

# Structural Aspects of Stable Dibenzyl Triselenides. The Crystal Structures of Bis(2,4-dichlorobenzyl) Triselenide and Bis(2,6-dichlorobenzyl) Triselenide

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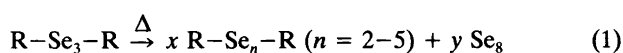
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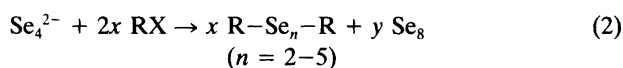
A number of substituted dibenzyl diselenides and dibenzyl triselenides have been studied. They have been classified according to their behaviour on heating.

The substituted dibenzyl triselenides with well-defined melting points have been characterized crystallographically. The sharply melting triselenides all crystallize with a short translational period (4.6–5.0 Å) parallel to a crystallographic two-fold axis. The crystal structure of bis(2,4-dichlorobenzyl) triselenide, which is isostructural with all but one of the triselenides, has been determined from low-temperature X-ray diffraction data. This triselenide is monoclinic, space group *C2/c*, *Z* = 4 with *a* = 13.423(5), *b* = 4.678(2), *c* = 27.696(11) Å and  $\beta$  = 92.13(13)°. The structure was also determined for bis(2,6-dichlorobenzyl) triselenide, which crystallizes in the orthorhombic space group *P22<sub>1</sub>*, with *Z* = 2, *a* = 4.578(2), *b* = 13.774(5) and *c* = 13.743(5) Å. Both triselenides crystallize with the molecule on a crystallographic two-fold axis, and have significant Se–Se intermolecular interactions between the central Se atom and the molecule related by translational symmetry along the two-fold axis. These interactions, as well as intramolecular interactions between Se and Cl in the *ortho* position, seem to be of importance for the stability of the triselenides.

An organic triselenide was first reported in 1929.<sup>1</sup> This class of compounds is described as thermally unstable, and the solid members generally display lower melting points than the corresponding triselenides.<sup>2</sup> The thermal reaction leads to an equilibrium mixture containing various dialkyl polyselenides and elemental selenium (eqn. 1).<sup>3</sup>



During an investigation<sup>4</sup> of the formation of dialkyl polyselenides by alkylation of tetraselenide ion (eqn. 2) we found that bis(2,4-dichlorobenzyl) triselenide is stable up to its melting point, which is higher than that of the corresponding diselenide.



This observation prompted a search for other stable benzylic triselenides. In our earlier investigations<sup>5</sup> we have found that intra- and intermolecular non-bonded selenium–selenium and selenium–halogen interactions play an important role for the stability of selenium compounds. To examine whether the unusual properties of the triselenides orig-

inate in similar interactions, we have used X-ray crystallographic methods to characterize the compounds structurally. Only a few triselenides have previously been characterized structurally by X-ray crystallography.<sup>6,7</sup>

## Experimental

**Preparations.** The dibenzyl polyselenide mixtures were prepared from elemental selenium by reduction to tetraselenide ion with hydrazine/sodium methanolate in DMSO and subsequent alkylation with the appropriate benzyl halide. The products were purified for NMR analysis by extraction from DMSO/water with dichloromethane followed by flash chromatography on silica gel (pentane-20% dichloromethane). This procedure removed a small amount of polar by-products but did not separate the polyselenides and caused no noticeable changes in the distribution among these. Product distributions among the dialkyl polyselenides as revealed by the NMR analyses (see later) are given in Table 3.

For isolation of the triselenides the crude polyselenide mixture was rechromatographed [silica gel; pentane/dichloromethane (95:5)] and the triselenides crystallized from hexane. The detailed procedure has been reported previously for bis(2,4-dichlorobenzyl) triselenide.<sup>4</sup>

Melting points and analyses are given in Table 1. The

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Table 1. Melting points of isolated dibenzyl di- and triselenides, RCH<sub>2</sub>Se<sub>2</sub>CH<sub>2</sub>R and RCH<sub>2</sub>Se<sub>3</sub>CH<sub>2</sub>R.

