R (observed reflections only)			0·063			0·061	

* In *Pnma*, C(4′) is omitted and atoms C(5) and C(6) are given weights of $\frac{1}{2}$.

Table 2. *Final temperature parameters from least-squares refinements**

		Pnma refinement			*Pn*2_1*a* refinement		
		Parameter	e.s.d.	Ratio of last shift to e.s.d.	Parameter	e.s.d.	Ratio of last shift to e.s.d.
I(1)	B_{11}	6·72	0·13	0·01	6·80	0·13	0·16
	B_{22}	4·20	0·16	0·00	4·67	0·21	0·17
	B_{33}	3·66	0·09	0·00	3·70	0·09	0·02
	B_{12}	—	—	—	1·70	0·70	0·42
	B_{13}	−0·30	0·15	0·01	−0·35	0·16	0·08
	B_{23}	—	—	—	−2·25	0·51	0·33
I(2)	B_{11}	3·93	0·09	0·00	3·95	0·09	0·09
	B_{22}	3·28	0·15	0·00	3·56	0·19	0·17
	B_{33}	3·94	0·09	0·01	4·05	0·09	0·07
	B_{12}	—	—	—	−2·10	0·43	0·25
	B_{13}	−0·11	0·13	0·01	0·02	0·13	0·07
	B_{23}	—	—	—	−2·04	0·43	0·07
Se(3)	B_{11}	2·35	0·11	0·00	2·36	0·11	0·01
	B_{22}	7·45	0·28	0·00	7·60	0·29	0·03
	B_{33}	3·25	0·12	0·00	3·25	0·12	0·02
	B_{12}	—	—	—	0·65	1·12	0·08
	B_{13}	0·11	0·19	0·00	0·00	0·19	0·04
	B_{23}	—	—	—	0·21	0·80	0·16
C(4)	B(iso)	5·28	0·50	0·00	2·28	0·62	0·05
C(4′)	B(iso)	—	—	—	6·99	1·60	0·03
C(5)	B(iso)	5·70	1·11	0·01	5·70	1·06	0·01
C(6)	B(iso)	3·79	0·78	0·01	3·78	0·75	0·03

* The relation between the B's above and the b's in the anisotropic temperature factor expression is given by $B_{11}=4a^2b_{11}$, $B_{12}=2abb_{12}$, *etc.*

C(5) is disordered, this atom was split into two 'half-atoms' designated C(5) and C(5′) and placed about 0.8 Å apart. These half-atoms were initially assigned anisotropic temperature factors, but in the ensuing least-squares cycles the e.s.d. values for these factors were of the order of magnitude of the factors themselves, hence isotropic factors were subsequently used for all carbon atoms. In the final stages of the least-squares refinement, the unobserved reflections were included with ΔF taken as $|F_c| - F_o\,(\min)$ with a weighting factor of $(1/70) = 1/4F_o\,(\min)$ if $|F_c| > F_o(\min)$ and $\Delta F = 0$ if $|F_c| < F_o\,(\min)$. Six additional least-squares cycles gave the positional and temperature parameters listed in Tables 1 and 2 respectively under columns headed '*Pnma* structure'.

Because of the ambiguity in the space group, it was considered of interest to carry out least-squares refinement in the space group *Pn*2_1*a*. This was done in each of two ways. In the first case, one of the components of the disordered structure was taken as a starting point. Since the two components are related by a mirror, it was unnecessary to carry out a separate refinement on each. The positional and temperature parameters listed in Tables 1 and 2 under '*Pn*2_1*a* structure' resulted from nine cycles of least-squares refinement. In the second case, the disordered structure which resulted from the *Pnma* refinement was refined in *Pn*2_1*a*. The results in this case differed little from the *Pnma* values so they were not listed in the tables. The most significant observation in this case was the failure of the least-squares refinement to move toward one of the ordered structures, even when one was favored in the input parameters.

