

In this way the values of  $q, r, s$  are determined:  $q = \frac{1}{2}$ ,  $r = 0, s = \frac{1}{2}$ . Putting these values for  $q, r, s$  into (3) gives

$$\begin{aligned} (a) \quad & A \sin 2\pi \left( \frac{n}{p} \right), y, z \\ (b) \quad & \frac{1}{2} - A \sin 2\pi \left( \frac{n}{p} \right), \frac{1}{2} + y, z \\ (c) \quad & A \sin 2\pi \left( \frac{n}{p} \right), \bar{y}, \frac{1}{2} + z \\ (d) \quad & \frac{1}{2} - A \sin 2\pi \left( \frac{n}{p} \right), \frac{1}{2} - y, \frac{1}{2} + z. \end{aligned} \quad (14)$$

By this atomic arrangement all symmetry elements of the space group of the subcell  $Cmc2_1$  are destroyed except the  $c$  glide plane. The remaining symmetry of the subcells of a supercell is therefore  $P1c1$ .

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Table 7, and to Dr Wedde for his careful inspection of the manuscript. The single-crystal diffractometer used for the measurement was made available by the Owens Illinois Co., Toledo, Ohio, USA, who also supported the work financially.

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## The Crystal Structure and Molecular Conformation of 3,7-Dichlorophenoselenazine

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The crystal structure of  $SeCl_2NC_{12}H_7$  has been solved by Patterson and Fourier methods and refined to an  $R$  of 7.5% by full-matrix least-squares methods. The unit cell is orthorhombic, with  $a = 7.995$  (3),  $b = 23.808$  (1),  $c = 6.028$  (2) Å and four molecules in the cell. The space group is  $Pnma$ . The structure contains layers of molecules centred on the mirror planes at  $b/4$  and  $3b/4$ .

### Introduction

The structural analyses of several phenazine derivatives have been carried out, especially of compounds including the phenothiazine heterocycle, but until now there has been no information about the structural details of the analogous selenium compounds. The structure determination of 3,7-dichlorophenoselenazine was undertaken as part of a series of structural analyses of organoselenium compounds. The determination of the Se–C bond lengths and the C–Se–C bond angles will provide information on the bonding characteristics of the selenium atom.

### Experimental

Crystals of 3,7-dichlorophenoselenazine were supplied by Professor Pino of the Departamento de Química

Analítica of this University. Single crystals used in this work were obtained by slow evaporation at room temperature from solutions in chloroform. The crystals are yellow-green and have laminar shape, the  $b$  axis being perpendicular to the plate. In spite of considerable effort it was not possible to grow crystals much wider than 0.1 mm. The density was determined by the flotation equilibrium method in an aqueous solution of zinc bromide.

Preliminary unit-cell dimensions were determined from rotation and Weissenberg photographs. The diagrams indicated orthorhombic symmetry and the systematic absences were consistent with either  $Pnma$  or  $Pn2_1a$  space groups. Accurate cell parameters were measured with Mo  $K\alpha$  radiation on a Philips PW 1100 four-circle diffractometer. The crystal data are summarized below.

$$\begin{aligned}
 a &= 7.995 \text{ (3) \AA} & Z &= 4 \\
 b &= 23.808 \text{ (1)} & D_m &= 1.84 \text{ (2) g cm}^{-3} \\
 c &= 6.028 \text{ (2)} & D_x &= 1.82 \text{ g cm}^{-3} \\
 \lambda(\text{Mo } K\alpha) &= 0.7107 \text{ \AA} & \mu(\text{Mo } K\alpha) &= 38.93 \text{ cm}^{-1}
 \end{aligned}$$

Systematic extinctions:  $0kl$  when  $k+l=2n+1$ ,  $hko$  when  $h=2n+1$ ,  $h00$  when  $h=2n+1$ ,  $0k0$  when  $k=2n+1$  and  $00l$  when  $l=2n+1$ .