R	Type	M.p. (°C)		Analysis (of triselenide)
		Diselenide	Triselenide	
Ph	A	91–92	66–80	C <sub>14</sub> H <sub>14</sub> Se <sub>3</sub> (CH)
2-ClPh	B	102–104	76–78	C <sub>14</sub> H <sub>12</sub> Cl <sub>2</sub> Se <sub>3</sub> (CHCl)
3,4-Cl <sub>2</sub> Ph	B	83–87	77–79	C <sub>14</sub> H <sub>10</sub> Cl <sub>4</sub> Se <sub>3</sub> (CHCl)
4-CH <sub>3</sub> Ph	C	64–65	90–92	C <sub>16</sub> H <sub>18</sub> Se <sub>3</sub> (C,H)
2,4-Cl <sub>2</sub> Ph	C	65–67	105–107	C <sub>14</sub> H <sub>10</sub> Cl <sub>4</sub> Se <sub>3</sub> (CHCl)
2,6-Cl <sub>2</sub> Ph	C	83–85	120–122	C <sub>14</sub> H <sub>10</sub> Cl <sub>4</sub> Se <sub>3</sub> (CHCl)
2,4-Br <sub>2</sub> Ph	C	79–81	95–97	C <sub>14</sub> H <sub>10</sub> Br <sub>4</sub> Se <sub>3</sub> (CHBr)
2-BrPh	D	101–102	(82–94)	–
2-IPh	D	94–96	(76–94)	–

A: Triselenide disproportionates during the heating. B: Triselenide stable up to the melting point but lower-melting than the diselenide. C: Triselenide stable and higher-melting than diselenide. D: Inseparable mixture of stable tri- and tetraselenides.

crystals for the X-ray analyses were obtained by recrystallization from hexane.

**NMR measurements.** <sup>1</sup>H (90 MHz) and <sup>77</sup>Se (17.1 MHz) NMR spectra were recorded in CDCl<sub>3</sub> on a JEOL FX 90Q instrument. The conditions for the recording of the <sup>77</sup>Se NMR spectra have been described previously.<sup>4</sup> A combination of <sup>77</sup>Se and <sup>1</sup>H NMR spectroscopy was used to identify and quantitatively estimate the individual homologues in the dibenzyl polyselenide mixtures in the following way. The <sup>77</sup>Se NMR spectra of a series of dialkyl polyselenide

Table 2. <sup>77</sup>Se and <sup>1</sup>H chemical shifts of dibenzyl polyselenides ArCH<sub>2</sub>Se<sub>n</sub>CH<sub>2</sub>Ar.

Ar	δ <sup>77</sup> Se (ppm)				
	n=2	n=3		n=4	
		CH <sub>2</sub> -Se	SeSeSe		CH <sub>2</sub> Se
Ph	411	543	589	554	725
3-MePh	411	540	595	550	728
4-MePh	409	539	590	551	726
2-ClPh	405	540	589	553	728
3-ClPh	421	550	593	564	726
4-ClPh	418	549	588	563	724
2-BrPh	407	541	590	555	728
2-IPh	408	540	589	556	728
2,4-Cl <sub>2</sub> Ph	408	543	585	557	724
2,6-Cl <sub>2</sub> Ph	409	536	622	–	–
2,4-Br <sub>2</sub> Ph	411	544	589	561	730

n	δ <sup>1</sup> H (CH <sub>2</sub> -Se)		
	2-unsubst.	2-subst.	2,6-disubst
2	3.68–3.75 <sup>a</sup>	3.87–3.97 <sup>a</sup>	4.45 <sup>a</sup>
3	+0.40±0.01 <sup>b</sup>	+0.35±0.01 <sup>b</sup>	+0.12 <sup>b</sup>
4	+0.13 <sup>b</sup>	+0.10 <sup>b</sup>	+0.11 <sup>b</sup>
5	+0.06 <sup>b</sup>	+0.06 <sup>b</sup>	

<sup>a</sup>Chemical shift (ppm). <sup>b</sup>Increment relative to the next lower (n–1) homologue (ppm).

mixtures, including the dibenzyl and the bis(2,4-dichlorobenzyl) polyselenides, have previously been analyzed and unequivocally assigned by observation of <sup>77</sup>Se-<sup>77</sup>Se and <sup>77</sup>Se-<sup>1</sup>H coupling constants.<sup>4</sup> These results and the signal connectivities, i.e. diselenide: one signal, triselenide: two signals with ratio 1:2, and tetraselenide: two signals with ratio 1:1, allowed the assignment of the observed <sup>77</sup>Se NMR signals to narrow and clearly separated chemical shift ranges (Table 2).

The ratios of the signals from the individual homologues gave a preliminary estimate of the mole fractions, which was used to identify the corresponding signals from the CH<sub>2</sub>Se protons in the <sup>1</sup>H NMR spectrum (Table 2). The relative intensities of the latter signals were used to determine the compositions of the dibenzyl polyselenide mixtures given in Table 3, since the <sup>77</sup>Se NMR spectra tend to underestimate the less abundant species in the mixture unless an exorbitant amount of time is used for the data collection.

**X-Ray crystallography.** Only some of the triselenides formed crystals of a quality sufficient for a crystallographic examination. Weissenberg photographs were used to characterize these compounds. The results obtained from the experiments are presented in Table 4. The crystal structures were determined for bis(2,4-dichlorobenzyl) triselenide and bis(2,6-dichlorobenzyl) triselenide, representing two different forms of crystalline triselenides. The crystal data for the two compounds are shown in Table 5, which also contains a summary of data collections and structure refinements. Additional details are given in the following.