Although unequivocal selections between the two space groups and an ordered *versus* a disordered structure cannot be made, the authors favor the solution involving the disordered structure in *Pnma* for the following reasons:

1. Within the significance of the experimental positional parameters in *Pn*2_1*a*, the three heavy atoms are located in planes normal to **b** and the atoms C(4) and C(4′) are located very close to positions of reflection in these same planes.
2. The carbon–carbon bond distances in the ring are more consistent with accepted values in the disordered *Pnma* structure. These distances are 1·55, 1·59 and 1·52 Å (average 1·55 Å) in *Pnma* against 1·52, 1·64 and 1·67 Å (average 1·61 Å) in the ordered *Pn*2_1*a* structure.
3. The slight decrease in R (0·063 to 0·061) in going from *Pnma* to *Pn*2_1*a* is less than might be expected to result from the addition of twelve more adjustable parameters.

The observed structure factors are compared in Table 3 with those computed on the basis of the final positional and temperature parameters for the disordered structure in *Pnma*. The atomic scattering factors used for iodine and selenium were those given in the *International Tables for X-ray Crystallography* (1962), Table 3.3.1*B*, while the diamond values of McWeeny (1954) were used for carbon. No corrections

Table 3. *Observed and calculated structure factors.*

The data are separated into groups having common values of k and l. The three columns in each group list values of h, $10F_o$ and $10F_c$, in that order. Unobserved reflections are indicated by U and the values of $10F_o$ given correspond to the minimum observable intensities