1237 unique reflexions (within the range  $2.5^\circ \leq \theta \leq 25^\circ$ ) were measured using Mo  $K\alpha$  radiation with a graphite monochromator and the  $\omega-2\theta$  scan mode on an automatic four-circle Philips PW1100 diffractometer. The scan width was  $1.20^\circ$  and the  $\omega$  scan speed  $0.024^\circ \text{ s}^{-1}$ . The background-counting time at each side of the peak was one half of scan time. Three standard reflexions were measured at regular intervals to provide a check on crystal and instrument stability. 201 reflexions were considered as unobserved according to the criterion  $I \leq 2\sigma(I)$  where  $\sigma = \sqrt{N + B_1 + B_2}$ ,  $N$  the peak count and  $B_1, B_2$  are the background counts. The appropriate

Lorentz-polarization correction was computed for each reflexion by our data reduction program. The intensities were not corrected for absorption.

The overall scale factor and temperature factor were determined by Wilson's (1942) method and normalized structure factors ( $|E|$ ) were calculated. The distribution of  $E$ 's was found to be centric.

### Structure determination and refinement

The structure was determined by the heavy-atom technique. The positions of the selenium and chlorine atoms were derived from a three-dimensional Patterson map. Two successive Fourier syntheses gave the coordinates of all non-hydrogen atoms, and resulted in a conventional  $R$  index of 18.0%. At this point least-squares refinement was begun, minimizing the function  $\sum w| \Delta F|^2$ . The non-hydrogen atoms were subjected to two cycles of isotropic temperature refinement followed by two cycles of anisotropic refinement. The  $R$  value

Table 1. Observed and calculated structure factors

The columns are in the order  $h, k, l, F_o$  and  $F_c$ .

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>																				
0	0	0	366.2	366.2	3	0	0	135.6	135.7	6	0	0	181.8	181.9	9	0	0	150.0	150.0	12	0	0	120.0	120.0	15	0	0	90.0	90.0	18	0	0	60.0	60.0	21	0	0	30.0	30.0	24	0	0	0.0	0.0
0	0	0	90.0	90.0	3	1	0	135.6	135.7	6	1	0	181.8	181.9	9	1	0	150.0	150.0	12	1	0	120.0	120.0	15	1	0	90.0	90.0	18	1	0	60.0	60.0	21	1	0	30.0	30.0	24	1	0	0.0	0.0
0	0	0	180.0	180.0	3	2	0	135.6	135.7	6	2	0	181.8	181.9	9	2	0	150.0	150.0	12	2	0	120.0	120.0	15	2	0	90.0	90.0	18	2	0	60.0	60.0	21	2	0	30.0	30.0	24	2	0	0.0	0.0

dropped to 7.4%. In the last cycles the weighting scheme used was based on counting statistics and complex scattering factors were introduced for the correction of anomalous dispersion for the Se and Cl atoms (Cromer, 1965). The space group was assigned after comparing refinement in  $Pn2_1a$ , where poorly conditioned normal equations were encountered, and in  $Pnma$ , where the atomic parameters were well behaved. Table 1 list the observed and calculated structure factors. Tables 2 and 3 list the positional coordinates and anisotropic temperature factors.

Table 2. Fractional coordinates ( $\times 10^4$ ) with standard deviations

	$x/a$	$y/b$	$z/c$
Se	1556 (1)	2500	7818 (1)
Cl	-886 (2)	336 (1)	7465 (3)
N	-460 (7)	2500	12274 (9)
C(1)	235 (5)	1903 (2)	9054 (8)
C(2)	132 (6)	1404 (2)	7873 (9)
C(3)	-694 (7)	964 (2)	8829 (9)
C(4)	-1420 (7)	999 (2)	11080 (9)
C(5)	1342 (6)	1530 (2)	12210 (9)
C(6)	-504 (6)	1980 (2)	11557 (8)

Scattering factors used were from *International Tables for X-ray Crystallography* (1962). The full-matrix least-squares refinement program used was that of Busing, Martin & Levy (1964), modified for the Univac 1108 computer.