**Bis(2,4-dichlorobenzyl) triselenide.** The compound crystallizes as yellow needles. The Weissenberg photographs revealed the systematically absent reflections: *hkl* for *h* + *k* = 2*n* + 1 and *h0l* for *l* = 2*n* + 1, which are consistent with the space groups *C2/c* or *Cc*. A modified Enraf-Nonius low-temperature device was used during data collection. The scan type and rate were selected on the basis of an analysis of the profiles of a number of reflections. The diffracto-

Table 3. Composition of crude polyselenide mixtures from alkylation of tetraselenide ion.  
 $2 \text{RCH}_2\text{X} + \text{Se}_4^{2-} \rightarrow \text{RCH}_2\text{Se}_n\text{CH}_2\text{R}$ .

R	X	Composition/%				$n_{\text{av}}^a$	Yield/% <sup>b</sup>
		$n = 2$	3	4	5		
Ph	Cl	89	7	3	1	2.15	96
—	Br	68	20	8	3	2.49	91
3-MePh	Br	75	17	6	2	2.33	92
4-MePh	Br	73	18	7	2	2.41	94
2-ClPh	Cl	63	21	12	4	2.57	91
3-ClPh	Br	78	15	5	2	2.34	98
4-ClPh	Cl	77	15	6	2	2.34	91
2-BrPh	Br	65	18	11	5	2.57	93
2-IPh	Cl	63	20	11	5	2.58	91
2,4-Cl <sub>2</sub> Ph	Cl	74	17	7	2	2.37	93
3,4-Cl <sub>2</sub> Ph	Cl	82	14	4	0	2.20	100
2,6-Cl <sub>2</sub> Ph	Br	83	12	5	0	2.17	97
2,4-Br <sub>2</sub> Ph	Br	74	17	7	2	2.32	100

<sup>a</sup>Average selenium chain length. <sup>b</sup>Selenium incorporation in polyselenides, calculated from  $n$  and sample weight.

Table 4. Unit cell dimensions at room temperature for the crystalline triselenides  $\text{RCH}_2\text{Se}_3\text{CH}_2\text{R}$ .

R	Crystal system	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$\beta$
2-ClPh	Monoclinic	13.63	4.76	25.03	96
4-CH <sub>3</sub> Ph	Monoclinic	12.16	4.93	28.00	96
2,4-Cl <sub>2</sub> Ph	Monoclinic	13.64	4.74	28.02	92
2,6-Cl <sub>2</sub> Ph	Orthorhombic	4.70	13.99	13.95	—
2,4-Br <sub>2</sub> Ph	Monoclinic	13.98	4.76	28.70	91.5

meter scans were performed at a constant rate of  $0.5^\circ \text{min}^{-1}$  in  $\theta$ . Background counts were made for 20 s at each end of the scan range. The intensities of three reflections were measured after every 50 reflections. These measurements did not show any significant variations. The data processing included corrections for Lorentz, polarisation, background and absorption effects. The latter correction was performed using a numerical Gaussian integration procedure.<sup>8</sup> The structure was solved by the heavy atom method. The Patterson syntheses showed positions of the Se atoms consistent with the centrosymmetric space group  $C2/c$ , and subsequent Fourier synthesis provided the positions of the other non-hydrogen atoms in the structure. The structure was refined by the method of least-squares, minimizing  $\sum w(|F_o| - |F_c|)^2$ . The X-Ray System<sup>9</sup> was used for the crystallographic computations. The atomic scattering factors used in the calculations were taken from the tabulation<sup>10</sup> of Cromer and Waber, except for hydrogen for which the values given by Stewart *et al.*<sup>11</sup> were employed. The anomalous dispersion corrections added to the scattering factors for Se and Cl were those calculated by Cromer and Liberman.<sup>12</sup>

A difference Fourier map calculated after an anisotropic refinement showed the positions of the hydrogen atoms. A common isotropic thermal parameter,  $B = 3.16 \text{Å}^2$ , was used for the hydrogen atoms, their positional parameters

being included in the refinement. In the final refinement cycles the weights were changed from unit weights to weights following the expression  $w^{-1} = 2 \cdot \sigma^2(F) + 0.1 |F| + 0.003 |F|^2$ . This weighting scheme was chosen as it did not give any systematic variations of  $\langle w\Delta F^2 \rangle$  with  $|F_o|$  and  $\sin\theta/\lambda$ . In the final refinement cycle the maximum shift was  $0.25 \sigma$ , and in the subsequent difference Fourier map the maximum peak of  $1 \text{ e Å}^{-3}$  was found close (ca.  $0.75 \text{ Å}$ ) to a Se atom.

