Crystal and Molecular Structures of Dimorpholino-tri- and -di-selane

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Crystals of the title compound $Se_3(NC_4H_8O)_2$ (1) are orthorhombic, space group *Pbcn* (no. 60) with a = 5.445(1), b = 9.473(2), c = 25.408(2) Å, and Z = 4. Crystals of $Se_2(NC_4H_8O)_2$ (2) are monoclinic, space group $P2_1/c$ (no. 14) with a = 8.871(1), b = 5.716(1), c = 23.820(3) Å, β = 98.59(1)°, and Z = 4. The structures have been determined by X-ray diffraction from Mo-K_α diffractometer data and refined by full-matrix least squares to R 0.035 and 0.035 for 899 and 2 017 observed reflections respectively. In (1) the molecules lie across crystallographic two-fold axes. The N–Se–Se–Se–N chains occur in the *trans* form, with N–Se 1.841(5), Se–Se 2.352(1) Å, N–Se–Se 105.2(2), Se–Se–Se 101.7(1)°, and NSeSe–SeSeSe 97.1°. Intermolecular Se ··· Se contacts of 3.404(2) Å occur across the two-fold axes. The N–Se–Se–N chains in (2) have N–Se 1.846(4) and 1.852(4), Se–Se 2.346(1) Å, N–Se–Se 109.0(1) and 109.2(1)°, and NSeSe–SeSeN 94.7°. The shortest intermolecular Se ··· Se contact in (2) is 3.588(1) Å. In both compounds the morpholine rings occur in the chair form, with N–Se equatorial.

We recently found that black selenium powder, when heated with piperidine or morpholine in the presence of Pb_3O_4, reacts to give diaminoselanes.[1] In the case of piperidine, only the tetraselane was obtained, whereas with morpholine the tri- and di-selane also crystallized. The crystal structures of the two tetraselanes have been reported,[1] and we describe here the structures of the tri- and di-selane, $Se_3(NC_4H_8O)_2$ and $Se_2(NC_4H_8O)_2$. A preliminary account has appeared.[1a] In the sulphur series, the crystal structures of dimorpholino- and dipiperidino-disulphane [2,3] and dimorpholinotetrasulphane [4] have been reported, but no structure of a diaminotrisulphane.

EXPERIMENTAL

The synthesis of dimorpholino-tri- and -di-selane has been described.[1] The triselane crystallizes as rhomb-shaped plates {001} bounded by {110}, sometimes elongated along the *a* axis, and with a tendency to cleavage along the *c* plane. The diselane crystallizes as prisms, extended along the *b* axis and bounded by {100} and {001}. Preliminary unit-cell and space-group data were derived from oscillation and Weissenberg photographs taken with Cu-K_α radiation. The crystals are less stable than those of dimorpholino- and dipiperidino-tetraselane,[1] and the crystals used for X-ray data collection were coated with epoxy-glue; the intensities of the reference reflections (three for each crystal, measured at intervals of 50 reflections) then showed no change. Data collection and treatment were as previously described [1] (Siemens AED diffractometer, niobium-filtered Mo-K_α radiation, λ = 0.710 7 Å). Reflections with $I > 3\sigma(I)$ were regarded as observed and were used in the solution and refinement of the structures. Unit-cell dimensions were based on the 2θ values of the Mo-$K_{\alpha(1)}$ peaks, λ = 0.709 26 Å, of *ca.* 15 reflections in the $40 < 2\theta < 50°$ range. Calculations were made by use of the 'X-Ray '72' programs,[5] and refinements were by full-matrix least squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w = 1/\sigma^2(F)$. Atomic scattering factors were from ref. 6 (from ref. 7 for H) with anomalous dispersion [8] for Se included. Anisotropic temperature factors were used for all atoms except hydrogen. Hydrogen atoms were placed geometrically by use of the 'X-Ray '72' BONDAT subroutine, at C–H 0.95 Å as for the tetraselanes,[1] and were given equal isotropic temperature factors; their parameters (positional and thermal) were not refined.

