

## The Crystal and Molecular Structure of Bisdiphenylmethyl Diselenide

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The crystal and molecular structure of bisdiphenylmethyl diselenide  $[(C_6H_5)_2CHSe]_2$  has been determined by X-ray single-crystal analysis, and refined by use of full-matrix least-squares techniques to a final  $R$  value of 6.7%. The observed Se–Se bond length is  $2.285 \pm 0.005$  Å. The Se–C bond length of  $1.97 \pm 0.01$  Å identifies it as an aliphatic Se–C bond. The distribution of bond lengths and angles around this carbon atom and its deviation of  $0.507$  Å from the plane containing the three heavy atoms bonded to it (Se and two carbon atoms) also supports the view that it is a substituted methyl carbon. The CSeSe/SeSeC dihedral angle is  $82^\circ$ . Both phenyl rings are planar but one of them is observed to be distorted out of the normal benzene configuration.

### Introduction

Bisdiphenylmethyl diselenide  $[(C_6H_5)_2CHSe]_2$  was obtained by Margolis & Pittman (1957) as the product of reduction of benzophenone by hydrogen selenide in the absence of oxygen. The expected product of this reaction, dimeric selenobenzophenone  $[(C_6H_5)_2CSe]_2$ , was not in fact observed. Proof that the diselenide had been formed was obtained (*loc. cit.*) by preparing an authentic sample independently by oxidation of the selenol, formed by treating diphenylmethyl bromide with sodium hydrogen selenide. Tests, including the determination of melting points and mixed melting points indicated that both products were one the same substance, and further evidence was put forward to suggest that the substance in question contained 'substituted methyl radicals and not substituted methylene radicals implicit in the ketonic structure' (*loc. cit.*). The crystal structure determination carried out with a sample kindly supplied by Dr R. W. Pittman supports the arguments put forward by Margolis & Pittman (1957) that the substance is bisdiphenylmethyl diselenide.

Margolis & Pittman (1957) also gave evidence to suggest that the C–Se bonds in the C–Se–Se–C chain in bisdiphenylmethyl diselenide (and also in a substance believed to be di(1-phenylethyl) diselenide) were relatively weak in comparison with those in two compounds reported to be di(isopropyl) diselenide and di(sec. butyl) diselenide respectively. The structure determination of bisdiphenylmethyl diselenide indicates a distorted tetrahedral distribution of bond lengths and angles around the carbon atoms in question in this substance and not a trigonal distribution which would be implicit in a ketonic structure. Furthermore, the C–Se bond length of  $1.97$  Å found in bisdiphenylmethyl diselenide is consistent with previously reported aliphatic C–Se bonds (Kruse, Marsh & McCullough, 1957), and while this is longer by  $0.04$  Å than the aromatic C–Se bond length of  $1.93$  Å, no conclusions may be drawn regarding the relative strength of C–Se

bonds in the three other compounds named above and reported by Margolis & Pittman (1957) without at least a knowledge of the C–Se bond lengths in these substances.

### Experimental

#### Crystal data

The crystals are pale-orange monoclinic needles with the unique axis  $b$  corresponding to the needle axis. The unit-cell parameters were measured initially from oscillation, precession and Weissenberg photographs and later refined by use of Main & Woolfson's (1963) method adapted for three-dimensional data (Darlow, 1967). Weissenberg photographs taken about the  $b$  axis provided the  $\alpha_1$ – $\alpha_2$  doublets necessary for the cell refinement and the doublet separations were measured with a Buerger–Supper precession photograph calibrator. The same films were also used for intensity measurements. Altogether 40 suitable doublets were found, having separations between  $0.26$  and  $1.245$  mm and a mean value of  $0.648$  mm. These measurements (taken as the mean of several readings) were accurate to about 3% on the average. Standard deviations for the unit-cell parameters were calculated in the least-squares refinement routine on the basis of a mean error in measurement for the  $\alpha_1$ – $\alpha_2$  doublets of  $\pm 0.02$  mm.

The crystal density  $D_m$  was measured by flotation in aqueous mercuric chloride solution. The relevant crystal data are summarized below:

Bisdiphenylmethyl diselenide:  $[(C_6H_5)_2CHSe]_2$ ,  
 $C_{26}H_{22}Se_2$ ,  $M = 492.4$ ; m.p.  $120$ – $123^\circ C$  [Margolis & Pittman (1957)]; Monoclinic, acicular  $b$ :

$$\begin{aligned} a &= 18.72 \pm 0.01 \text{ \AA}, \\ b &= 5.773 \pm 0.008 \text{ \AA}, \\ c &= 12.594 \pm 0.005 \text{ \AA}; \\ \beta &= 125.47 \pm 0.03^\circ; \\ V &= 1107.4 \text{ \AA}^3; \\ D_m &= 1.49 \pm 0.01 \text{ g.cm}^{-3}; \\ Z &= 2, \\ D_x &= 1.48 \text{ g.cm}^{-3}. \end{aligned}$$

Ni-filtered Cu radiation used for intensity and unit-cell measurements.

$$\lambda = 1.542 \text{ \AA},$$

$$\mu(\text{Cu } K\alpha) = 47.8 \text{ cm}^{-1};$$

$N_0 = 1053$  non-zero intensities measured;

Number of 'less-thans' = 33;

91% of radiation sphere explored.

$$F(000) = 244.$$

Absent spectra:  $hkl$  when  $h+k=2n+1$ ;

Space group  $C^*/2$  ( $C2$  confirmed by structure analysis).