K= 0, L= 0		
2	3289	-3183
4	717	702
6	1613	1515
8	1905	-1877
10	827	758
12	234U	27
14	248U	-305
K= 0, L= 1		
3	844	-800
4	731	-686
5	414	351
6	1023	1064
7	274	259
8	827	-839
9	702	-685
10	657	635
11	619	638
12	234U	114
13	341	-338
14	320	-314
K= 0, L= 2		
0	489	-374
1	702	-736
2	932	-906
3	602	594
4	561	441
5	543	-563
6	165U	-222
7	351	380
8	185U	-54
9	287	-263
10	536	538
11	219U	28
12	438	-425
13	248U	128
K= 0, L= 3		
1	128U	85
2	2266	2524
3	143U	-63
4	2655	-2861
5	438	433
6	1716	1765
7	549	-519
8	331	-332
9	482	475
10	657	-636
11	227U	-181
12	446	453
13	248U	-64
K= 0, L= 4		
0	844	-837
1	1104	1231
2	1104	1278
3	262	-193
4	811	-808
5	836	-784
6	287	259
7	1056	1070
8	203U	96
9	602	-560
10	523U	-531
11	234U	-26
12	446	442
13	320	329
K= 0, L= 5		
1	234	218
2	165U	-94
3	536	-517
4	185U	-146
5	461	396
6	203U	126
7	203	-223
8	219U	-73
9	219U	90
10	234U	7
11	248U	-170
K= 0, L= 6		
0	1655	-1839
1	510	531
2	1020	1153
3	608	-595
4	203U	-156
5	475	517
6	646	-562
7	203	-182
8	914	813
9	234	-190
10	388	-370
11	361	384
K= 0, L= 7		
1	536	-547
2	351	-301
3	1069	1106
4	602	620
5	910	-890
6	549	-552
7	234U	186
8	414	390
9	361	361
10	260U	-197
11	379	-395
K= 0, L= 8		
0	219U	105
1	430	400
2	219U	-55
3	219U	-180
4	227U	166
5	234U	-82
6	234	-262
7	248U	74
8	248U	145
9	262U	10
K= 0, L= 9		
1	234U	7
2	351	-307
3	234U	163
4	388	350
5	310	-291
6	310	-266
7	379	400
8	262U	55
9	341	-334
K= 0, L= 10		
0	475	367
1	785	-730
2	379	-335
3	370	316
4	260U	115
5	260U	207
6	274U	74
7	438	-375
8	274U	-96
9	287	281
K= 1, L= 0		
2	3538	3159
4	4370	-3835
6	2202	2114
8	417	-410
10	780	-726
12	545	536
14	230U	-145
K= 1, L= 1		
0	417	-460
3	307	302
4	880	-807
5	924	-842
6	510	488
7	955	909
8	174U	120
9	489	-456
10	613	-622
11	195U	-23
12	531	543
13	307	294
14	282	-250
K= 1, L= 2		
1	95U	-8
2	103U	-15
3	269	-235
4	170	-225
5	225	225
6	659	646
7	371	-372
8	531	-517
9	417	414
10	351	334
11	442	-422
12	213U	162
13	318	314
14	282	-307
K= 1, L= 3		
0	3589	-4037
1	450	455
2	2451	2490
3	545	-555
4	371	-446
5	434	431
6	1262	-1189
7	190	-197
8	1428	1419
9	195U	-168
10	653	-638
11	282	294
12	213U	-0
13	255	-247
14	282	249
K= 1, L= 4		
1	545	-563
2	329	-345
3	1276	1305
4	717	739
5	880	-860
6	872	-946
7	174U	24
8	746	757
9	642	605
10	417	-436
11	577	-595
12	230U	-23
K= 1, L= 5		
0	151U	112
1	691	772
2	151U	57
3	380	-440
4	174U	-18
5	174U	120
6	174U	-90
7	195U	-9
8	195U	154
9	195U	82
10	255	-262
11	230U	-102
12	230U	140
K= 1, L= 6		
1	174U	-21
2	1006	-1066
3	170	177
4	1244	1324
5	442	-448
6	807	-854
7	577	607
8	213U	141
9	466	-523
10	318	305
11	230U	195
12	329	-296
K= 1, L= 7		
0	798	768
1	1109	-1160
2	648	-702
3	380	401
4	371	410
5	466	471
6	213U	-48
7	691	-733
8	213U	-146
9	417	461
K= 1, L= 8		
1	195U	-171
2	195U	-53
3	295	277
4	213U	68
5	213U	-216
K= 1, L= 9		
0	474	439
1	399	-350
2	282	-289
3	361	347
4	230U	29
5	230U	-304
K= 1, L= 10		
1	380	305
2	230U	204
3	613	-608
4	318	-293
5	571	545
K= 2, L= 0		
0	4540	-4497
2	3738	3243
4	694	-578
6	1681	-1500
8	1658	1504
10	704	-763
12	209U	5
14	231	293
K= 2, L= 1		
3	762	674
4	303	373
5	360	-338
6	1098	-1013
7	276	-232
8	791	833
9	630	610
10	446	-414
11	532	-584
12	209U	-38
13	303	314
14	276	294
K= 2, L= 2		
0	566	-438
1	612	575
2	371	384
3	546	-531
4	599	-396
5	471	493
6	371	326
7	360	-378
8	170U	231
9	262	243
10	454	-428
11	190U	-28
12	338	361
13	225U	-127
K= 2, L= 3		
1	120U	-62
2	2049	-1945
3	124	114
4	2650	2741
5	371	-373
6	1462	-1523
7	487	482
8	276	247
9	371	-404
10	454	460
11	200U	158
12	410	-473
13	225U	57
K= 2, L= 4		
0	1088	1136
1	1074	-1067
2	921	-927
3	214	197
4	665	700
5	677	703
6	290	-339
7	895	-945
8	181U	-224
9	510	514
10	381	435
11	209U	13
12	360	-383
13	276	-289
K= 2, L= 5		
1	148U	-169
2	148U	-87
3	437	418
4	170U	9
5	360	-345
6	181U	-177
7	181U	187