*Bis(2,6-dichlorobenzyl) triselenide.* Weissenberg photographs taken of the yellow needle-like crystals showed that bis(2,6-dichlorobenzyl) triselenide crystallizes in the orthorhombic crystal system. The systematically absent reflections  $0k0$  for  $k = 2n + 1$  and  $00l$  for  $l = 2n + 1$  are only consistent with the space group  $P2_21_2_1$  (a non-standard setting of  $P2_12_12$ ).

On the basis of a detailed profile analysis the scan type and range was selected. The scan range was extended by 25% at each end to define the background. The maximum scan time was 240 s, and the maximum  $\sigma(I)/I$  requested was 0.01.

The data processing and structure determination followed the lines described previously. The Enraf-Nonius SDP-system<sup>13</sup> was used for the crystallographic calculations. The scattering factors and anomalous dispersion

Table 5. Crystal data and a summary of the structure determinations.

Compound	Bis(2,4-dichlorobenzyl) triselenide	Bis(2,6-dichlorobenzyl) triselenide
Formula	C <sub>14</sub> Cl <sub>4</sub> H <sub>10</sub> Se <sub>3</sub>	C <sub>14</sub> Cl <sub>4</sub> H <sub>10</sub> Se <sub>3</sub>
Formula weight/g mol <sup>-1</sup>	556.93	556.93
Space group	C2/c	P2 <sub>2</sub> ,2 <sub>1</sub>
Temperature	105K	110K
Diffractometer	Picker FACS-1	CAD4
Cell parameters (low temperature)		
a/Å	13.423(5)	4.578(2)
b/Å	4.678(2)	13.774(5)
c/Å	27.696(11)	13.743(5)
β/°	92.13(3)	—
V/Å <sup>3</sup>	1738(2)	866.5(9)
D <sub>calc</sub> /g cm <sup>-3</sup>	2.123	2.134
Molecules per cell	4	2
Radiation	MoKα (graphite monochromated)	MoKα (Zr-filtered)
Crystal size/mm	0.14 × 0.33 × 0.05	0.33 × 0.10 × 0.09
Developed faces	{100}, {101}, {001}	{100}, {011}
Linear absorption coeff./cm <sup>-1</sup>	68.87	69.16 cm <sup>-1</sup>
Range of transmission factors	0.382–0.692	0.236–0.566
Scan mode	ω-2θ	ω-2θ
θ-range/°	1.2–22.5	1–32
Scan range (Δω)	0.95 + 0.35 tanθ	1.5 + 0.35 tanθ
Internal R-value from averaging	0.025	0.030
Number of unique reflections	1107	3020
Number of observed reflections I > 2σ(I)	1031	2065
Number of variables	111	96
Weights w <sup>-1</sup>	2σ <sup>2</sup> (F) + 0.1 F  + 0.0003 F  <sup>2</sup>	σ <sup>2</sup> (F) + 0.0016 F  <sup>2</sup>
R	0.038	0.046
R <sub>w</sub>	0.052	0.064

terms were taken from the same sources as mentioned above, and were used as contained in the program. A difference Fourier calculated after an anisotropic refinement clearly showed the positions of the hydrogen atoms. They were introduced in idealized positions with a common isotropic thermal parameter,  $B = 2\text{\AA}^2$ . The weights used in the final cycles were of the form  $w^{-1} = \sigma^2(F) + 0.0002|F|^2$ . This weighting scheme gave a uniform distribution of  $\langle w\Delta F^2 \rangle$  as a function of  $F_0$  and  $\sin\theta/\lambda$ . The polarity of the

crystal was established as described by Rogers.<sup>14</sup> In the last refinement cycle the maximum shift was 0.02  $\sigma$ . The final difference Fourier was featureless, the maximum peak being 1.3 e/Å<sup>3</sup>.

The positional parameters for the two compounds are listed in Tables 6 and 7. Anisotropic thermal parameters, hydrogen positions, and lists of observed and calculated structure amplitudes can be obtained from the authors on request.

Table 6. Positional<sup>a</sup> parameters for bis(2,4-dichlorobenzyl) triselenide.

Atom	x	y	z
Se1	0.5000	0.4060(2)	0.2500
Se2	0.36281(5)	0.7091(2)	0.25584(2)
C1	0.3764(5)	0.6386(15)	0.3612(2)
C2	0.2843(5)	0.5435(15)	0.3764(3)
C3	0.2762(5)	0.3405(15)	0.4126(3)
C4	0.3627(6)	0.237(2)	0.4348(3)
C5	0.4551(6)	0.327(2)	0.4213(3)
C6	0.4607(5)	0.528(2)	0.3845(3)
C7	0.3855(6)	0.8586(15)	0.3225(3)
Cl1	0.1743(12)	0.6797(4)	0.35026(6)
Cl2	0.35315(15)	-0.0160(4)	0.48059(6)

<sup>a</sup>Coordinates for the symmetry-related part of the molecule are generated by the symmetry operation (1-x, y, 1/2-z).