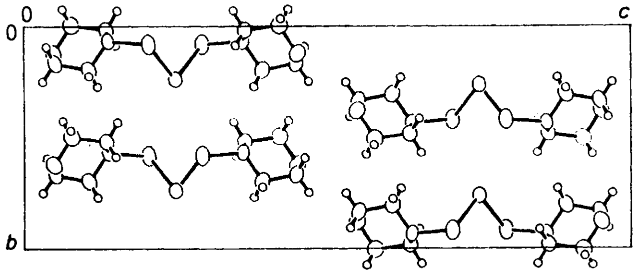

FIGURE 1 The structure of dimorpholinotriselane as seen along the *a* axis

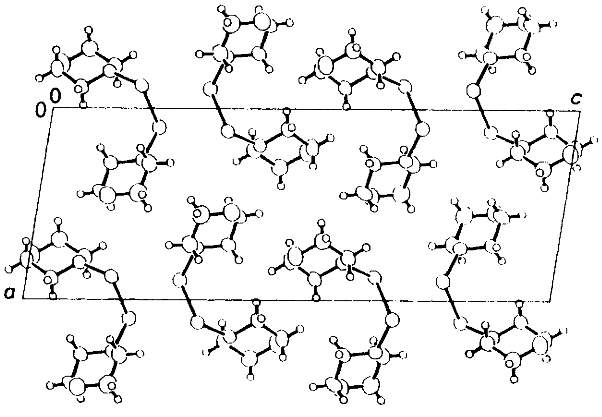

FIGURE 2 The structure of dimorpholinodiselane as seen along the *b* axis

Crystal Data.—(1), $C_8H_{16}N_2O_2Se_3$ M = 409.1, Orthorhombic, space group *Pbcn* (no. 60), a = 5.445(1), b = 9.473(2), c = 25.408(2) Å, U = 1 310.4 Å^3, Z = 4, D_c = 2.07 g cm^{-3}, $F(000)$ = 784, μ(Mo-K_α) = 90.4 cm^{-1}, 899 observed unique reflections within 2θ = 60°. The crystal used was an elongated plate with cross-section 0.252 × 0.028 mm; absorption corrections ranged from 1.287 to 6.044.

(2), $C_8H_{16}N_2O_2Se_2$, M = 330.1, Monoclinic, space group $P2_1/c$ (no. 14), a = 8.871(1), b = 5.716(1), c = 23.820(3) Å, β = 98.59(1)°, U = 1 194.3 Å^3, Z = 4, D_c = 1.84 g cm^{-3}, $F(000)$ = 648, μ(Mo-K_α) = 66.4 cm^{-1}, 2 017 observed unique reflections within 2θ = 56°. The crystal used was 0.084 × 0.492 × 0.200 mm; absorption corrections ranged from 1.721 to 4.049.

The structures were solved by direct and Fourier methods.

The 'X-Ray '72' SINGEN and PHASE sub-programs gave the signs of 286 reflections for (1) and 421 reflections for (2) and the E maps gave the positions of the Se atoms. The N, C, and O atoms were located from the subsequent Fourier maps. The refinements converged at $R = 0.035$ and 0.035, $R' = 0.028$ and 0.040, $\sigma_1 = [\Sigma w\Delta^2(F)/(n - m)]^{\frac{1}{2}} = 1.57$ and 1.41, for (1) and (2) respectively. The largest shift-to-error ratio in the last cycle was 0.004 4 for (1) and 0.005 4 for (2), and the largest peaks and holes in the $\Delta(F)$ map based on the final parameters were 1.4 and -1.0 e Å^{-3} for (1) and 0.9 and -0.9 e Å^{-3} for (2). Final co-ordinates for non-hydrogen atoms are in Table 1. Lists of structure factors, thermal parameters, and hydrogen co-ordinates are in Supplementary Publication No. SUP 22697 (30 pp.).*

RESULTS AND DISCUSSION

Molecular dimensional data are in Tables 2 and 3, and views of the structures are in Figures 1—4.

The N-Se-Se-Se-N *and* N-Se-Se-N *Chains*.—The dimorpholinotriselane molecules lie across crystallographic two-fold axes and thus occur as *trans* rotamers [9] in the crystals. So do the molecules in one of the two X-Se-Se-Se-X structures reported earlier, $Se_3(PEt_2Se)_2$,[10] whereas in the other, $Se_3(CN)_2$,[11,12] the molecules have mirror-plane symmetry and the *cis* form. From isomorphism with $Te[S(ts)_2]$ (ts = toluene-*p*-sulphonyl) of known structure,[13] $Se_3(ts)_2$ [14] has two-fold axis symmetry and the *trans* form. The Se-Se bond lengths in $Se_3(PEt_2Se)_2$ and $Se_3(CN)_2$ are [10,12] 2.352(2) and 2.334(1) Å respectively, the bond angles at the central Se atom are 103.9(2) and 103.0(1)°, and the SeSeSe-SeSeX dihedral angles are 92.5 and 93.2°. These are close to the values in $Se_3(NC_4H_8O)_2$.