8	181U	95
9	200U	-112
10	209U	74
11	217U	165
K= 2, L= 6		
0	1538	1481
1	510	-508
2	1008	-1144
3	479	532
4	190U	163
5	419	-450
6	573	595
7	190U	148
8	510	-658
9	209U	186
10	360	375
11	290	-338
K= 2, L= 7		
1	446	462
2	400	360
3	912	-999
4	487	-478
5	747	804
6	487	540
7	209U	-169
8	371	-371
9	262	-308
10	233U	136
11	360	361
K= 2, L= 8		
0	190U	2
1	315	-339
2	190U	99
3	200U	158
4	209U	-162
5	209U	53
6	217U	191
7	217U	-60
8	225U	-185
K= 2, L= 9		
1	209U	27
2	175	243
3	217U	-150
4	360	-373
5	231	279
6	231	228
7	350	-367
K= 2, L= 10		
0	371	-379
1	660	661
2	290	274
3	276	-287
4	233U	-102
5	241U	-176
6	241U	-39
7	381	347
K= 3, L= 0		
2	2325	-2141
4	3103	2994
6	1743	-1722
8	365	259
10	471	443
12	590	-510
K= 3, L= 1		
0	1054	1070
3	192	-199
4	672	686
5	689	674
6	455	-395
7	740	-728
8	258	-257
9	422	395
10	404	453
11	187U	12
12	394	-427
K= 3, L= 2		
1	102U	-13
2	192	-205
3	149	73
4	132U	172
5	149	-165
6	577	-524
7	333	275
8	447	478
9	375	-369
10	187U	-127
11	385	367
K= 3, L= 3		
0	2373	2710
1	439	-408
2	2177	-2172
3	447	416
4	333	341
5	365	-337
6	1075	1007
7	162U	110
8	1033	-1051
9	187U	136
10	537	593
11	198U	-240
K= 3, L= 4		
1	487	457
2	455	424
3	1000	-990
4	584	-552
5	720	717
6	770	792
7	175U	-19
8	655	-648
9	455	-461
10	258	264
11	471	493
K= 3, L= 5		
0	148U	140
1	577	-548
2	148U	30
3	385	349
4	162U	-2
5	162U	-130
6	162U	37
7	187U	57
8	211	-229
9	187U	-87
10	209U	185
K= 3, L= 6		
1	162U	57
2	798	796
3	162U	-188
4	1180	-1150
5	375	390
6	699	688
7	487	-503
8	209U	-105
9	404	394
K= 3, L= 7		
0	667	-727
1	970	932
2	577	533
3	365	-328
4	365	-322
5	355	-355
6	187U	78
7	577	603
8	209U	177
9	375	-375
K= 3, L= 8		
1	187U	89
2	187U	92
3	209U	-208
4	209U	-29
5	209U	146
K= 3, L= 9		
1	365	315
2	285	279
3	209U	-301
4	219U	-28
5	219U	219
K= 3, L= 10		
1	228	-221
2	229U	-184
3	590	515
4	258	221
5	430	-444
K= 4, L= 0		
0	2722	2883
2	2281	-2246
4	126U	326
6	931	914
8	1158	-1131
10	596	610
K= 4, L= 1		
3	470	-467
4	569	-575
5	251	282
6	634	623
7	178U	155
8	634	-620
9	444	-444
10	205U	235
11	444	449
K= 4, L= 2		
0	444	451
1	251	-313
2	308	-295
3	355	358
4	320	334
5	397	-374
6	178U	-65
7	355	341
8	235	-194
9	205U	-195
10	320	312
K= 4, L= 3		
1	126U	26
2	1421	1443
3	145U	-168
4	1841	-1797
5	294	277
6	1234	1211
7	366	-358
8	199	-191
9	235	266
10	308	-317
K= 4, L= 4		
0	1032	-861
1	727	749
2	738	711
3	162U	-155
4	510	-519
5	494	-491
6	235	149
7	646	676
8	205U	182
9	407	-406
10	344	-318
K= 4, L= 5		
1	162U	98
2	178U	58
3	178U	-215
4	192U	-137
5	192U	210
6	192U	108
7	205U	-136
K= 4, L= 6		
0	1087	-1125
1	444	424
2	847	829
3	407	-412
4	192U	-125
5	320	285
6	461	-418
K= 4, L= 7		
1	366	-316
2	178	-254
3	748	733
4	407	412
5	569	-591
6	397	-391
K= 4, L= 8		
0	205U	0
1	251	213
2	205U	-47
3	217U	-94
4	229U	121
5	229U	10
K= 4, L= 9		
1	229U	-59
2	229U	-213
3	229U	132
4	229U	278
K= 4, L= 10		
0	320	276
1	533	-499
K= 5, L= 0		
2	1474	1491
4	1579	-1657
6	1269	1273
8	237U	-209
10	265U	-300
K= 5, L= 1		
0	595	-656
3	168U	105
4	475	-476
5	430	-442
6	206U	38
7	507	498
8	237U	145
9	323	-297
10	359	-322
K= 5, L= 2		
1	130U	-1
2	168U	60
3	168U	46
4	411	-413
5	188U	61
6	269	269
7	237	-171
8	336	-291
9	336	279
10	278U	66
K= 5, L= 3		
0	1474	-1840
1	298	308
2	1236	1327
3	269	-277
4	269	-207
5	206U	193
6	531	-537
7	237U	-30
8	812	780
9	265U	-94
10	449	-423
K= 5, L= 4		
1	311	-312
2	201	-221
3	595	623
4	581	566
5	507	-491
6	507	-477
7	252U	36
8	457	410
9	284	289
K= 5, L= 5		
0	206U	-62
1	237	289
2	222U	83
3	222U	-207
4	237U	-4
5	237U	138
6	252U	-135
7	265U	-96
8	265U	144
K= 5, L= 6		
1	237U	-62
2	628	-607
3	252U	184
4	750	704
5	381	-303
6	567	-528
7	311	335
K= 5, L= 7		
0	475	447
1	653	-625
2	411	-417
3	265U	217
4	265U	222
5	265U	206
6	291U	-2
7	449	-409
K= 5, L= 8		
1	265U	-29
K= 5, L= 9		
0	359	285