Table 7. Positional<sup>a</sup> parameters for bis(2,6-dichlorobenzyl) triselenide.

Atom	x	y	z
Se1	0.1989(12)	1.000	0.000
Se2	0.51227(2)	1.04863(6)	0.12299(5)
C1	0.428(2)	0.8645(6)	0.2216(6)
C2	0.337(2)	0.8913(6)	0.3188(6)
C3	0.138(2)	0.8379(7)	0.3706(7)
C4	0.015(2)	0.7550(5)	0.3285(6)
C5	0.091(2)	0.7275(6)	0.2371(8)
C6	0.298(2)	0.7779(6)	0.1841(6)
C7	0.655(2)	0.9208(6)	0.1698(6)
Cl1	0.4860(5)	0.9937(2)	0.3700(1)
Cl2	0.4024(5)	0.7382(2)	0.0706(2)

<sup>a</sup>Coordinates for the symmetry-related part of the molecule are generated by the symmetry operation (x, 2-y, -z).

The accuracy of the structure determinations is not as high as normally achieved from low-temperature diffraction data. This can be attributed partly to the strong absorption of the crystals and to their poor quality, especially in the case of the 2,4-dichloro compound. The pronounced anisotropic vibration of Cl in the 2,4-dichloro compound which is apparent in Fig. 2 may also be influenced by these factors.

## Results and discussion

The triselenide which have been separated from the corresponding diselenides and isolated as pure materials have been divided into three classes according to their behaviour on heating. The class A compounds display unsharp melting points, indicating that Se-Se bond exchanges occur below this temperature. The class B compounds have sharp melting points, although lower than those of the corresponding diselenides, while the class C compounds melt sharply and at a higher temperature than the diselenides. An additional class, D, contains two systems where also the tetraselenide is resistant to decomposition on the column, and an inseparable mixture of tri- and tetraselenide is isolated.

The quality of the crystals of type A, which disproportionate during heating, is so poor that it was impossible to characterize them by X-ray crystallographic methods. Consequently, the triselenides listed in Table 4 are all of the types B and C. It is remarkable that the triselenides which yield crystals of a reasonable quality all have a crystallographic two-fold axis with a short translational period of 4.7–5.0 Å.

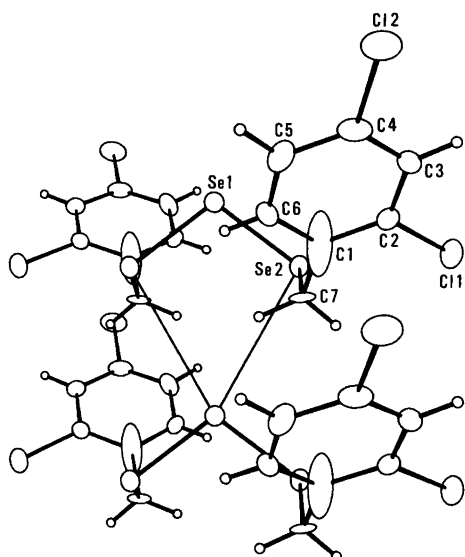


Fig. 1. An ORTEP drawing showing two molecules of bis(2,4-dichlorobenzyl) triselenide related by translational symmetry along the short *b* axis. The intermolecular Se-Se interactions are drawn as thin lines. The thermal ellipsoids are scaled to include 50% probabilities. The hydrogen atoms are drawn as spheres with an arbitrary radius.

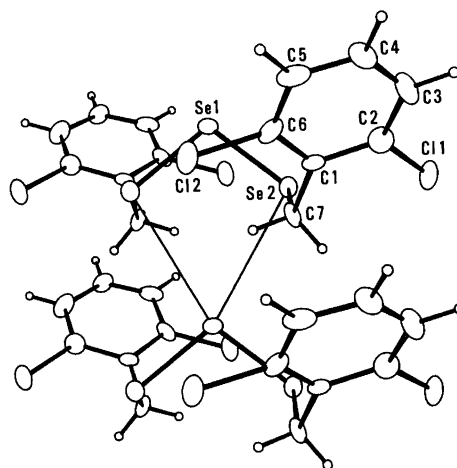


Fig. 2. An illustration of the labelling and interactions in bis(2,6-dichlorobenzyl) triselenide drawn as described for Fig. 1.