Molecular symmetry, point group 2.

### Intensity data

Intensities of  $hkl$  and  $h\bar{k}l$  reflexions were measured visually on zero to fourth-layer  $b$  axis Weissenberg photographs and corrected empirically for spot size. Equivalent pairs were averaged to give 1053 out of 1196 accessible unique intensities, together with estimates of their error (all found to be less than 8.5%). A further 33 reflexions too weak to measure were given intensities equal to half the minimum observable value. No extinction or absorption corrections were applied. Poorer quality  $Ok\bar{l}$  and  $lkl$  intensity data obtained from  $a$  axis Weissenberg films were used to scale and, in a few cases, to supplement the  $b$  axis data.

The scale factor  $K_j$  for a given film or layer  $j$  may be estimated (Palmer, 1962) from the expression:

$$K_j = \frac{1}{N} \sum_{r=1}^N S_{jr}, \quad (1)$$

where  $N$  = number of films to be scaled and

$$S_{jr} = \frac{1}{m} \sum_{n=1}^m (R_{nr}) (R_{jn}), \quad (2)$$

where  $R_{jr}$  = intensity ratio of film  $r$  to film  $j$  calculated from the terms common (if any) to the two films.  $m$  = the number of terms contributing to the summation in (2), *i.e.* for which both  $R_{nr}$  and  $R_{jn} \neq 0$ , and  $R=0$  if there are no terms common to the two films in question.

Unfortunately in the present case, because of the  $C$ -face lattice centring, only  $b$ -axis layers with  $k$  even could be scaled to the zero level  $a$ -axis intensities, and  $b$ -axis layers with  $k$  odd could be scaled to the first level  $a$ -axis intensities. Hence, no scaling was effected

between the  $k$  even and odd layers. Common  $F_0(hkl)$  values agreed on the average to about  $\pm 9\%$ . The seven scale factors were subsequently refined during refinement of the structure.

## Determination of the structure

### Preliminary

An unsharpened three-dimensional Patterson function calculated at grid intervals of 1/30 along each axis contained a main peak of height 40 on section  $v=0$ , and several other peaks of height between 6 and 8. The dominant peak which was at a vector distance of about 2.3 Å from the origin, corresponding approximately to the known Se-Se bond length, was taken to be indicative that the substance was in fact the diselenide. An Se-Se vector interaction lying on  $v=0$  precludes space group  $Cm$  but still leaves an ambiguity. If the space group is actually  $C2$  the molecular symmetry would be required to be at least point group 2 with Se atoms at  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + x, y, z; \bar{x}, y, \bar{z}$ . If the space group is  $C2/m$  the molecular symmetry would have to be at least point group  $2/m$  with Se coordinates as above but with  $y$  necessarily equal to zero. The second alternative imposes more restrictions on the possible structural arrangements than the first, requiring the methyl carbon atom C(1) to have a  $y$  parameter of zero which in turn would involve an unlikely CSeSe/SeSeC dihedral angle of zero. The Se(i)-C(1) peak did not in fact occur on the Patterson section  $v=0$ , as would be required for  $C2/m$ , and the space group was accordingly taken to be  $C2$ . (See Table 5 for notation.)

The above Patterson function contained two strong but confused images of the organic part of the structure, owing to the various Se-C and Se(i)-C interactions, most of which were accounted for by the subsidiary peaks. In order to resolve the two images, a three-dimensional minimum function,  $M_2$  (Buerger, 1959), was computed from the Patterson, with the Se positions as superposition points. The map was calculated initially at intervals of 1/30 and repeated subsequently at intervals of 1/50 along each axis to improve resolution. Interpretation of the  $M_2$  function was straightforward in spite of the presence of an unwanted

Table 1. Refinement stages

Stage	Parameters varied	No. of cycles $N_c$	No. of variables $N_v$	Initial $R$	Final $R$
1	Layer scaling factors $S(k)$ . Overall temperature factor $B_0$	2	7	0.243	0.207
2	Atomic positions only $(x, y, z)$	2	42	0.207	0.120
3	$(x, y, z)$ and $S(k)$	2	49	0.120	0.116
4	Individual isotropic temperature factors $B_r$	2	14	0.116	0.106
5	$(x, y, z)$ and $B_r$	1	56	0.106	0.106
6	$(x, y, z)$ and $S(k)$	1	49	0.106	0.105
7	Individual anisotropic temperature factors $\beta_{ij}$	3	84	0.105	0.075
8	$(x, y, z)$	2	42	0.075	0.072
9	$S(k)$	1	7	0.072	0.070
10	$(x, y, z)$ , $\beta_{ij}$ for all atoms	4	126	0.070	0.067

