Acta Cryst. (1950). **3**, 41

The Crystal Structure of Di-*p*-tolylselenium Dichloride and Di-*p*-tolylselenium Dibromide*

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(*Received* 28 *February* 1949 *and in revised form* 25 *July* 1949)

Crystals of the dichloride and dibromide of di-*p*-tolylselenium have been studied by means of rotation and Weissenberg photographs, using copper radiation. The substances are isomorphous and have structures based on $P2_12_12-D_2^3$ with two molecules to the unit cell. The molecular structure is that of a slightly distorted trigonal bipyramid with a selenium atom at the center, halogen atoms at the apices, and two *p*-tolyl groups plus an unshared pair of electrons in the equatorial positions. As in the diphenylselenium dihalides, the selenium–halogen separations are approximately 0·23 A. longer than the sums of the normal single-bond covalent radii.

Introduction

In previous communications from this Laboratory, the crystal structures of diphenylselenium dibromide (McCullough & Hamburger, 1941) and diphenylselenium dichloride (McCullough & Hamburger, 1942) have been described. The dibromide was found to have a four-molecule unit based on the space group *Pbcn*, while the dichloride proved to have an eight-molecule unit based on *Pbca*. In spite of the differing crystal structures, the molecular structures were the same within the experimental errors and were essentially that of a trigonal bipyramid with the selenium atom at the center, the two halogen atoms in the apical positions, and the three equatorial positions occupied by the two phenyl groups and the unshared pair of electrons. An unusual feature of both molecules is the unexpectedly long selenium–halogen separations observed, which are 2·52 A. for Se–Br and 2·30 A. for Se–Cl, as compared with the sums of the normal single-bond radii, 2·31 and 2·16 A. respectively. The observed halogen–selenium–halogen bond angles were 180° ± 3° in the dibromide and 180° ± 5° in the dichloride.

As a check on these interesting structures, and with the object of obtaining more accurate information on the bond distances and bond angles, the dihalides of two *para*-substituted diphenylselenides were investigated. The present communication deals with the dichloride and the dibromide of di-*p*-tolylselenium.

Preparation of the crystals

Di-*p*-tolylselenium was prepared from *p*-toluidine and potassium selenide by the method of Leicester & Bergstrom (1929). The crude selenide was purified by means of several recrystallizations from a solvent consisting of two volumes of methanol in one volume of benzene. The dihalides were precipitated by addition of carbon tetrachloride solutions of the pure halogens to solutions of the selenide in that solvent. After recrystallization from carbon tetrachloride the equivalent weights were taken by the method of McCullough (1942) and found to be within 0·1 % of theoretical, which is about the experimental error of the method. Crystals suitable for X-ray analysis were prepared by the slow evaporation of solutions of the dihalides in pure carbon bisulfide, in which the substances are very soluble.

Determination of the structure

Rotation and Weissenberg photographs of both substances were prepared about all three axes of the orthorhombic crystals by use of copper radiation filtered through nickel foil. Needles about 2 mm. in length and about 0·2 mm. across were used in the preparation of photographs about the *c* axis. In order to minimize undesired absorption effects, it was necessary to cleave crystals across the *c* axis in the preparation of photographs about the *a* and *b* axes. The zero-layer Weissenberg photographs were carefully prepared by use of a double-film technique, and all intensities were estimated visually with the aid of a calibrated scale.

Photographs for the two compounds were nearly identical, differing only slightly in the relative intensities and in lattice dimensions. We shall accordingly limit our discussion to the dichloride, with the understanding that the features of the structure analysis of the dibromide were essentially identical with those of the dichloride. The lattice constants given in Table 1 were computed from measurements taken from rotation and Weissenberg photographs about all three axes.

Table 1. *Lattice constants for di-*p*-tolylselenium dihalides*

(Cu $K\alpha = 1{\cdot}5418$ A.)

	a (A.)	*b* (A.)	*c* (A.)
Dichloride	14·20 ± 0·03	8·43 ± 0·02	5·81 ± 0·02
Dibromide	14·60 ± 0·03	8·64 ± 0·02	5·82 ± 0·02

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* Contribution from the Department of Chemistry, University of California. Based on research performed under Task Order I of Contract N6 onr-275 between the Office of Naval Research and the University of California at Los Angeles.