Bis(2,6-dichlorobenzyl) triselenide, which is the highest melting compound, differs from the other triselenides by crystallizing in the orthorhombic crystal system, and it also has the shortest two-fold axis. The remaining triselenides in Table 4 crystallize in the monoclinic system with very similar unit cell dimensions, indicating that these structures are isostructural; e.g., the crystal structure of the bis(2,4-dichlorobenzyl) triselenide can be regarded as representative for the monoclinic triselenides. A comparison of the results in Table 4 with the melting points in Table 2 for the 2-chloro-substituted triselenides reveals that a decrease in the length of the two-fold axis is accompanied by an increase in the melting point. This indicates that the interactions in the direction of the two-fold axis are important for the stability of the triselenides.

The crystal structure determination for bis(2,4-dichlorobenzyl) triselenide and bis(2,6-dichlorobenzyl) triselenide showed that both triselenides crystallize with the molecule on a crystallographic two-fold axis. The central selenium atom on the two-fold axis, Se1, is covalently bonded to the two Se2 atoms, and interacts weakly with two Se2 atoms related by translational symmetry along the short axis, as shown in the drawings in Figs. 1 and 2.

Table 8. Selected interatomic distances (Å) in the two structures.

2,4-Dichloro		2,6-Dichloro	
Se1-Se2 <sup>a</sup>	3.751(2)	Se1-Se2 <sup>s</sup>	3.6296(11)
Se2-Cl1	3.708(2)	Se2-Cl1	3.480(2)
Se1-Cl1 <sup>b</sup>	3.718(2)	Se1-Cl2	3.849(2)
Se2-Se2 <sup>c</sup>	3.709(2)	Se2-Se2 <sup>f</sup>	3.6360(14)
Se2-Cl1 <sup>d</sup>	3.691(2)		
Se2-Se2 <sup>d</sup>	3.831(14)		

<sup>a</sup>(*x*, *y*-1, *z*). <sup>b</sup>(1/2 + *x*, *y*-1/2, *z*). <sup>c</sup>(1-*x*, *y*, 1/2-*z*). <sup>d</sup>(1/2-*x*, 1/2+*y*, 1/2-*z*). <sup>e</sup>(*x*-1, *y*, *z*). <sup>f</sup>(*x*, 2-*y*, -*z*).

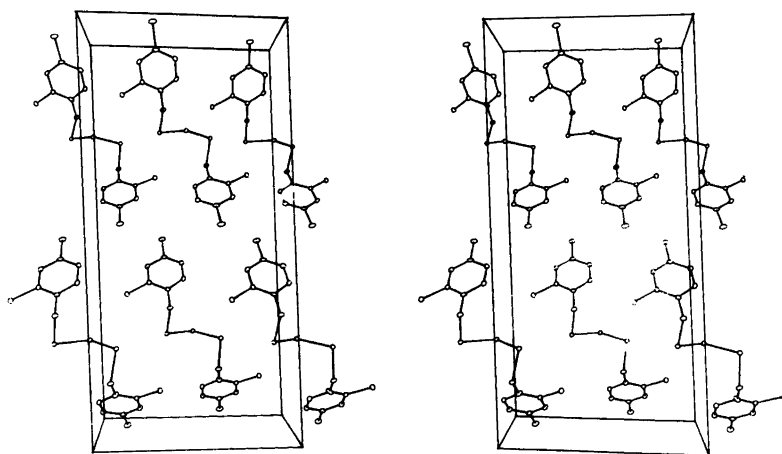


Fig. 3. A stereo pair illustrating the packing in bis(2,4-dichlorobenzyl) triselenide seen along the short *b* axis.

In both structures, this arrangement of Se2 atoms around Se1 forms planar sheets of selenium atoms with each layer sandwiched between two benzyl groups. Table 8 contains the interatomic distances, which are similar to or smaller than the sum of the van der Waals radii.<sup>15</sup> The interatomic distances between Se1 and the Se2 atoms of the molecule translated along the short axis are, as expected, shortest in the 2,6-dichloro compound, viz. 3.630 Å compared to 3.751 Å found in crystals of the 2,4-dichloro-substituted triselenide. Both distances are shorter than the sum of the van der Waals radii,  $d_{vdw}$  (Se-Se) = 3.80 Å. The Se2'-Se2 distance within the triselenide is of the same order of magnitude and also shortest in the 2,6-dichloro compound, viz. 3.636 Å compared to 3.709 Å in the 2,4-dichloro compound. This arrangement of the Se atoms seems to play an important role for the stability of the triselenide. The triselenides in Table 4 all crystallize as needles with the short axis parallel to the needle axis, indicating that the strongest interactions are in the direction of the short axis, i.e. intermolecular Se2-Se1 interactions.