were made for dispersion as the indicated corrections for molybdenum radiation are probably less than uncertainties in the atomic scattering factors. A final, three-dimensional difference Fourier synthesis showed no significant maxima or minima.

Computing procedures

The Patterson, Fourier and difference syntheses involved in this study were computed by use of an unpublished routine written for the IBM 7090 by P. K. Gantzel and Håkon Hope in these laboratories. In its present form, the routine is applicable only to the calculation of structure factors and three-dimensional Fourier syntheses for centrosymmetric structures. The coefficients for the Fourier synthesis can be F_o, F_c or the difference between F_o and the contributions of any or all atoms present. The phases used are those calculated in the structure factor part which provides for either isotropic or anisotropic temperature factors. The contribution and phase of each atom is printed out for each reflection.

The least-squares refinements were carried out by use of ACA Computer Program No. 317 (UCLALS-1) written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood for the IBM 7090. This program minimizes the weighted sum of the squares of the quantity $(KF_o - G|F_c|)$ by a full-matrix routine, where K and G are scale factors. The program provides for several weighting options and for either isotropic or anisotropic temperature factors on the individual atoms. The anisotropic temperature factors are of the form:

$$\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$$

The weighting scheme used for the observed reflections was that of Hughes (1941) with $4F_o(\text{min})=70$. Unobserved reflections were omitted in the earlier stages of the refinement but were introduced in the final stages with the weighting scheme mentioned earlier.

The standard deviations of the positional and temperature parameters were estimated from the inverse matrix of the normal equations. The shifts in parameters indicated in the last cycles of the least-squares refinements are given in Tables 1 and 2 as fractions of their respective e.s.d. values.

Discussion of the structure

A projection of the crystal structure of $C_4H_8Se.I_2$ on (010) is shown in Fig.1, while a view of a molecule of