The individual anisotropic temperature factors are  $\beta_{ij} = 2\pi a^* i a^* j U_{ij}$ .

centre of symmetry which could have been eliminated by the use of higher order  $M$  functions with postulated carbon positions. However, since a plausible structure was suggested by  $M_2$  in which most of the carbon atoms could be placed with reasonable confidence, and in any case the images arising from carbon-carbon vector interactions were weak in comparison with selenium-carbon peaks, no attempt was made to form high order weighted minimum functions. Two spurious peaks were present in the  $M_2$  function, one of which was later identified with a diffraction ripple effect from the Se atoms along the  $y$  direction (which was present also on the Patterson and subsequent electron density maps) and the other occurred near the position of C(10). As a result of this interpretation, coordinates were assigned to all the atoms in the asymmetric unit, although some carbon atoms, particularly C(5), C(9) and C(10) were not represented as strongly on the minimum function map as the others, and were therefore less accurately located.

The method of successive Fourier syntheses was used in order to confirm and establish more accurate atomic positional parameters. The first structure factor calculation was based on the atoms located with greatest confidence from  $M_2$ , *i.e.* Se, C(1), C(3), C(4), C(6), C(7), C(8) and C(13). Isotropic temperature factors of  $4.0 \text{ \AA}^{-2}$  for Se and  $2.5 \text{ \AA}^{-2}$  for C atoms were used in these calculations and the corresponding atomic scattering factors were determined by means of Forsyth-Wells coefficients (Forsyth & Wells, 1959).

Electron density maps were calculated at intervals of  $1/50$  along each axis for  $\frac{1}{4}$  of the unit cell. After five rounds of structure factor and Fourier calculations reliable coordinates were obtained for all atoms and the conventional  $R$  factor had dropped from 30% to 24%.

### Refinement of the structure

At this stage it was considered that sufficiently accurate fractional coordinates had been obtained for all atoms in the structure (excluding hydrogen) to allow the various scale, positional and temperature factor parameters to be refined by least-squares. An Atlas Autocode version of the *ORFLS* full-matrix least-squares program (Busing, Martin & Levy, 1962) was used to perform the necessary calculations (Pawley, 1967). The quantity minimized is  $\sum_{hkl} \omega(|F_o| - |F_c|)^2$ , where  $|F_c|$  incorporates

all scale factors.

The refinement was executed in several stages as set out in Table 1. Relative weights were assigned to each reflexion according to the expression:

$$\omega(hkl) = [1 + (|F_o| - a)^2/b^2]^{-1}$$

(Mills & Rollett, 1960) with  $a=40.0$  and  $b=67.0$ , chosen so that  $\omega^{-1/2}$  was proportional to  $\sigma(F_o)$  the mean estimated standard deviation in a selected range of  $F_o$ , indicated from the intensity measurements. Greatest weight is given in this scheme to medium

range intensities ( $\omega_{\min}=0.54$ ,  $\omega_{\text{mean}}=0.83$  and  $\omega_{\max}=1.00$ ). Each refinement stage was taken through two or three cycles to ensure convergence.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), no allowance being made for anomalous scattering. The results for the various refinement stages are summarized in Table 1, and values of various pertinent quantities derived in the final cycle are given in Tables 2 and 3. Scale factors  $S(k)$  were never refined along with individual isotropic or anisotropic temperature factors because of the expected high correlation with  $\beta_{22}$  (Lingafelter & Donohue, 1966).

Table 2. Values from final least-squares cycle

$\Sigma \omega(\Delta F)^2/(N_o - N_v)$	1.17
Number of observations $N_o$	1086
Number of variables $N_v$	126
Residual	0.067
Weighted residual	0.069
Mean shift/error for $x, y, z$	0.02
Mean shift/error for $\beta_{ii}$	0.015
Mean shift/error for $\beta_{ij}$	0.015

Table 3. Reflexion statistics

Group ( $hkl$ )	Number of reflexions	Scale factor $S(k)$	$R$
$h0l$	232	2.01	0.068
$h1l$	237	2.00	0.059
$h2l$	223	2.01	0.059
$h3l$	201	2.18	0.064
$h4l$	174	3.12	0.067
$0kl$	12	6.06	0.085
$1kl$	7	4.03	0.079

A final electron density map (Fig. 1) and a weighted difference map were calculated at intervals of 94ths along  $a$ , 30ths along  $b$  and 60ths along  $c$  for approximately one quarter of the unit cell. The electron density map showed a trace of the diffraction ripple mentioned previously but no other unexpected features. The difference map contained several regions of density between 0.3 and 0.4 e. $\text{\AA}^{-3}$ , only three of which were at expected hydrogen positions. This latter result is not too unexpected since, according to the criteria proposed by Cruickshank (1960), the predicted coordinate estimated standard deviations for the hydrogen atoms would be about 0.2 to 0.3  $\text{\AA}$ . Tables of  $F_o$  and  $F_c$  may be obtained from the authors.