Table 8 shows how differences in substitution of the benzyl group lead to differences in the Se-Cl interactions in the crystal. In bis(2,6-dichlorobenzyl) triselenide, the conformation of the molecule is influenced by Se-Cl interactions. The intramolecular Se2-Cl1 distance of 3.480 Å in the 2,6-dichloro compound is significantly shorter than the sum of the van der Waals radii,  $d_{vdw}$  (Se-Cl) = 3.65 Å. The equivalent distance in the 2,4-dichloro-substituted trisele-

nide is 3.708 Å. This difference in intramolecular Se-Cl interactions is reflected in the torsion angles listed in Table 9. In the bis(2,4-dichlorobenzyl) triselenide only the chlorine in the *ortho* position interacts with Se. Apart from the intramolecular interaction with Se2, it has an intermolecular distance to Se1 of similar magnitude. Though the chlorine atoms in bis(2,6-dichlorobenzyl) triselenide in principle are equivalent, Table 8 shows the difference in interatomic contacts. The stereo pairs in Figs. 3 and 4 illustrate the packing in the two structures seen along the two-fold axis.

An inspection of the bond lengths and angles listed in Table 9 reveals that the two triselenides have similar molecular geometries. The Se1-Se2 distance is shorter in the 2,6-dichloro compound, 2.317 Å, than in the 2,4-dichloro, 2.334 Å, but both are within the range of Se-Se distances (2.31–2.35 Å) found in the structures of other triselenides.<sup>6,7</sup>

The Se2'-Se1-Se2 angles are significantly smaller than the equivalent angle found in the aliphatic triselenide  $\text{Se}_3\{\text{CH}[\text{C}(\text{CH}_3)_2]_2\}_2$ , 107.65(4).<sup>6</sup> It is likely that the decrease in this angle in the benzyl triselenides is caused by the intramolecular Se-Cl interactions. The two C-Cl distances are shorter in the 2,6-dichloro compounds,  $\langle\text{C-Cl}\rangle = 1.720$  Å, than the C-Cl distances in the 2,4-dichloro structure,  $\langle\text{C-Cl}\rangle = 1.743$  Å. This difference is hardly significant but it could originate in the closer interactions in the 2,6-dichloro compound. The torsion angles involving

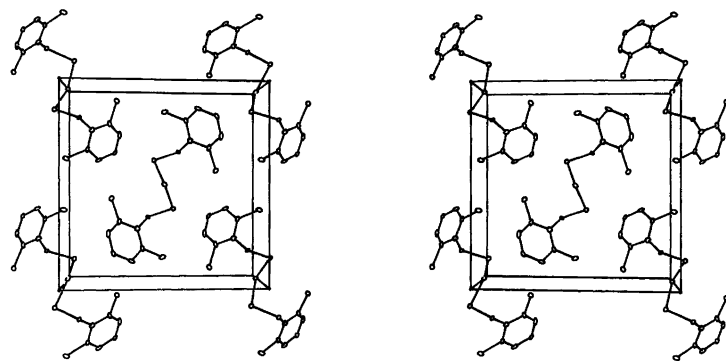


Fig. 4. A stereo pair showing the packing in bis(2,6-dichlorobenzyl) triselenide seen in the direction of the short *a* axis.

Table 9. Bond lengths (Å), and bond and torsion angles (°) in the two triselenides.

	2,4-Dichloro	2,6-Dichloro
Se1-Se2	2.3344(11)	2.3169(9)
Se2-C7	1.987(7)	1.984(7)
C7-C1	1.495(10)	1.478(9)
C1-C2	1.393(10)	1.447(10)
C2-C3	1.388(10)	1.371(11)
C3-C4	1.380(10)	1.399(12)
C4-C5	1.374(11)	1.357(12)
C5-C6	1.392(11)	1.383(11)
C6-C1	1.381(10)	1.430(10)
C2-Cl	1.741(7)	1.718(8)
C4(6)-Cl2	1.744(8)	1.721(8)
Se2-Se1-Se2'	105.20(5)	103.38(5)
Se1-Se2-C7	100.6(2)	100.6(2)
Se2-C7-C1	114.2(5)	113.1(5)
C7-C1-C2	122.2(6)	120.9(7)
C7-C1-C7	120.3(6)	123.8(7)
C2-C1-C6	117.4(6)	115.2(6)
C1-C2-C3	122.0(6)	122.3(7)
C1-C2-Cl1	120.4(5)	118.3(6)
Cl1-C2-C3	117.6(5)	119.4(6)
C2-C3-C4	118.3(7)	119.4(8)
C3-C4-C5	121.7(7)	120.4(7)
C4-C5-C6	118.6(7)	121.6(7)
C5-C6-C1	121.9(7)	112.0(7)
C3(1)-C4(6)-Cl2	118.5(6)	118.4(6)
C5-C4(6)-Cl2	119.8(6)	120.6(6)
Torsion angles		
Se2'-Se1-Se2-C7	-72.1(2)	-73.9(2)
Se1-Se2-C7-C1	-66.4(5)	-70.2(5)
Se2-C7-C1-C2	-78.2(8)	-73.6(8)
C7-C1-C2-C3	-179.6(7)	-176.9(8)