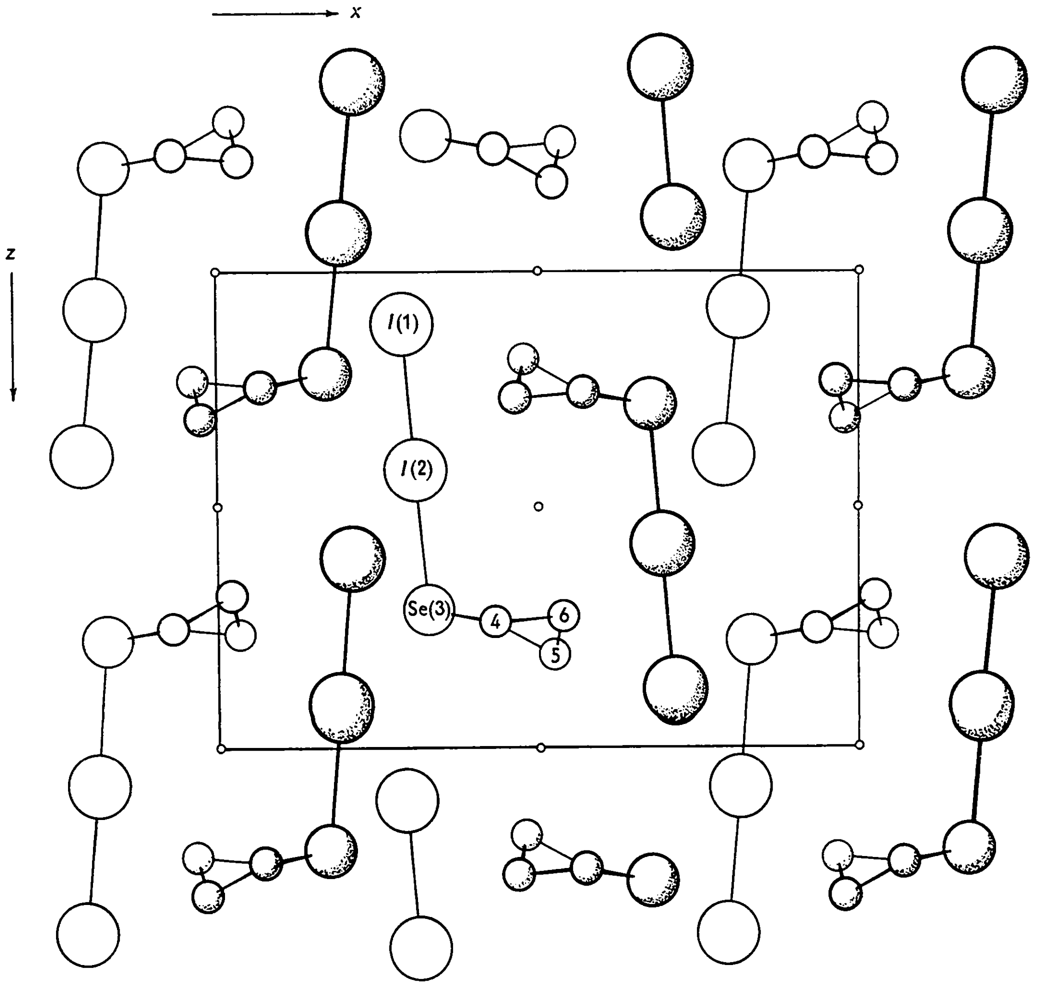

Fig. 1. Projection of the structure of $C_4H_8Se.I_2$ on (010). The heavy atoms in the shaded molecules are in the mirror at $y=\frac{3}{4}$, while those in the unshaded molecules are in the mirror at $y=\frac{1}{4}$.

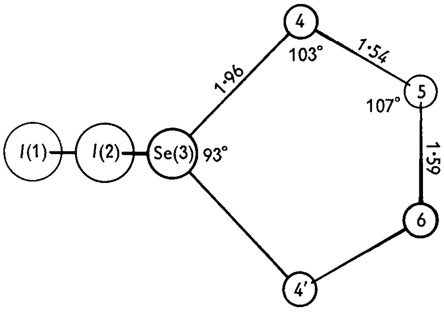

Fig. 2. View of the molecule of $C_4H_8Se.I_2$ perpendicular to the plane of the atoms C(4)–Se(3)–C(4).

the complex perpendicular to the plane of the C–Se–C bonds is shown in Fig. 2. The structurally interesting bond distances, bond angles and intermolecular packing distances are given in Tables 4, 5 and 6 respectively.

The individual molecules which make up the disordered structure have no symmetry, but they collectively achieve the symmetry *m* in a statistical manner. Thus the individual molecules are of two kinds which are mirror images of each other. Although the structure of $C_4H_8Se.I_2$ is definitely of the molecular complex type involving Se.I–I bonding, there are strong indications that the structure is tending toward the axial X–Se–X bonding found in R_2SeBr_2 and R_2SeCl_2 compounds. These indications include (*a*) the short Se.I bond of 2·762 Å, (*b*) the long I–I bond of 2·914 Å and (*c*) the short intermolecular contact of 3.638 Å which Se shows with the I(1) atom of a neighboring molecule. The position of this second iodine atom is such that the angle I(2)–Se–I(1) is 167°, not far from the 172–180° found in the axial type compounds.