TABLE 1

Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	10^4x	10^4y	10^5z
(a) $Se_3(NC_4H_8O)_2$			
Se(1)	2 354.2(11)	814.7(7)	29 406(2)
Se(2)	5 000	2 382.4(8)	25 000
N	3 596(8)	673(4)	36 126(17)
C(1)	6 112(12)	181(6)	36 397(24)
C(2)	6 805(13)	−39(6)	42 165(24)
O	6 529(9)	1 215(4)	45 102(17)
C(4)	4 040(14)	1 658(6)	44 882(24)
C(5)	3 276(11)	1 961(6)	39 273(21)
(b) $Se_2(NC_4H_8O)_2$			
Se(1)	−1 193.6(5)	938.5(8)	16 120(2)
Se(2)	999.4(5)	2 817.0(9)	20 724(2)
N(1)	−1 928(4)	2 574(6)	9 602(13)
C(1)	−1 102(5)	2 265(8)	4 784(17)
C(2)	−2 043(6)	3 382(10)	−414(18)
O(1)	−2 297(4)	5 789(7)	433(14)
C(4)	−3 090(6)	6 084(9)	5 164(20)
C(5)	−2 208(5)	5 049(8)	10 484(18)
N(2)	2 707(4)	1 432(6)	18 531(14)
C(6)	2 860(5)	1 801(9)	12 534(18)
C(7)	4 392(6)	874(11)	11 570(22)
O(2)	4 569(4)	−1 528(7)	12 924(15)
C(9)	4 421(7)	−1 890(10)	18 672(22)
C(10)	2 887(6)	−1 029(9)	19 945(20)

The dimorpholinodiselane molecules lie in general positions in the crystals but have approximate two-fold axis symmetry. The Se-Se bond length, 2.346(1) Å, compares with 2.352(1) Å in the triselane. No X-ray structures are available for other tri- and di-selanes with the same terminal groups. The crystals of the diselane are not isomorphous with those of dimorpholinodisulphane [2] or dipiperidinodisulphane,[3] but the molecular structures are equivalent. The S-S bond lengths in

TABLE 2

Distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) $Se_3(NC_4H_8O)_2$

(i) Bond lengths

Se(1)-Se(2)	2.352(1)	C(2)-O	1.411(7)
Se(1)-N	1.841(5)	O-C(4)	1.420(9)
N-C(1)	1.449(8)	C(4)-C(5)	1.512(9)
C(1)-C(2)	1.528(9)	C(5)-N	1.469(7)

(ii) Bond angles

N-Se(1)-Se(2)	105.2(2)	N-C(1)-C(2)	108.9(5)
Se(1)-Se(2)-Se(1′) [a]	101.7(1)	C(1)-C(2)-O	111.5(5)
Se(1)-N-C(1)	114.5(4)	C(2)-O-C(4)	109.2(5)
Se(1)-N-C(5)	113.6(4)	O-C(4)-C(5)	110.8(6)
C(1)-N-C(5)	110.7(5)	C(4)-C(5)-O	108.8(5)

Dihedral angle [b] at Se(1)-Se(2) 97.1.

(b) $Se_2(NC_4H_8O)_2$

(i) Bond lengths

Se(1)-Se(2)	2.346(1)	Se(2)-N(2)	1.852(4)
Se(1)-N(1)	1.846(4)	N(2)-C(6)	1.470(6)
N(1)-C(1)	1.462(6)	C(6)-C(7)	1.508(7)
C(1)-C(2)	1.526(6)	C(7)-O(2)	1.414(8)
C(2)-O(1)	1.413(7)	O(2)-C(9)	1.410(7)
O(1)-C(4)	1.425(7)	C(9)-C(10)	1.520(8)
C(4)-C(5)	1.507(7)	C(10)-N(2)	1.450(7)
C(5)-N(1)	1.457(6)		

(ii) Bond angles

N(1)-Se(1)-Se(2)	109.0(1)	N(2)-Se(2)-Se(1)	109.2(1)
Se(1)-N(1)-C(1)	116.4(3)	Se(2)-N(2)-C(6)	114.3(3)
Se(1)-N(1)-C(5)	114.6(3)	Se(2)-N(2)-C(10)	114.6(3)
C(1)-N(1)-C(5)	110.3(4)	C(6)-N(2)-C(10)	110.0(4)
N(1)-C(1)-C(2)	108.0(4)	N(2)-C(6)-C(7)	108.3(4)
C(1)-C(2)-O(1)	111.8(4)	C(6)-C(7)-O(2)	112.2(5)
C(2)-O(1)-C(4)	109.6(4)	C(7)-O(2)-C(9)	109.9(5)
O(1)-C(4)-C(5)	111.3(4)	O(2)-C(9)-C(10)	111.2(5)
C(4)-C(5)-N(1)	109.8(4)	C(9)-C(10)-N(2)	109.8(5)

Dihedral angle [b] at Se(1)-Se(2) 94.7

[a] Se(1′) across molecular two-fold axis. [b] Zero for planar *cis*.