the triselenide moiety are very similar in the two structures,  $\langle \text{Se2}'\text{-Se1-Se2-C7} \rangle = -73^\circ$ , and significantly smaller than in the other aliphatic polyselenide characterized structurally,  $\text{Se}_3\{\text{CH}[\text{C}(\text{CH}_3)_3]_2\}_2$ , in which the two angles are  $-100.6(2)^\circ$  and  $-86.9(2)^\circ$ . This apparently fixed geometry of the C-Se-Se-Se-C fragment in the dibenzyl triselenides is probably due to the interaction between Se and Cl in the *ortho* position.

The most prominent chemical property setting the triselenides of classes B, C and D apart from the normally behaving class A compounds is the reluctance of the former to undergo equilibration according to eqn. (1). This property accounts for the fact that the crystals melt sharply, i.e. without preceding equilibration at around  $100^\circ\text{C}$ .

More strikingly, the class B-D triselenides can be separated from the corresponding diselenides with virtually no loss of material by chromatography on silica gel, whereas the same procedure applied to class A triselenides produces only occasionally, and with high material losses, a pure triselenide. The possibility that the added stability of class B-D triselenides reflects an extraordinary thermodynamic stabilization can be ruled out. Equilibration is observed on exposure of the crystals to daylight at room temperature or

on addition of strongly electrophilic (e.g.  $\text{CF}_3\text{CO}_2\text{H}$ ) or nucleophilic (e.g.  $\text{PhCH}_2\text{Se}^-$ ) catalysts.

The product distributions among the polyselenides given in Table 3 support the same conclusion. These data reveal no significant trends towards a higher triselenide content among the group B, C and D compounds. In fact the variation caused by the replacement of benzyl chloride with benzyl bromide in the preparation of the dibenzyl polyselenides is comparable to the variation found between the individual polyselenide mixtures. Thus the situation we observe is presumably one where equilibration catalyzed by selenolate species in the reaction mixture has progressed to an extent depending on the rate of capture of the latter species by the benzyl halide. It is likely that the added stability of the type B and D triselenides is kinetic rather than thermodynamic in origin and importantly, the factor or factors responsible must be operating on the dissolved molecules as well as in the crystalline structures.

It is evident from the present investigation that one structural element, viz. the presence of a 2-halogeno substituent, generally leads to triselenide stabilization. The X-ray data reveal that such a substituent in one benzyl moiety interacts attractively with the selenium atom bonded to the other benzyl moiety. The  $^{77}\text{Se}$  NMR data (Table 2) contain information suggesting that a specific interaction between a  $\text{CH}_2$ -bound selenium atom and a 2-halogeno substituent prevails even in solution. While the chemical shifts of the central selenium atoms in the tri- and tetraselenides display only slight and apparently unsystematic substituent effects, a systematic trend emerges for the selenium bound to  $\text{CH}_2$  in di-, tri- and tetraselenides.

This is most clearly seen when the unsubstituted compounds ( $\text{Ar} = \text{Ph}$ ) are compared to the 2-, 3- and 4-chloro-substituted analogues. Both the 3- and 4-chloro substituents cause a deshielding amounting to 6–10 ppm. This effect is in accord with the electron-accepting nature of the substituent. In contrast, the 2-chloro substituent causes a shielding of the selenium atom (6 ppm in the di-, 3 ppm in the tri- and 1 ppm in the tetraselenide). The same type of shielding effect is seen when the 2-bromo and 2-iodo compounds are compared to the unsubstituted, or the 2,4-dichloro to the 4-chloro compounds.

The bis(2,6-dichlorobenzyl) triselenide displays the strongest shielding in this group (7 ppm) and is at the same time the compound with the shortest intramolecular Se-Cl contact. It is thus evident that a 2-halogeno substituent exerts a specific influence, presumably via direct contact which more than counterbalances the normal electronic effects transmitted through the carbon framework. The indicated additional bonding, although weak, might conceivably impose a kinetic barrier by keeping the reaction partners formed by (catalyzed, thermal or photochemical) disruption of a Se-Se bond together. In this way recombination might be favoured over reaction chains leading to polyselenide equilibration. This point of view might lend support from the fact that the strongest stabilization which affects even the tetraselenides is exerted by the 2-bromo

and 2-iodo substituents. In view of their increased size and polarizability these are expected to provide particularly efficient bonding of the type suggested.

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