Table 4. *Bond distances in* $C_4H_8Se.I_2$

	Pnma structure		*Pn*2*a* structure	
Bond	Distance	e.s.d.	Distance	e.s.d.
Se(3)–I(2)	2·762 Å	0·005 Å	2·765 Å	0·005 Å
I(1)–I(2)	2·914	0·004	2·913	0·004
Se(3)–C(4)	1·960	0·025	1·957	0·035
Se(3)–C(4′)	(1·960)	(0·025)	1·945	0·060
C(4)–C(5)	1·55	0·05	1·52	0·07
C(5)–C(6)	1·59	0·07	1·64	0·07
C(4′)–C(6)	1·52	0·05	1·67	0·10
Se(3)–I(1)*	3·638	0·005	3·636	0·005

* Intermolecular, between two molecules related by the lattice translation along **c**.

Table 5. *Bond angles and dihedral angles in* $C_4H_8Se.I_2$ *in degrees. Estimated deviations in parenthesis*

(*a*) Bond angles

	Pnma structure	$Pn2_1a$ structure
I(1)–I(2)–Se(3)	179·4 (0·3)	179·1 (0·3)
I(2)–Se(3)–I(1)*	167·2 (0·4)	167·2 (0·4)
I(2)–Se(3)–C(4)	100·5 (1·0)	97·0 (1·8)
I(2)–Se(3)–C(4′)	100·5 (1·0)	108·0 (5·0)
C(4)–Se(3)–C(4′)	93·2 (1·8)	93·9 (5·5)
Se(3)–C(4)–C(5)	102·1 (2·2)	102·1 (2·5)
C(4)–C(5)–C(6)	107·8 (3·0)	105·2 (3·5)
C(5)–C(6)–C(4′)	105·8 (3·0)	98·0 (6·0)
C(6)–C(4′)–Se(3)	104·6 (2·2)	101·3 (3·0)

* Intermolecular, between two molecules related by the lattice translation along **c**.

(*b*) Dihedral angles

C(4)–Se(3)–C(4′)–C(6)	14·4°
C(4′)–Se(3)–C(4)–C(5)	16·0
Se(3)–C(4)–C(5)–C(6)	42·4
Se(3)–C(4′)–C(6)–C(5)	40·5
C(4)–C(5)–C(6)–C(4′)	57·1

Table 6. *Packing distances in* $C_4H_8Se.I_2$

Refer to Fig. 1 for atom numbering

Atom in numbered molecule	Atom in neighboring molecule	Symmetry operation converting numbered molecule to neighbor*	Observed distance	Sum of van der Waals radii
Se(3)	I(1)	I	3·64 Å	4·15 Å
C(4)	I(1)	I	4·08	4·15
C(5)	I(1)	I	4·11	4·15
I(2)	I(1)	II	4·37	4·30
Se(3)	I(1)	II	4·23	4·15
I(1)	C(4)	II	3·91	4·15
I(1)	C(5)	III	4·02	4·15
I(1)	C(6)	III	4·07	4·15
I(2)	C(6)	III	3·94	4·15
C(5)	Se(3)	IV	3·96	4·00
C(6)	Se(3)	IV	3·82	4·00

* I: Lattice translation along *c* axis.
II: *n*-glide plane at $x=\frac{1}{4}$.
III: Center of symmetry at $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$.
IV: 2_1 axis at $y=\frac{1}{4}$, $z=\frac{3}{4}$.

It is of interest to compare the structure of $C_4H_8Se.I_2$ with that of di-*p*-chlorodiphenyltellurium diiodide (Chao & McCullough, 1962). The latter compound has axial I–Te–I bonds but there are indications of tendencies toward molecular complex type bonding. One Te–I bond is significantly longer than the other and both are longer than expected for axial type bonding. Also the intermolecular I–I packing distance in the line of the Te–I bonds is only 3·85 Å, considerably shorter than the sum of the van der Waals radii, 4·30 Å. The bonding arrangements of the heavy atoms in the two compounds are compared in Fig. 3 and the bond distances are compared in Tables 7 and 8.