### Description and discussion

The molecule of dichlorophenoselenazine consists of two groups of atoms related by a mirror plane in which

lie the selenium and nitrogen atoms. Bond lengths and angles in the molecule are shown in Fig. 1 and listed in Table 4.

The observed value of 1.921 (5) Å for the Se-C distance is in good agreement with the average value for Se-C(aromatic) of 1.92 Å reported by Aleby (1972). The angle C-Se-C of 95.4 (2)° can be compared with similar C-Se-C distances in other organoselenium compounds reported in the same paper. On the other hand this observed value is analogous to that found in the structural analysis of phenothiazine (99.6°) (Bell, Blount, Briscoe & Freeman, 1968) and phenothiazine derivatives (average 98.3°) (Marsau, 1972). These results suggest that some type of hybridization involving the rings and the  $d$  orbitals of the selenium atom may occur. The availability of bonding schemes for sulphur containing heterocyclic compounds which either involve or reject the use of the  $3d$  orbitals of sulphur has been commented on by Salmond (1968).

The bond length N-C of 1.410 (5) Å agrees well with the values observed in phenothiazine (1.406 Å) and

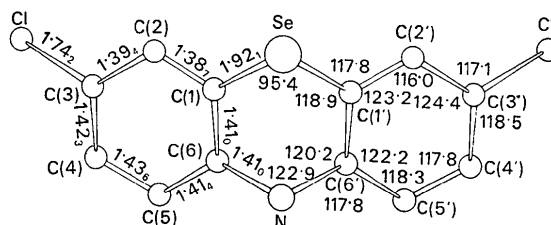


Fig. 1. Bond lengths and angles for 3,7-dichlorophenoselenazine.

Table 3. Anisotropic thermal parameters ( $\times 10^4$ ) with estimated standard deviations

The form of the temperature factor is  $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Se	91 (2)	19 (1)	181 (4)	0	28 (3)	0
Cl	330 (8)	22 (1)	625 (9)	-2 (3)	14 (6)	-39 (3)
N	172 (9)	17 (1)	209 (15)	0	-17 (9)	0
C(1)	92 (8)	18 (1)	239 (12)	2 (2)	-23 (9)	1 (3)
C(2)	116 (8)	16 (1)	396 (18)	3 (2)	-39 (9)	-9 (4)
C(3)	157 (9)	15 (1)	423 (19)	11 (3)	8 (9)	-18 (4)
C(4)	204 (9)	21 (1)	405 (20)	26 (3)	-22 (9)	2 (4)
C(5)	119 (9)	21 (1)	479 (22)	9 (3)	1 (9)	23 (5)
C(6)	112 (8)	18 (1)	220 (15)	8 (2)	-17 (8)	10 (4)

Table 4. Bond lengths and angles with e.s.d.'s in parentheses

(a) Bond lengths (Å)

Se—C(1)	1.921 (5)	C(2)—C(3)	1.394 (7)
Cl—C(3)	1.742 (5)	C(3)—C(4)	1.423 (8)
N—C(6)	1.410 (5)	C(4)—C(5)	1.436 (7)
C(1)—C(2)	1.387 (7)	C(5)—C(6)	1.415 (7)

(b) Bond angles (°)

C(1)—Se—C(1)	95.4 (2)	N—C(6)—C(1)	122.2 (4)
Se—C(1)—C(2)	117.8 (3)	C(1)—C(2)—C(3)	116.0 (4)
Se—C(1)—C(6)	118.9 (3)	C(2)—C(3)—C(4)	124.4 (5)
Cl—C(3)—C(2)	117.1 (4)	C(3)—C(4)—C(5)	117.8 (5)
Cl—C(3)—C(4)	118.5 (4)	C(4)—C(5)—C(6)	118.3 (4)
C(6)—N—C(6')	122.9 (4)	C(5)—C(6)—C(1)	120.3 (4)
N—C(6)—C(5)	117.6 (4)		

phenothiazine derivatives (average 1.415 Å) showing an  $sp^2$  type hybridization. This result is common in the case of non-planar molecules and may indicate a trigonal bond character (Trueblood, Goldish & Donohue, 1961).