The only systematic absences observed were $h00$ with h odd and $0k0$ with k odd. The space group was thus uniquely determined to be $P2_12_12\text{–}D_2^3$. The density of the dichloride was found by flotation in a mixture of carbon tetrachloride with methylene chloride to be approximately 1·55 g.cm.$^{-3}$. The calculated density for two molecules in the unit cell is 1·57 g.cm.$^{-3}$. From the similarities of the cell constants and appearance of the photographs it was assumed that there were also two molecules per unit cell in the dibromide.

We must, then, place two selenium atoms, four halogen atoms, and twenty-eight carbon atoms within the unit cell. The selenium atoms must lie in one of the two sets of special positions, $(0, 0, z; \frac{1}{2}, \frac{1}{2}, \bar{z})$ or $(\frac{1}{2}, 0, z; 0, \frac{1}{2}, \bar{z})$, the set actually employed being arbitrary. It then appears likely that the other atoms should occupy sets of general positions $(x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2}-x, \frac{1}{2}+y, \bar{z}; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$. Although this space group is polar, projections along each axis possess a center of symmetry and it was therefore possible to make Fourier projections along all three axes.

The most striking feature of the Weissenberg photographs about the c axis is the general weakness or complete absence of reflections from planes with $h+k$ odd. If these reflections were entirely absent, centering of the c face of the unit cell would be indicated. This, in turn, would indicate that the X–Se–X and C–Se–C bonds probably project parallel to the a and b axes. This situation must be very nearly fulfilled, and it appeared that a Fourier projection on (001) should afford good resolution of the molecule.

Reflections of the type $hk0$ were observed for approximately 115 planes out of a possible total of 154 within the reflecting circle. The maximum observed value of $\sin\theta$ was 0·98. After correcting the observed intensities for Lorentz and polarization factors, the resultant F^2 values were used to construct a Patterson projection on (001). As in all projections involved in this investigation, Patterson–Tunell strips (Patterson & Tunell, 1942) were used to perform the summation at intervals of $\frac{1}{60}$ of the cell edge. The resulting summation showed, besides a peak at the origin, a large peak at $y=0{\cdot}284$ and a smaller peak at $y=0{\cdot}44$ (and, by symmetry, at $y=0{\cdot}56$). The size of the peaks strongly indicated that they represented Se–Cl and Cl–Cl interactions respectively. By placing the selenium atom at $0, 0, z$, chlorine parameters of $(x, 0{\cdot}28, z)$ were indicated with the value of x very close to zero. The algebraic sign of x may be assigned arbitrarily, and in order to fix the signs of the F values of $hk0$ with $h+k$ odd, the chlorine atom was placed at $x=0{\cdot}02$. The F values thus obtained were used to construct a Fourier projection on (001). From the carbon parameters indicated by this projection, the signs of about five of the F terms were revised, and a final Fourier projection was constructed. For both the dichloride and the dibromide, the resolution of carbon atoms was quite good, with the dichloride yielding a slightly better result. The chlorine parameters obtained from this projection are

$$x_{\text{Cl}}=0{\cdot}010, \quad y_{\text{Cl}}=0{\cdot}281.$$

Zero-layer Weissenberg photographs about the b axis were used for determination of the z parameters. Ninety-five out of a possible 115 reflections were observed on these photographs with a maximum $\sin\theta$ of 0·98. The Patterson projection on (010) showed a very large peak at $x=\frac{1}{2}$, $z=0{\cdot}144$. From this and other features of the projection it was inferred that the selenium atom and the two chlorine atoms in a given molecule have the same or nearly the same z parameter. This would be the case if, as expected, the Cl–Se–Cl bond angle were close to 180°.

In order to determine the signs of the F values, the z parameters for both the selenium and chlorine atoms were given the tentative value 0·072. The resulting Fourier projection yielded final parameters which did not change the sign of any F term. However, in this projection the selenium and chlorine atoms nearly coincided, making it impossible to determine the exact z parameters of these atoms, although the resolution of carbon atoms was excellent. For this reason, a Fourier projection on (100) was also constructed. Owing to the shortness of the b and c axes, there were but sixty-eight possible planes within the diffraction circle and, of these, only thirty-eight were actually observed. The resulting Fourier projection thus showed little detail; but it did indicate that the chlorine atoms were at a slightly higher z value than the selenium atom. The parameters determined from this projection were

$$y_{\text{Se}}=0, \quad z_{\text{Se}}=0{\cdot}072, \quad y_{\text{Cl}}=0{\cdot}286, \quad z_{\text{Cl}}=0{\cdot}078.$$