### Results and discussion

The atomic parameters and their associated errors (e.s.d.'s) obtained from the final least-squares cycle are given in Table 4. Intramolecular bond lengths and angles are listed in Tables 6 and 7 and are also shown in Fig. 2. The computations during this stage of the analysis were made using the X-ray '63 system of crystallographic programs (Stewart & High, 1964) in operation at Imperial College London.

Table 4. Atomic parameters for bisdiphenylmethyl diselenide

	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{23}$	$\beta_{31}$	$\beta_{12}$
Se	0.0676 (1)	0.0*	0.0191 (1)	0.0048 (0)	0.0327 (4)	0.0110 (1)	-0.0008 (4)	0.0038 (1)	0.0016 (2)
C(1)	0.1241 (7)	0.2530 (23)	0.14691 (1.3)	0.0037 (5)	0.0111 (40)	0.0151 (16)	0.0028 (21)	0.0044 (8)	0.0014 (12)
C(2)	0.1250 (7)	0.2134 (21)	0.2667 (11)	0.0035 (5)	0.0140 (45)	0.0106 (12)	-0.0015 (18)	0.0030 (7)	-0.0013 (11)
C(3)	0.1546 (8)	0.0005 (58)	0.3404 (12)	0.0066 (7)	0.0351 (49)	0.0135 (14)	0.0021 (58)	0.0060 (8)	0.0010 (39)
C(4)	0.1522 (10)	0.9748 (54)	0.4521 (14)	0.0063 (7)	0.0463 (84)	0.0123 (15)	0.0080 (42)	0.0044 (9)	0.0010 (30)
C(5)	0.1194 (11)	0.1579 (45)	0.4855 (17)	0.0055 (8)	0.0814 (109)	0.0135 (20)	-0.0091 (43)	0.0048 (11)	-0.0019 (27)
C(6)	0.0882 (11)	0.3534 (43)	0.4110 (18)	0.0059 (9)	0.0740 (100)	0.0170 (24)	0.0061 (13)	0.0061 (13)	0.0014 (27)
C(7)	0.0892 (10)	0.3863 (28)	0.2992 (15)	0.0056 (7)	0.0402 (64)	0.0154 (19)	-0.0071 (28)	0.0056 (10)	-0.0011 (17)
C(8)	0.2173 (8)	0.2820 (22)	0.1761 (12)	0.0046 (6)	0.0153 (47)	0.0177 (13)	0.0000 (19)	0.045 (8)	0.0024 (13)
C(9)	0.2790 (9)	0.0993 (29)	0.2444 (16)	0.0045 (7)	0.0532 (88)	0.0169 (20)	0.0149 (30)	0.0046 (10)	0.0052 (17)
C(10)	0.3641 (10)	0.1442 (40)	0.2666 (19)	0.0038 (7)	0.0764 (98)	0.0228 (28)	0.0170 (46)	0.0048 (12)	0.0054 (23)
C(11)	0.3795 (10)	0.3291 (25)	0.2200 (17)	0.0050 (7)	0.0545 (85)	0.0184 (22)	0.0030 (36)	0.0067 (11)	-0.0019 (20)
C(12)	0.3161 (13)	0.5220 (61)	0.1514 (20)	0.0110 (12)	0.0359 (83)	0.0310 (31)	0.0012 (68)	0.0151 (18)	0.0005 (43)
C(13)	0.2319 (10)	0.4646 (45)	0.1270 (17)	0.0076 (8)	0.0265 (91)	0.0236 (23)	0.0100 (34)	0.0103 (12)	0.0032 (23)

\* Kept constant to define space group origin.

Table 5. Symmetry operations used in generating positions from original asymmetric unit

Subscript	Symmetry operation
(i)	$(-x, y, -z)$
(ii)	$(\frac{1}{2}-x, -\frac{1}{2}+y, -z)$
(iii)	$(x, -1+y, z)$
(iv)	$(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$
(v)	$(-x, y, 1-z)$
(vi)	$(x, y, 1+z)$
(vii)	$(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$

Table 6. Intramolecular bond lengths and standard deviations

Atoms	Distance	e.s.d
Se—Se(i)	2.285 Å	0.0027 Å*
Se—C(1)	1.97	0.01
C(1)—C(2)	1.52	0.02
C(2)—C(3)	1.45	0.03
C(3)—C(4)	1.44	0.03
C(4)—C(5)	1.40	0.04
C(5)—C(6)	1.36	0.03
C(6)—C(7)	1.43	0.03
C(7)—C(2)	1.39	0.03
C(1)—C(8)	1.57	0.02
C(8)—C(9)	1.43	0.02
C(9)—C(10)	1.47	0.03
C(10)—C(11)	1.33	0.03
C(11)—C(12)	1.48	0.03
C(12)—C(13)	1.46	0.03
C(13)—C(8)	1.33	0.03

\* This value must be doubled to account for the twofold relationship between the Se atoms.

