Hoerni & Ibers (1954) for carbon, modified by a temperature factor $B = 3{\cdot}0$. The form factors f_H for the 4 atoms determining α_H were deduced from the relation

$$r = \Sigma_H/\Sigma_L = (f_H/f_L)(4/5)^{\frac{1}{2}} ,$$

r being assigned values of 0·5, 1·0 and 1·5 in turn. Values of $|F|$, $|F_H|$ and α_H were calculated for $h \leq 30$ and the appropriate values of W obtained by interpolation in Table 2.

Electron-density distributions ϱ' and ϱ'' were calculated for the three values of r: ϱ' was calculated from the structure amplitudes $|F|$ with phase angles α_H and ϱ'' was calculated from the suitably scaled weighted structure amplitudes $kW|F|$ with phase angles α_H, the same $F(0)$ term being used in each series and the scale factor k being defined by

$$\sum_{h=1}^{30} |F| = k \sum_{h=1}^{30} W|F| \, .$$

A fair comparison of the two distributions can then be made directly. The resultant distributions are shown in Fig. 1, and an examination of this shows the improved resolution in ϱ'', especially at the lowest value of r, of the atoms which make no contribution to α_H.

In order to provide a quantitative measure of the improvement a comparison was made of the average peak heights of the known atoms, that is, those contributing to α_H, and the unknown atoms in the weighted and unweighted Fourier series of Fig. 1. Values of $\overline{(\varrho_W/\varrho_U)}_H$ and $\overline{(\varrho_W/\varrho_U)}_L$, the ratios of the average peak height in the weighted series to the average peak height in the unweighted series of the known and unknown atoms, respectively, were calculated for the various values of r and are listed in Table 3. The results show that the average peak height of an unknown atom is increased considerably more in the weighted series than is the peak height of a known atom. The greatest improvement in resolution is associated with the smallest value of r, in agreement with Woolfson's conclusions concerning the centrosymmetrical case.

Table 3. *Comparison of the average peak heights in the weighted and unweighted Fourier series*

r	$\overline{(\varrho_W/\varrho_U)}_H$	$\overline{(\varrho_W/\varrho_U)}_L$
0·5	1·11	1·42
1·0	1·05	1·13
1·5	1·03	1·08

In view of these results it would appear that there is a greater possibility of recognizing the structure in the weighted than in the unweighted series and it would seem worthwhile, therefore, in the application of the heavy-atom method to non-centrosymmetrical structures, particularly when the parameter r is small, to weight each structure amplitude according to the function tabulated in Table 2 rather than to include indiscriminately each structure amplitude at its face value.

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The structure of the compounds of iodine with 1,4 diselenane and 1,4 dithiane.*

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A long term project in these laboratories has been the investigation of the structures of compounds of the type $R_2\mathrm{Se}X_2$ and $R_2\mathrm{Te}X_2$ where X is one of the halogens. The previously reported studies have involved only dichlorides and dibromides and the structures have, in all cases, involved nearly linear X–Se–X and X–Te–X axial bonds in molecules with pseudo trigonal bipyramidal structures (see Christofferson, Sparks & McCullough, 1958, for references to earlier studies). Preliminary studies on several iodides in the tellurium series showed these to be structurally complex. In contrast, the iodides of 1,4 diselenane and 1,4 dithiane proved to be crystallographically simple. Work on these compounds indicated that they are molecular complexes, rather than true diiodides. This unexpected result gave added interest to the study and prompted this preliminary report.

Crystallographic data for the isomorphous compounds are given in Table 1. Due to the presence of only two molecules per unit cell in $P2_1/c$, the molecules are required to be centrosymmetric. Satisfactory trial structures were obtained by means of Patterson summations on (010) and (100) and Fourier summations on these faces of the unit cells in the two compounds gave the positional parameters listed in Table 2. Although approximate carbon positions were indicated in the two-dimensional summations, reliable parameters must await the three-dimensional refinement of the structures now in progress. A projection of the structure of the selenium

Table 1. *Crystallographic data*

	$C_4H_8S_2 . 2\,I_2$	$C_4H_8Se_2 . 2\,I_2$
a (Å)	6·83	6·88
b (Å)	6·39	6·33
c (Å)	16·78	17·68
β (°)	117° 30′	118° 30′
$\varrho_{\mathrm{obs.}}$ (g.cm^{-3})	—	3·4
$\varrho_{\mathrm{calc.}}$ (g.cm^{-3})	3·22	3·53

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Table 2. *Atomic positional parameters*

(*a*) $C_4H_8S_2.2\,I_2$

	x	*y*	*z*
S	0·208	0·451	0·100
I_1	0·525	0·140	0·147
I_2	0·825	0·817	0·183

(*b*) $C_4H_8Se_2.2\,I_2$

	x	*y*	*z*
Se	0·192	0·607	0·110
I_1	0·472	0·259	0·139
I_2	0·770	0·920	0·173

Table 3. *Bond distances in* $C_4H_8S_2.2\,I_2$, $C_4H_8Se_2.2\,I_2$ *and related compounds*