TABLE 3

Least-squares planes of the carbon atoms of the morpholino-groups, with equations of the planes in direct space

(a) $Se_3(NC_4H_8O)_2$

$$3.8911x + 6.5846y - 1.9744z = 1.7843$$

Distances from plane: Se(2) 1.236, Se(1) −0.912, N −0.655, C(1) −0.005, C(2) 0.006, O 0.666, C(4) −0.007, C(5) 0.006 Å; angles with plane C(1)-N-C(5) 52.2, C(2)-O-C(4) 54.4, N-Se(1)-Se(2) 84.0°; angle of normal to plane with two-fold axis 46.0°

(b) $Se_2(NC_4H_8O)_2$

$$(i)\ 6.8487x + 3.6085y - 4.4812z = -0.1562$$

Distances from plane: Se(2) 0.924, Se(1) −1.045, N(1) −0.666, C(1) 0.004, C(2) −0.004, O(1) 0.653, C(4) 0.004, C(5) −0.004 Å; angles with plane C(1)-N(1)-C(5) 53.0, C(2)-O(1)-C(4) 53.0, N(1)-Se(1)-Se(2) 79.1°

$$(ii)\ 3.2268x + 3.7445y + 14.3032z = 3.3944$$

Distances from plane: Se(1) −1.123, Se(2) 0.917, N(2 0.666, C(6) −0.005, C(7) 0.005, O(2) −0.644, C(9) −0.005 C(10) 0.005 Å; angles with plane C(6)-N(2)-C(10) 52.7 C(7)-O(2)-C(9) 52.6, N(2) -Se(2)-Se(1) 86.9°

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

the disulphanes [2,3] are 2.069(1) and 2.067(4) Å; compared with Se–Se and S–S bond lengths in different forms of cyclo-octaselenium [15] and cyclo-octasulphur [16] (overall averages, 2.335 and 2.045 Å), the bonds in the diaminodiselane and diaminodisulphanes are long, especially so in the disulphanes.

The Se–N bonds in the tri- and di-selane have the same lengths within error limits. The weighted average of the three independent values, and the two in dimorpholino- and dipiperidino-tetraselane,[1b] is 1.843(2) Å.

Conformation of the Morpholinoseleno-groups.—The morpholino-groups occur in the chair form, with N–Se equatorial. The bonds at the nitrogen atom are distorted pyramidal, slightly flattened, the average bond angle at nitrogen being 112.9° in the triselane and 113.3° in the diselane (in dimorpholino- and dipiperidino-tetraselane,[1b] 113.8°). The N and Se(1) atoms lie on the same side, and Se(2) on the other side, of the least-squares plane of the carbon atoms, *cf*. Table 3, and the N–Se(1)–Se(2) plane makes an angle close to 90° with the least-squares plane, as in the tetraselanes.[1b] The rotational positions of the nitrogen lone pair and Se(2) relative to the N–Se(1) bond are thus approximately planar *trans*. This is also the preferred conformation of the aminothio group,[17] and occurs in dimorpholino- and dipiperidino-disulphane [2,3] and dimorpholinotetrasulphane.[4]

Molecular Packing.—In dimorpholinotriselane, the two-fold rotation axes of the space group run parallel to the b crystal axis, at $x = 0$ and $\frac{1}{2}$, $z = \frac{1}{4}$ and $\frac{3}{4}$; their spacings $\frac{a}{2}$ along a and $\frac{c}{2}$ along c are 2.72 and 12.70 Å respectively. The four molecules of the unit cell lie across the two-fold axes, with the central atom Se(2) on the axes, and with O · · · O 10.35 Å at an angle of 9.3° with the c axis. No bonds extend across the c plane at $z = 0$ and $\frac{1}{2}$, and layers of thickness $\frac{c}{2}$ are held together through H · · · H and H · · · O van der Waals contacts. This accounts for the thin {001} plate growth and the cleavage along the c plane.