Table 7. Intramolecular angles and standard deviations

Atoms	Angle	e.s.d.
Se(i)—Se—C(1)	100.1°	0.5°
Se—C(1)—C(2)	113.1	1.0
Se—C(1)—C(8)	105.5	1.0
C(1)—C(2)—C(3)	123.1	1.4
C(1)—C(2)—C(7)	117.1	1.3
C(1)—C(8)—C(9)	117.6	1.4
C(1)—C(8)—C(13)	118.5	1.2
C(2)—C(1)—C(8)	114.5	0.9
C(2)—C(3)—C(4)	119.6	2.2
C(3)—C(4)—C(5)	119.0	2.2
C(4)—C(5)—C(6)	120.3	2.3
C(5)—C(6)—C(7)	122.9	2.3
C(6)—C(7)—C(2)	118.4	1.6
C(7)—C(2)—C(3)	119.7	1.6
C(8)—C(9)—C(10)	113.1	1.7
C(9)—C(10)—C(11)	123.1	1.7
C(10)—C(11)—C(12)	123.7	2.1
C(11)—C(12)—C(13)	110.7	2.4
C(12)—C(13)—C(8)	124.9	2.0
C(13)—C(8)—C(9)	123.7	1.7

## Se—Se bonding

The bonded selenium atoms lie across a crystallographic twofold axis of symmetry and the standard deviation of the bond length will, therefore, be twice the normal calculated standard deviation given in Table 6. Hence, the Se—Se bond length is  $2.285 \pm 0.005$  Å, which is in agreement with that of  $2.29 \pm$

0.01 Å found in diphenyl diselenide by Marsh (1952), confirming the existence of an Se-Se bond significantly shorter than twice the assigned single-bond radius. Se-Se bond lengths usually lie in the range 2.32 to 2.34 Å (Kruse, Marsh & McCullough, 1957; Foss, Johnsen & Reistad, 1964).

The dihedral angle between the planes defined by C(1) (i)-Se(i)-Se and Se(i)-Se-C(1) is 82° (Table 8) which is close to the theoretical value of 90° (Bergson, 1962).

Table 8. *Dihedral angles in bisdiphenylmethyl diselenide*

Plane 1	Plane 2	Interplanar angle
C(1) (i)-Se(i)-Se	Se(i)-Se-C(1)	81.99°
Ring A	Ring B	56.87
Se-C(1)-C(2)	Ring A	52.18
Se-C(1)-C(8)	Ring B	69.99
Ring A	(010)	56.31
Ring B	(010)	30.02

### Se-C bonding

Kruse *et al.* (1957) have discussed the differences between aromatic Se-C bonds (usually around 1.93 Å) and aliphatic Se-C bonds (1.98 to 2.01 Å). The Se-C(1) bond distance of  $1.97 \pm 0.01$  Å in bisdiphenylmethyl diselenide places it in the aliphatic class, and the carbon atom C(1) is further typified by the distorted tetrahedral distribution of bond lengths and angles around it and the resulting deviation of 0.507 Å of atom C(1) from the plane containing atoms Se, C(2) and C(8).

### Molecular overcrowding

Fig. 2(c) and (d) shows the disposition of the carbon atoms constituting phenyl rings A [C(2) to C(7)] and B [C(8) to C(13)] with respect to the Se atom. Atoms C(2) and C(3) in ring A and atoms C(8) and C(9) in ring B are all well within the non-bonded approach distance of 3.85 Å from the selenium atom, and the molecule is, therefore, very much overcrowded. The effects of the resulting strain on such a system are difficult to predict in view of the various factors to be accounted for (Harnik, Herbstein, Schmidt & Hirshfeld, 1954) and can only be properly described when hydrogen positions have been determined. However, several features of the present structure are of interest although the limits of accuracy do not permit detailed discussion.

Atoms C(12) and C(13) of ring B are involved in the only intermolecular Se---C contacts (Table 9 and Figs. 3 & 4), there being no intermolecular contact between selenium and ring A carbon atoms. It would appear that atoms C(8), C(9) and C(13) of ring B have been pulled closer to the selenium atom than the corresponding ring A atoms C(2), C(3) and C(7) respectively (Table 10). This is accompanied by an increase in the bond length C(1) to C(8) from the methyl carbon to ring B compared with the corresponding bond length C(1) to C(2) between the methyl carbon and ring A, and a decrease between bond angles Se-C(1)-C(2) and Se-C(1)-C(8).

Table 9. *The shorter intermolecular distances*

Atoms	Distance	Sum of van der Waals radii
Se ···· C(11) (ii)	3.81 Å	3.85 Å
Se ···· C(12) (ii)	3.85	3.85
C(3) ···· C(7) (iii)	3.68	3.70
C(4) ···· C(6) (iii)	3.72	3.70
C(4) ···· C(7) (iii)	3.74	3.70
C(9) ···· C(12) (iii)	3.73	3.70
C(10) ···· C(12) (iii)	3.78	3.70
C(9) ···· C(13) (iii)	3.86	3.70
C(5) ···· C(9) (iv)	3.76	3.70

Table 10. *Short non-bonded intramolecular distances*

Atoms	Distance	e.s.d.	Sum of van der Waals radii
Se ··· C(2)	2.92 Å	0.01 Å	3.85 Å
Se ··· C(3)	3.37	0.01	
Se ··· C(7)*	3.99	0.02	
Se ··· C(8)	2.82	0.01	
Se ··· C(9)	3.31	0.01	
Se ··· C(13)	3.70	0.03	

\* Included for comparison.