Table 7. *Comparison of* M–I *and* I–I *distances in* $C_4H_8Se.I_2$, $C_4H_8Se_2.2I_2$ *and* $(p\text{-}ClC_6H_4)_2TeI_2$

	$C_4H_8Se.I_2$	$C_4H_8Se_2.2I_2$	$(p\text{-}ClC_6H_4)_2TeI_2$
Shorter M–I distance	2·762 Å	2·829 Å	2·922 Å
Longer M–I distance	3·638	3·889	2·947
Shortest I–I distance	2·914	2·870	3·85

Table 8. *Comparison of* M–X *distances in various compounds with sums of single bond covalent radii*

Bond	Observed distance	Sum of radii	Difference	Compound	Reference
Se–Cl	2·38 Å	2·16 Å	0·22 Å	$(p\text{-tolyl})_2SeCl_2$	McCullough & Marsh (1950)
Se–Br	2·55	2·31	0·24	$(p\text{-tolyl})_2SeBr_2$	McCullough & Marsh (1950)
Se–I	2·76	2·50	0·26	$C_4H_8Se.I_2$	Present work
Te–Cl	2·51	2·36	0·15	$(CH_3)_2TeCl_2$	Christofferson, Sparks & McCullough (1958)
Te–Br	2·68	2·51	0·17	$(C_6H_5)_2TeBr_2$	Christofferson & McCullough (1958)
Te–I	2·93	2·70	0·23	$(p\text{-ClC}_6H_4)_2TeI_2$	Chao & McCullough (1962)

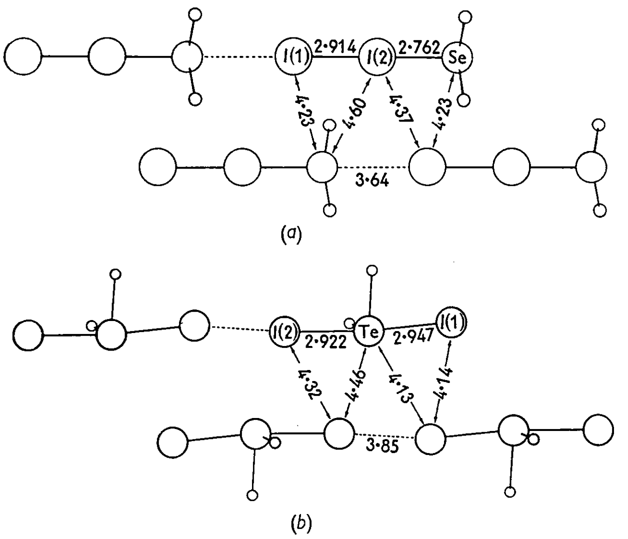

Fig. 3. (*a*) View of part of the structure of $C_4H_8Se.I_2$ along the *a* axis showing the packing of the heavy atoms. Carbon atoms C(5) and C(6) are omitted. (*b*) View of part of the structure of $(p\text{-ClC}_6H_4)_2TeI_2$ along the *b* axis showing the packing of the Te and I atoms. Only the central portions of the molecules are shown.

Another interesting result of the present study is the structure of the five-membered tetrahydroselenophene ring. If the plane of the atoms C(4)–Se(3)–C(4′) is used as a reference, C(5) is displaced 0·42 Å from the plane on one side and C(6) is displaced 0·37 Å on the other. In view of the standard deviations of about 0·03 Å in the positional parameters of these atoms, the difference in the displacements is probably not significant. The puckering of the ring is equally probable in either of two ways, giving rise to two molecular conformations, and the disorder in the structure. For symmetry reasons, the packing contacts of these atoms are not changed in going from one configuration to the other and no strong barrier is apparent which would prevent interchange of the two forms, even in the solid.

Except for an unexpectedly high value for B_{22} for the selenium atom, the temperature parameters in $C_4H_8Se.I_2$ follow the same pattern found in the iodine complexes of dithiane (Chao & McCullough. 1960) and diselenane (Chao & McCullough, 1961). In these cases B_{ii} for I(1) > B_{ii} for I(2) > B_{ii} for Se, that is the vibrations of the iodine atom at the end of the Se–I–I sequence are most pronounced, in fact, greater than those of any other atoms in the crystals. Analysis of the B's for I(1) shows that the major axis of the vibrational ellipsoid (which is required by symmetry to be normal to **b**) makes an angle of 87°($\sigma \sim 3°$) with the line of the bond between I(1) and I(2). Thus the implied vibration of I(1) is largely normal to its bond with I(2) with an r.m.s. amplitude of 0·3 Å.

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