Across the a plane at $x = 0$ and $\frac{1}{2}$, intermolecular Se(1) · · · Se(1) contacts of 3.404(2) Å, generated by the two-fold axes, occur in directions which make angles of 152.4° with the Se(1)–N bonds and angles of 98.5° with the Se(1)–Se(2) bonds. This results in infinite helical –Se(2)–Se(1) · · · Se(1)– chains running through the crystal parallel to the a axis, at y and $\frac{1}{2} + y$ at $z = \frac{1}{4}$, and $\frac{1}{2} - y$ and $1 - y$ at $z = \frac{3}{4}$ (see Figure 3). The Se(1) · · · Se(1) contacts are *ca*. 1 Å longer than the Se(2)–Se(1) bonds, but the angle at Se(1) is in the normal range, and so are the dihedral angles along the helix, 97.0° at Se(2)–Se(1) and 100.7° at Se(1) · · · Se(1). The senses of screw of adjacent helixes alternate. The helix has three atoms per turn, as in trigonal selenium, and the pitch, *i.e*. the distance along the axis after one turn, is $a = 5.446$ Å; in trigonal selenium, the three-fold screw axis is 4.958 Å.[18] The angles in the triangle seen when looking along the helix are 74.0° at the central atom and 53.0° at the terminal atoms of the triselane group. The picture is that of a helix of trigonal selenium broken at each turn, the triselane fragments being rotated slightly about the two-fold axis and moved slightly apart to give space for the morpholino-groups. The nearly linear N–Se(1) · · · Se(1)–N sequences are indicative of four-centre four-electron interactions at the broken bonds.

The Se(1) · · · Se(1) atoms of a helix each lie 3.670(1) Å from the Se(2) atom of a helix $\frac{b}{2}$ removed, located on the two-fold axis across which Se(1) · · · Se(1) extends. This makes the environment of Se(2) distorted *cis* square-planar: Se(1)–Se(2) · · · Se(1) 156.7°, Se(1) · · · Se(2) · · · Se(1) 55.3°, and the angle between the Se(1) · · · Se(2) · · · Se(1) and Se(1)–Se(2)–Se(1) planes, intersecting in the two-fold axis, is 3.2°. A tendency of bivalent selenium toward square-planar four-co-ordination is evident in numerous crystals, *e.g*. in $Se_3(CN)_2$,[11,12] $Se_3(PEt_2Se)_2$,[10] and $K_2[Se_4(CN)_3]_2 \cdot H_2O$.[12,19] These contacts, in the present case, lead to infinite –Se(2) · · · Se(1)– chains, crossing at Se(2) and parallel to [110] and $[\bar{1}10]$, *i.e*. to the boundary faces of the rhomb-shaped plates.

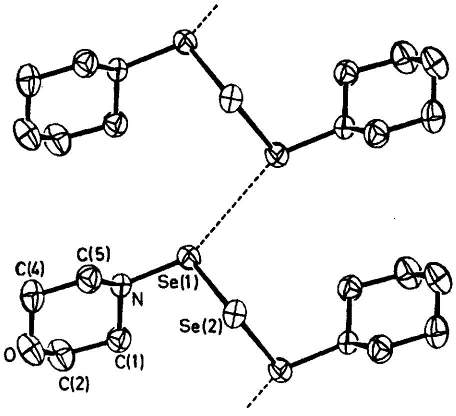

FIGURE 3 Two dimorpholinotriselane molecules, at x and $1 + x$, as seen along the two-fold axes (thermal ellipsoids drawn to enclose 50% probabilities). The infinite –Se–Se · · · Se– helix (four per unit cell) running parallel to the a axis is indicated

In dimorpholinodiselane the shortest intermolecular Se · · · Se contacts are generated by the two-fold screw axes, and are 3.588(1) *A* between Se(1) and Se(2) atoms. They give rise to helixes along the screw axes, with two diselane groups per turn, and pitch $b = 5.716$ Å. Se(2) · · · Se(2) contacts of 4.067(1) Å occur within the helixes.

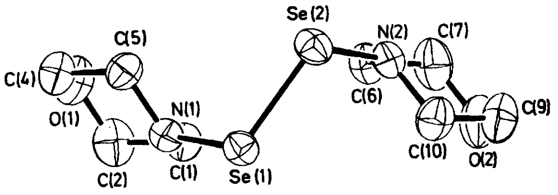

FIGURE 4 The dimorpholinodiselane molecule (thermal ellipsoids as in Figure 3)

There is no intermolecular N · · · Se contact within 4.0 Å in either compound.

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