### The phenyl rings

The bond lengths and angles in the phenyl rings are less accurately determined than those for the rest of the structure. Nevertheless the dimensions of ring B indicate a degree of distortion from the normal benzene configuration whereas ring A shows no detectable deformation. This is presumably due to the differences in environment of the two rings.

The two rings yield independently average C-C bond lengths of 1.41 Å and C-C-C bond angles of 120°, but with a wider distribution of values in B than in A. The largest distortion has taken place in the bond

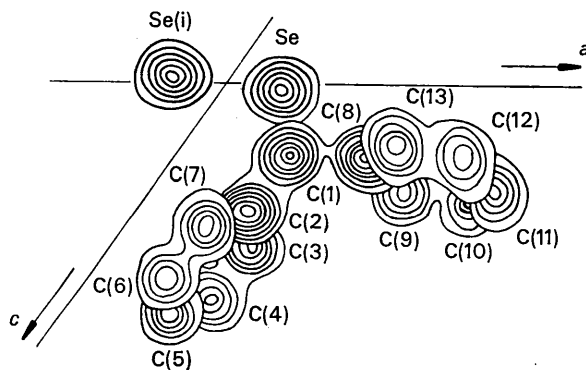


Fig. 1. Bisdiphenylmethyl diselenide, final composite electron density map in projection down *b*, showing the carbon atoms in one asymmetric unit and the two bonded selenium atoms. Contours are at intervals of 1 e.Å<sup>-3</sup> for C, starting at 1, and intervals of 10 e.Å<sup>-3</sup> for Se, starting at 2.

angles C(11)–C(12)–C(13) and C(8)–C(9)–C(10) both of which are significantly less than  $120^\circ$ . Some of the deviations in bond length may be significant but further comparison is not possible without correcting for thermal vibration.

Both rings are planar within experimental error (Table 11) and their mean planes also contain the methyl carbon atom C(1) which was not included in the least-squares calculations for the equations of the planes. However, the deviations of the atoms from the mean plane of ring *B* are noticeably, if not significantly, greater than those for ring *A*. The acute angle between the ring planes is  $56.9^\circ$ .

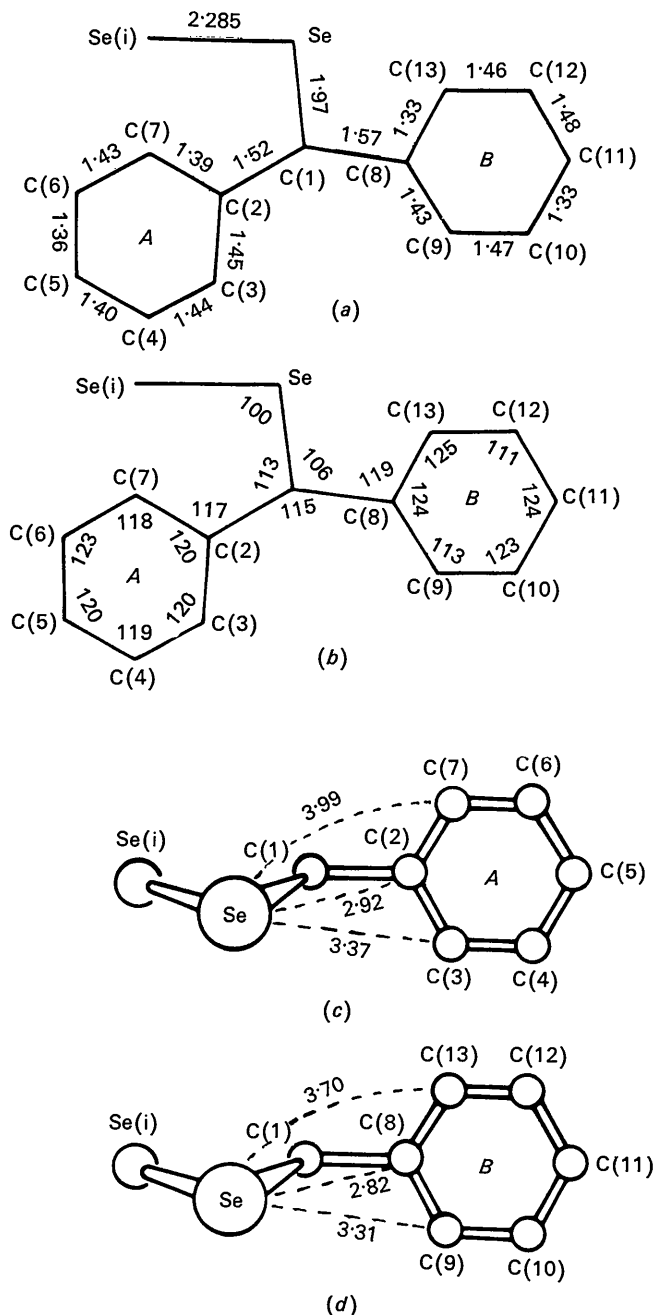


Fig. 2. (a) Bond lengths and (b) bond angles showing the carbon atoms in one asymmetric unit and the two bonded selenium atoms in the molecule. (c) Interatomic distances between Se and ring *A* atoms and (d) interatomic distances between Se and ring *B* atoms for comparison. Dihedral angles are listed in Table 8.