Compound	Bond	Obs. dist. (Å)	Radius sum (Å)	Diff. (Å)
$C_4H_8S_2.2\,I_2$	S–I_1	2·77	2·37	0·40
	I_1–I_2	2·77	2·66	0·11
$C_4H_8Se_2.2\,I_2$	Se–I	2·81	2·50	0·31
	I_1–I_2	2·83	2·66	0·17
$C_4H_8O_2.2\,ICl$	O–I	2·6	1·99	0·6
(Hassel & Hvoslef)	I–Cl	2·3	2·32	0·0
$C_4H_8O_2.Br_2$	O–Br	2·71	1·80	0·91
(Hassel & Hvoslef)	Br–Br	2·31	2·28	0·03
CsI_3	I_1–I_2	3·04	2·66	0·38
(Tasman & Boswijk)	I_2–I_3	2·83	2·66	0·17
$(C_6H_5CH_2)_2S.I_2$	S–I_1	2·84	2·37	0·47
(Hassel)	I_1–I_2	2·81	2·66	0·15

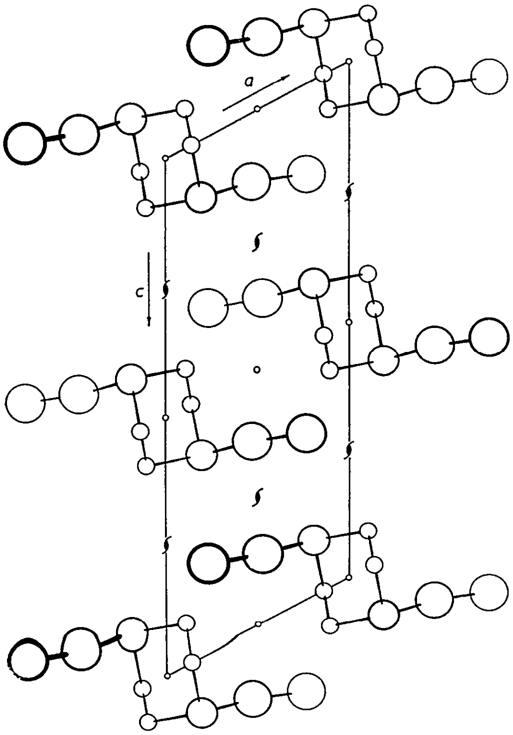

Fig. 1. Projection of the structure of $C_4H_8Se_2.2\,I_2$ on (010). Circles represent, in order of decreasing size, I, Se and C atoms respectively.

compound on (010) is shown in Fig. 1. Tentative bond distances between heavy atoms are given in Table 3.

The results of Hassel & Hvoslef for the 1,4 dioxane complexes $C_4H_8O_2.Br_2$ (1954) and $C_4H_8O_2.2\,ICl$ (1956) and the results of Tasman & Boswijk (1955) for CsI_3 are included in Table 3 for comparison with the results of the present study. The angles Se–I–I and S–I–I both have values within a degree or two of 176°, the angle found in the I_3^- ion. The O–I–Cl and O–Br–Br angles in the dioxane complexes are also nearly linear.

The sums of the normal single covalent bond radii are given in Table 3 for comparison with the observed bond distances. The differences in bond lengths (observed minus calculated) are listed in the last column of the table. If one makes the reasonable assumption that a smaller difference in these quantities implies a stronger bond, then it follows that 1,4 diselenane forms a stronger iodine complex than 1,4 dithiane which in turn forms a stronger complex than the ICl and Br_2 complexes of 1,4 dioxane. Also the halogen molecule entering a stronger complex should become itself more loosely bonded (lengthened X–X or X–X' bond), while a halogen molecule entering a weak complex should be only slightly disturbed. These latter considerations lead to the same conclusions with respect to the stabilities of the complexes. The observed Se–I bond distance of 2·81 Å is actually only about 0·1 Å longer than the anticipated length of an Se–I bond in axial I–Se–I bonding. In the latter case Se would be expected to have a covalent radius of 1·39 Å (McCullough, 1953).

As a result of correspondence with Professor O. Hassel, it was learned that he is also studying the structure of the iodine compound with 1,4 dithiane. He indicated that the S–I bonds are in the equatorial positions, in contrast with the axial Se–I bonds shown in our Figure 1. A review of our results after receiving his communication indicated that the angle S–S–I is 130° in the 1,4 dithiane complex and that the angle Se–Se–I is 90° in the 1,4 diselenane complex. The two molecules accordingly have different conformations and the apparent isomorphism of the compounds is surprising.

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