The Cl-C bond of 1.742 (5) Å is within experimental error of the values determined for 2,8-dichlorodibenzo-*p*-dioxin (1.75 Å: Boer, Neuman & Aniline, 1972) and for 2,7-dichlorodibenzo-*p*-dioxin (1.742 Å: Boer & North, 1972). In this paper it is shown that the bond length C-Cl in chlorinated dibenzo-*p*-dioxins is a function of the degree of chlorine substitution.

The bond lengths and angles in the aromatic rings are normal and the average values agree with the values reported in the literature.

The structure is not planar, as expected from the different hybridization of the selenium and nitrogen atoms bounding the rings. However, the coplanarity of the carbon atoms of each benzene ring is fairly good, as illustrated in Table 5, the maximum deviation from the least-squares plane being 0.02 Å. The selenium and nitrogen atoms lie slightly outside the dihedral angle made by the two benzene ring. The dihedral angle was found to be 146.5°. This value is intermediate between the observed value of 153.3° in phenothiazine and the average value of 137.3° found in the phenothiazine derivatives.

Table 5. Deviations (Å) of the atoms from least-squares plane

The atoms indicated with asterisks were omitted from the calculation of the least-squares plane.  
 $0.860X - 0.288Y + 0.422Z + 1.137 = 0$

Se*	0.202
Cl*	-0.080
N*	-0.051
C(1)	0.018
C(2)	-0.010
C(3)	-0.007
C(4)	0.016
C(5)	-0.009
C(6)	-0.008

The packing of the structure, illustrated in Fig. 2, consists of two different layers of molecules centred on

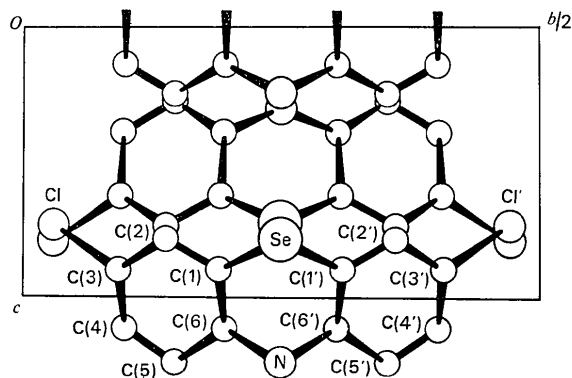


Fig. 2. Packing of the structure as viewed down the *a* axis.

the mirror planes at  $b/4$  and  $3b/4$ . Within each layer herring-bone packing occurs. The intermolecular contacts less than 4 Å are listed in Table 6. Molecules in adjacent layers are aligned head-to-tail and make contacts Se-C(1) and Se-C(6). This packing is analogous to that found in 2,8-dichlorodibenzo-*p*-dioxin, apart from the lack of planarity of the molecule in the present structure.

Table 6. Intermolecular contacts less than 4 Å

Se-N(i)	3.709	Cl—C(4)(iv)	3.931
Se-N(ii)	3.888	C(2)—C(3)(v)	3.664
Se-C(1)(ii)	3.457	C(2)—C(4)(v)	3.770
Se-C(2)(ii)	3.893	C(2)—C(5)(i)	3.623
Se-C(6)(ii)	3.578	C(5)—C(6)(vi)	3.666
Cl-Cl(iii)	3.660		

Symmetry code

(i)	$x$	$y$	$-1+z$	(iv)	$-\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$
(ii)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{3}{2}-z$	(v)	$\frac{1}{2}+x$	$y$	$\frac{3}{2}+z$
(iii)	$-x$	$-y$	$1-z$	(vi)	$x$	$\frac{1}{2}-y$	$z$

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