Table 11. *Least-squares planes and deviations*

Ring *A* [defined by atoms C(2) to C(7)]. Equation of plane in direct space:  $13.15X + 2.32Y + 0.88Z = 2.35$ . Distances of atoms from plane:

Atom	Distance
C(2)	–0.025 Å
C(3)	0.015
C(4)	0.006
C(5)	–0.017
C(6)	0.007
C(7)	0.015

(Standard deviation of ring atoms from mean plane = 0.017 Å)

C(1)	0.0007
Se	1.44

Ring *B* [defined by atoms C(8) to C(13)]. Equation of plane in direct space:  $-3.90X + 2.27Y + 10.30Z = 1.71$ . Distances of atoms from plane:

Atom	Distance
C(8)	–0.025 Å
C(9)	0.008
C(10)	–0.011
C(11)	0.026
C(12)	–0.040
C(13)	–0.041

(Standard deviation of ring atoms from mean plane = 0.031 Å)

C(1)	–0.009
Se	1.78

#### Molecular packing

No intermolecular Se---Se contacts are present in the structure. The shortest intermolecular distances are listed in Table 9 and indicated in Figs. 3 and 4, all being compatible with normal van der Waals contacts. The closest intermolecular Se---C distances are between Se and ring *B* carbon atoms C(11) and C(12) generated by symmetry operation (ii) (Table 5). Phenyl rings *A* and *B* form independent stacks along the *b* direction while the closest approach between the two rings is through C(5) in ring *A* and C(9) (iv) in ring *B*.

The authors wish to thank Dr C. H. Carlisle for suggesting the problem and Dr R. W. Pittman for supplying the sample of crystals. The authors are also indebted to Drs S. F. Darlow and G. S. Pawley for permission to use their computer programs. Unless stated otherwise, all computations were made on the London University Atlas Computer with original Fortran programs.

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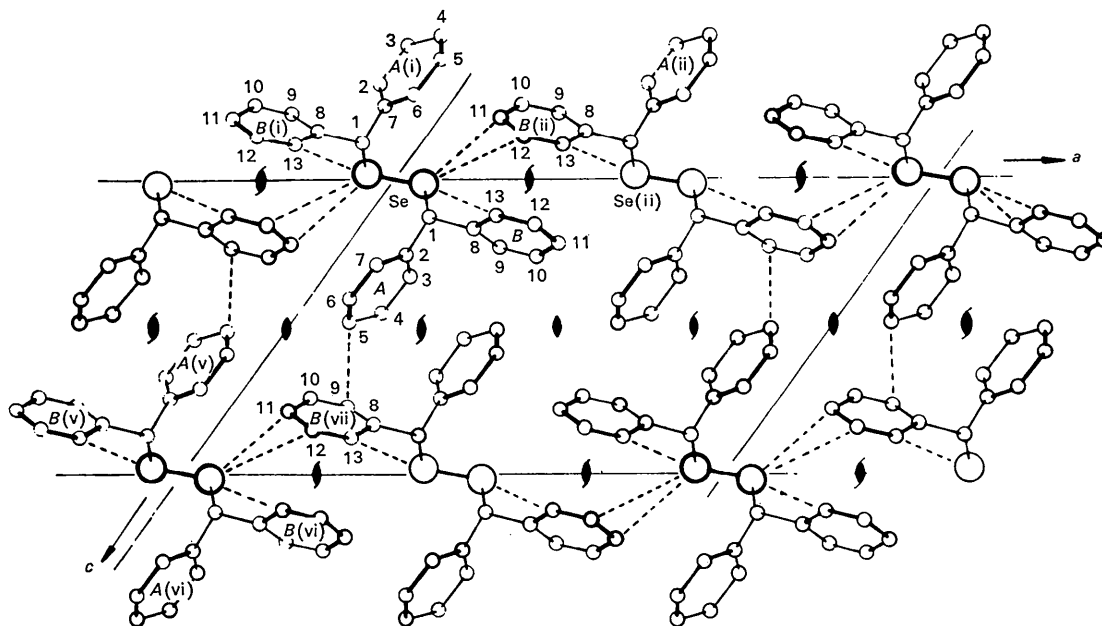


Fig. 3. Bisdiphenylmethyl diselenide, projection of the structure down the  $b$  axis. Important intermolecular distances are indicated by dashes.