The final step in the structure determination consisted in adjusting the values of the various co-ordinates until the best fit for all three projections was obtained. It was found that reflections of the type $h0l$ were the most sensitive to changes in the z parameters of the selenium and halogen atoms, while reflections of the type $hk0$ were of most use in locating the carbon atoms. For the preliminary determination of the carbon parameters, the benzene ring was considered to be a regular hexagon with an edge of 1·39 A., while the Se–C and C_4–C_7 distances were taken as the sums of the normal covalent radii, 1·94 and 1·54 A. respectively. From Fourier projections, there was some evidence in both crystals that the latter distance might be somewhat shorter, perhaps about 1·50 A. However, the intensity agreement obtained from assuming the longer distance was very good, and the accuracy of the observed intensities was not considered great enough to allow closer refinement of the carbon parameters. In general, the position of the carbon atoms assigned in the above manner agreed very closely with the maxima in the Fourier projections, and it is probable that the C–C bond distances are accurate within 0·05 A. The accuracy of these determinations was greatly increased by the fact that the planes of projection (010) and (001) both show essentially complete resolution of the phenyl groups. The final Fourier projections on the three faces of the unit cell for the dichloride are shown in Figs. 1, 2 and 3. The Fourier projections obtained for the dibromide show essentially the same features. (Note that in the projection on (010), the halogen and selenium atoms are closely superimposed.)

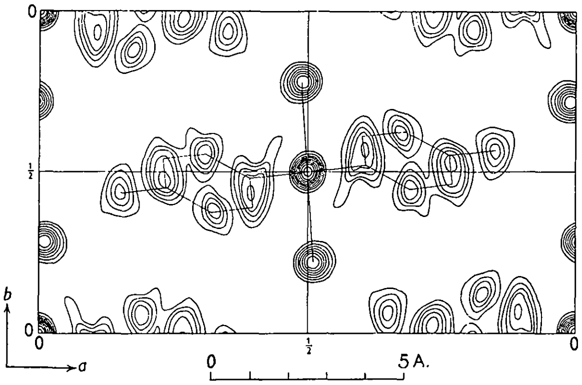

Fig. 1. Fourier projection of di-*p*-tolylselenium dichloride on (001).

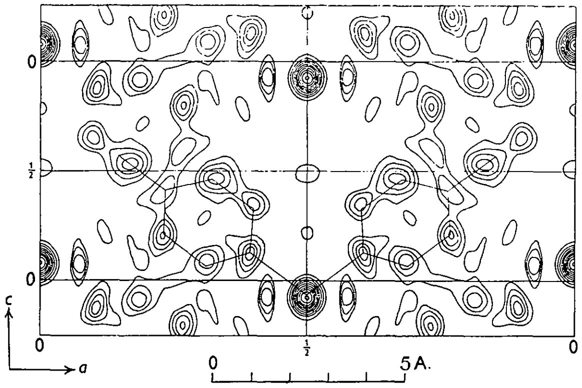

Fig. 2. Fourier projection of di-*p*-tolylselenium dichloride on (010).

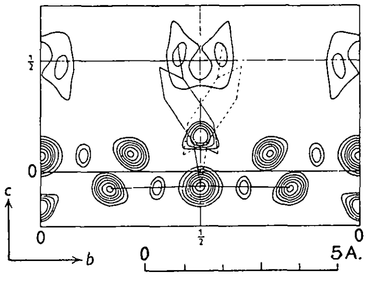

Fig. 3. Fourier projection of di-*p*-tolylselenium dichloride on (100).

In the final comparison of calculated and observed F values, it became apparent that a temperature correction was necessary, as the calculated intensities at large angles were, in general, much too strong. This condition was especially pronounced with reflections having a large value of k or l. In the former case, reflections of the type h,10,0 were quite weak, although for these planes the selenium and halogen atoms both show nearly the maximum positive phase. Thus, if a constant normalization factor is used for all reflections, these last reflections calculate to be about three times as strong as they actually appear. This effect is noted even more strongly for high values of l, while it is much less evident at high values of h. As a consequence, it seemed advisable to make anisotropic temperature corrections which differed along the three axes.