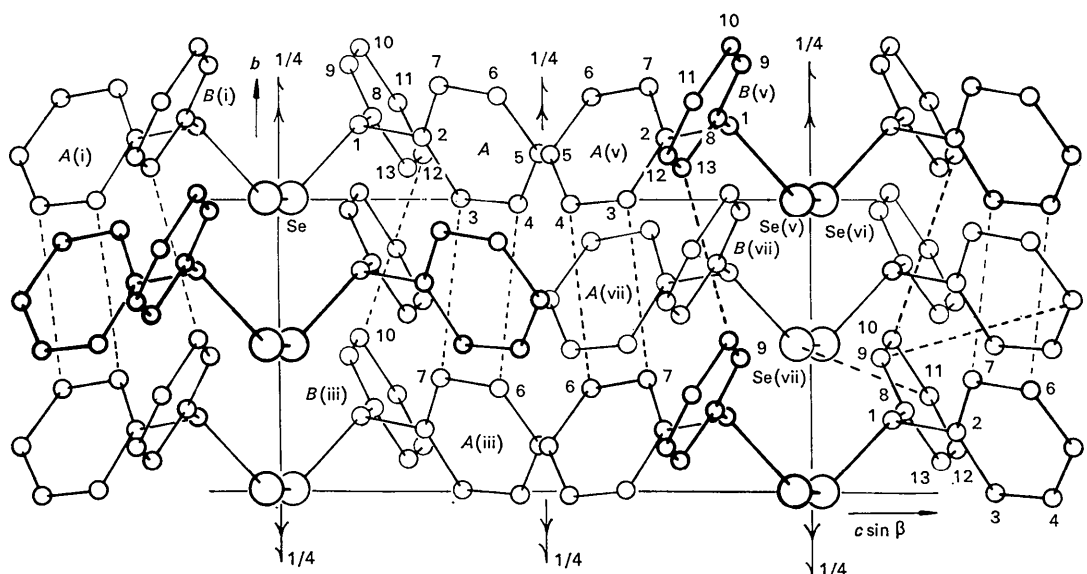


Fig. 4. The structure as seen in projection down the  $a$  axis. The positive direction of  $a$  is away from the observer.

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## The Structural Formula and Crystal Structure of Pentachloroethoxycodide, $C_{20}H_{24}NO_3Cl_5$

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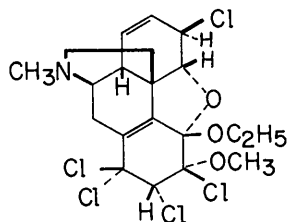
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$\alpha$ -Chlorocodide treated with cold  $SO_2Cl_2$  yields the unusual product pentachlorooxycodide. X-ray analysis has established the structural formula of the ethoxy derivative. The four additional Cl atoms have been added to ring I of the codide in equatorial positions on C(1), C(2) and C(3) and in an axial position on C(1), the ethoxy group has been added to C(4) in an axial position *trans* to the methoxy group on C(3). The prismatic crystals are in space group  $P2_12_12_1$  with  $a=13.38 \pm 0.02$ ,  $b=9.50 \pm 0.02$  and  $c=17.58 \pm 0.03$  Å. The symbolic addition procedure was used to obtain the initial phases for the structure determination.

### Introduction

An unusual chemical reaction takes place when  $\alpha$ -chlorocodide is treated with cold  $SO_2Cl_2$ . The end product has a total of five chlorine atoms and an extra oxygen atom. Spectroscopic data show conclusively that the end product no longer contains the aromatic ring present in the codide molecule. The extreme sensitivity of the product to most agents precluded the establishment of the structural formula by chemical means; hence the purpose of this investigation was to elucidate the structure and configuration by an X-ray diffraction analysis. The original product was in the form of thin, silky needles; however, quenching the reaction mixture with cold  $C_2H_5OH$  rather than ice produced the ethoxy derivative which forms good prismatic crystals. The molecule is identified to be



A preliminary account of this work has been published (Eisner, Batterham, Weiss & Karle, 1968).

### Experimental

Samples of pentachlorooxycodide and the ethoxy analog were prepared by Drs U. Eisner and U. Weiss of the National Institutes of Health. The oxy-compound did not form good crystals whereas the ethoxy analog crystallized into well-shaped stout prisms elongated about the  $b$  axis with good optical extinctions. The crystals, however, deteriorated fairly rapidly in the X-ray beam. The diffraction spots became fuzzy and lost intensity and the optical extinctions disappeared. For this reason, the data were obtained from several different crystals. Large crystals,  $\sim 0.5 \times 0.5 \times 0.5$  mm, were used so as to minimize exposure time to X-rays. Cell parameters listed in Table 1 were determined from precession photographs. The intensity data were collected by the multiple-film equi-inclination Weissenberg technique and estimated visually by comparison with a calibrated film strip. Layers 0-6 about the  $b$  axis and layers 0-1 about the  $c$  axis were recorded. Corrections were made for spot size and Lorentz and polarization factors. The data were cross-correlated, put on an absolute scale and corrected for vibrational motion by means of a  $K$ -curve (Karle & Hauptman, 1953) and normalized structure factor magnitudes  $|E|$  were derived.