The form of this correction was indicated by a plot of the logarithm of the ratio of $F_{\text{calc.}}$ to $F_{\text{obs.}}$ against various powers of h, k and l. That is, an average ratio was obtained for every value of h (varying k or l), and the logarithm of this ratio was plotted against h^2, h^3 and h^4; this was repeated for values of k and l. In every case (six plots for each crystal) the third-power curve provided the closest fit to a straight line; moreover, the slope of the line remained constant for reflections both of the type $h0l$ and $hk0$. From the intercept of this line with the axis $h=0$ was obtained the absolute ratio (the constant film correction factor), while the slope of the line determined the variation of this factor as the running index was increased. The total correction may be summed in the following manner:

$$F_{\text{corr.}} = F_{\text{calc.}}\, e^{-\alpha(h/a)^3}\, e^{-\beta(k/b)^3}\, e^{-\gamma(l/c)^3}.$$

Here, $F_{\text{calc.}}$ is the calculated F value corrected by a factor constant for any photograph, varying from 16 to 23 for the dibromide and from 9 to 13 for the dichloride. The Miller indices are divided by their respective cell dimensions for purposes of normalization. The values of α, β and γ are as follows:

	Dichloride	Dibromide
α	0·25	0·24
β	0·71	0·51
γ	0·89	0·64

It is interesting to note that the ratio $\alpha:\beta:\gamma$ is nearly constant for the two crystals. The fact that the three correction factors are so clearly separable in the two crystals is no doubt due to the alignment of the molecule along the three crystallographic axes. It should be pointed out that if these corrections are indeed due to thermal disturbances within the molecule, the peaks on the Fourier projections should show some enlargement in the direction of vibration. Little such enlargement is actually observed. However, this empirical anisotropic correction fits the data, whereas a correction term depending upon $\sin^2\theta$ gives less satisfactory results.

The parameters finally chosen are given in Table 2. The reliability of the structure is expressed in Table 3 in terms of the correlation factor, R, defined as

$$R = \frac{\sum^{N}\{|F|_{\text{obs.}} - |F|_{\text{calc.}}\}}{\sum^{N}|F|_{\text{obs.}}}.$$

In addition to values of R defined as above, values of R' which include the empirical correction factor, are also given.

Table 2. *Parameter values for di*-p-*tolylselenium dichloride and dibromide*

		Se	*X*	C_1	C_2	C_3	C_4	C_5	C_6	C_7
Dichloride	*x*	0	0·012	0·108	0·102	0·180	0·264	0·270	0·192	0·350
	y	0	0·281	0·979	0·888	0·872	0·948	0·039	0·054	0·931
	z	0·069	0·078	0·870	0·672	0·529	0·584	0·782	0·925	0·426
Dibromide	*x*	0	0·008	0·107	0·101	0·178	0·259	0·265	0·188	0·344
	y	0	0·294	0·977	0·888	0·871	0·944	0·032	0·049	0·925
	z	0·058	0·070	0·863	0·665	0·525	0·583	0·781	0·921	0·428

A detailed comparison of observed, calculated and corrected *F* values is given for the *hk*0 data from the dichloride in Table 4. The complete tabulation of intensity data is omitted in the interest of economy of space.

Table 3. *Correlation factors for di*-p-*tolylselenium dihalides*

	Dichloride			Dibromide		
	R	*R′*	*N*	*R*	*R′*	*N*
*hk*0	0·29	0·12	111	0·28	0·15	112
*h*0*l*	0·33	0·13	92	0·32	0·12	98
0*kl*	0·43	0·16	39	0·38	0·20	37

Table 4. *Comparison of calculated with observed F values for hk*0 *reflections of di*-p-*tolylselenium dichloride*

*hk*0	$F_{\text{calc.}}$	$F_{\text{corr.}}$	$F_{\text{obs.}}$	*hk*0	$F_{\text{calc.}}$	$F_{\text{corr.}}$	$F_{\text{obs.}}$	*hk*0	$F_{\text{calc.}}$	$F_{\text{corr.}}$	$F_{\text{obs.}}$
200	+63	+63	53	830	+1	+1	<11	10,6,0	+34	+25	22
400	+102	+101	80	930	+64	+59	57	11,6,0	+14	+10	13
600	+91	+89	86	10,3,0	+21	+19	18	12,6,0	+23	+16	17
800	+95	+91	85	11,3,0	+64	+56	62	13,6,0	+18	+11	<11
10,0,0	+87	+80	81	12,3,0	+38	+32	28	14,6,0	+20	+12	17
12,0,0	+74	+65	66	13,3,0	+34	+28	26	15,6,0	+33	+19	11
14,0,0	+37	+29	32	14,3,0	+28	+21	18				
16,0,0	+44	+31	29	15,3,0	+54	+39	38	170	+91	+61	55
18,0,0	+43	+26	24	16,3,0	+10	+7	<9	270	−7	−4	<13
				17,3,0	+28	+18	20	370	+66	+44	49
110	+88	+88	75					470	+10	+7	13
210	+6	+6	5	040	+85	+80	99	570	+71	+47	49
310	+37	+37	42	140	+4	+4	<9	670	−1	−1	<13
410	−12	−12	11	240	+82	+76	80	770	+76	+49	51
510	+28	+28	35	340	+10	+8	14	870	+2	+1	<13
610	−24	−24	23	440	+94	+87	103	970	+66	+42	41
710	+43	+42	43	540	−18	−16	13	10,7,0	+16	+10	12
810	−31	−30	29	640	+62	+57	52	11,7,0	+51	+31	28
910	+44	+42	47	740	−33	−30	29	12,7,0	−7	−4	<9
10,1,0	−29	−27	25	840	+82	+72	72	13,7,0	+58	+32	24
11,1,0	+80	+71	71	940	−1	−1	<13				
12,1,0	−17	−14	13	10,4,0	+59	+50	53	080	+34	+19	23
13,1,0	−2	−2	<13	11,4,0	−28	−23	14	180	−9	−5	<13
14,1,0	−29	−23	14	12,4,0	+49	+40	37	280	+54	+30	26
15,1,0	+40	+30	29	13,4,0	−16	−12	<13	380	−3	−2	<13
16,1,0	−41	−29	15	14,4,0	+52	+38	35	480	+27	+15	18
17,1,0	+31	+20	17	15,4,0	−16	−11	<11	580	−13	−7	<13
18,1,0	−28	−17	8	16,4,0	+39	+25	24	680	+36	+19	18
								780	−20	−11	13
020	+98	+98	98	150	+17	+14	11	880	+32	+17	17
120	+41	+41	33	250	−22	−19	16	980	−20	−10	<11
220	−37	−36	38	350	+22	+19	21	10,8,0	+50	+25	15
320	+29	+29	30	450	+16	+13	15	11,8,0	−21	−10	<8
420	+12	+12	8	550	+13	+11	<12	12,8,0	+31	+15	9
520	−10	−10	9	650	−17	−14	18				
620	+3	+3	<9	750	+30	+26	26	190	+13	+6	<12
720	0	0	<10	850	−21	−17	19	290	+18	+8	<12
820	+33	+32	33	950	+19	+16	16	390	−7	−3	<12
920	+12	+11	12	10,5,0	−2	−2	<13	490	−6	−2	<11
10,2,0	+24	+22	29	11,5,0	+11	+9	14	590	−4	−2	<11
11,2,0	+7	+6	<13	12,5,0	−20	−15	<13	690	0	0	<11
12,2,0	+23	+20	26	13,5,0	+23	+17	15	790	+6	+2	<10
13,2,0	+26	+21	20	14,5,0	−14	−10	<11	890	+1	0	<9
14,2,0	+16	+12	14	15,5,0	+26	+17	16	990	+20	+8	<8
15,2,0	+9	+6	<12					10,9,0	+7	+3	<6
16,2,0	+21	+15	13	060	+22	+17	20				
17,2,0	+2	+2	<9	160	−10	−8	<12	0,10,0	+28	+9	16
				260	+40	+31	33	1,10,0	+7	+2	<9
130	+87	+84	89	360	+13	+10	13	2,10,0	+64	+20	20
230	+11	+11	18	460	+33	+26	31	3,10,0	+18	+5	<9
330	+95	+93	100	560	+14	+11	16	4,10,0	+28	+8	<9
430	+31	+30	35	660	+27	+20	22	5,10,0	+7	+2	<8
530	+62	+60	62	760	+4	+3	<13	6,10,0	+39	+12	9
630	+8	+7	9	860	+31	+23	30	7,10,0	+12	+3	<5
730	+77	+72	69	960	+40	+29	24				

Discussion of the structure

The molecular structure of the di-*p*-tolylselenium dihalides is essentially identical with that previously found for the diphenylselenium dihalides (McCullough & Hamburger, 1941, 1942). However, owing to better data and smaller unit cells, the details of the structure are given more accurately in the present study. In particular, the selenium–halogen separations and the *X*–Se–*X* as well as the C–Se–C bond angles are more accurately determined. Values for the more important bond distances and bond angles are shown in Table 5.

Table 5. *Bond distances and bond angles in di-*p*-tolylselenium dihalides*

	Bond distances (A.)		Bond angles (°)	
	Se–*X*	Se–C	*X*–Se–*X*	C–Se–C
Di-*p*-tolylselenium dichloride	2·38 ± 0·02	1·93 ± 0·03	177·5 ± 1	106·5 ± 1
Di-*p*-tolylselenium dibromide	2·55 ± 0·02	1·95 ± 0·03	177 ± 1	108 ± 1

The radius of selenium is especially interesting. If one subtracts the normal single-bond covalent radii for chlorine and bromine from the observed separations for Se–Cl and Se–Br, the results are 1·39 and 1·41 A. respectively, which agree closely with the octahedral covalent radius for selenium, 1·40 A., as found in K_2SeCl_6 and K_2SeBr_6 (Pauling, 1940, p. 184). On the other hand, the Se–C separation in both crystals leads to a selenium radius of 1·17 A. which is the accepted normal single-bond radius for selenium. This suggests that, although the Se–C bonds are of the $4s4p^2$ type, the Se–*X* bonds probably involve the 5*s* orbital of selenium as proposed by Beach & Pauling (Pauling, 1940, p. 184) for the octahedral $SeBr_6^{--}$ ion, leading to the much larger radius. It occurred to the present authors that the Se–*X* bonds in the diarylselenium dihalides might be the result of 4*p*5*s* hybridization. This would account both for the large radius of selenium and the near linearity of the *X*–Se–*X* bond angle. However, recent calculations by Pauling (private communication) indicate that the 4*d* and 5*s* orbitals enter about equally into hybridization with 4*p* in forming the axial bonds. This is brought about by the fact that, although the 4*d* orbital is slightly less stable, it has greater hybridizing tendencies than has the 5*s* orbital.

Other interesting features of the structure are the deviations from an ideal trigonal bipyramid. The first of these is a slight deviation from linearity in the *X*–Se–*X* bond. In both crystals this deviation amounts to 2–3° and in the same direction, namely, so that the halogen atoms are bent away from the side of the selenium atom bonded to the *p*-tolyl groups. The agreement between the two crystals lends weight to the observed displacement. The second feature involves the dihedral angle between the plane of the C–Se–C bonds and that of the *X*–Se–*X* bonds. In the dichloride this dihedral angle has the value 87 ± 2°, while in the dibromide it is 85 ± 2°. The ideal value is 90°. In both crystals the displacement is in such a direction as partially to relieve the strain brought about by the close approach of a halogen atom on one molecule with a methyl group of another molecule. The observed separations are 3·67 A. in the dichloride and 3·79 A. in the dibromide, compared with the sums of the van der Waals radii (Pauling, 1940, p. 189) of a methyl group and the halogen atom of 3·8 and 3·95 A. respectively.

The non-bonded halogen–halogen separations are also of interest. In the dichloride this separation is 3·72 ± 0·04 A., while in the dibromide the value is only 3·58 ± 0·04 A. Again by use of Pauling's van der Waals radii, the calculated distances are 3·6 and 3·9 A. respectively. However, the non-bonded Br–Br separation in crystalline bromine (Vonnegut & Warren, 1936) is even shorter, namely, 3·3 A., so that the present value of 3·58 A. is not unique in its shortness.

Because of the good resolution of the carbon atoms in two of the Fourier projections, it has been possible to determine the angle of rotation of the benzene rings about the Se–C bonds. In both crystals the dihedral angle between the plane of the ring and the plane of the C–Se–C bonds was found with be 40 ± 5°.

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