

Crystal Structure of 1,4-Diselenocyanatobenzene: the Co-ordination of Selenium(II)

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The crystal structure of 1,4-diselenocyanatobenzene has been determined by single-crystal *X*-ray diffraction, and refined by least-squares methods to $R = 11.4\%$. The crystals are monoclinic, space group $P2_1/c$, with two centrosymmetric molecules in a cell of dimensions $a = 9.12$, $b = 4.12$, $c = 11.84$ Å, $\beta = 95.7^\circ$. The C-Se-C bond angle is 94.4° and each selenium atom makes intermolecular contacts, $\text{Se} \cdots \text{N}$, of 3.08 and 3.27 Å, which are appreciably less than the sum of the van der Waals radii. Each of these weak intermolecular bonds is nearly co-linear with a C-Se bond, giving approximately square-planar co-ordination around the selenium atom.

A refinement of the structure of selenium diselenocyanate by use of the published data shows that in this compound also both kinds of selenium atom show approximately square-planar co-ordination, closely similar to that found in the title compound, and resembling that already established for tellurium(II).

Information on the bond lengths and angles of organic compounds of selenium(II) is limited. Electron-diffraction measurements on dimethyl selenide gave only an approximate bond angle,¹ and *X*-ray crystal structure determinations reported² show large standard deviations. Few measurements of the Se-C bond length have been made since Abrahams' review.³ No full crystal-structure determinations are available for organic selenocyanates although Aksnes and Foss have reported the structure of selenium diselenocyanate.⁴ We describe here the structure of 1,4-diselenocyanatobenzene, $p\text{-C}_6\text{H}_4(\text{SeCN})_2$, together with a least-squares refinement of the structure reported for selenium diselenocyanate, $\text{Se}(\text{SeCN})_2$.⁴

EXPERIMENTAL

1,4-Diselenocyanatobenzene was prepared from diazotized 4-selenocyanatoaniline by a method similar to that described for the preparation of 1,4-selenocyanatothiocyanatobenzene⁵ which used potassium selenocyanate in place of the thiocyanate. We thank Prof. F. Challenger for his description of the compound, details of which have not been published previously. The product was recrystallized from ethanol as yellow-orange plates (Found: C, 33.5; H, 1.5. $\text{C}_6\text{H}_4\text{N}_2\text{Se}_2$ requires C, 33.6; H, 1.4%).

Crystal Data.— $\text{C}_6\text{H}_4\text{N}_2\text{Se}_2$, $M = 286.01$, m.p. 156° (decomp.), monoclinic, $a = 9.12 \pm 0.02$, $b = 4.12 \pm 0.01$, $c = 11.84 \pm 0.02$ Å, $\beta = 95.7^\circ \pm 0.2^\circ$, $U = 442.7$ Å³, $D_m = 2.12$, $Z = 2$, $D_c = 2.15$, $F(000) = 268$ electrons. Space group, $P2_1/c$ (C_{2h}^2 , No. 14). $\text{Cu-K}\alpha$ radiation, single-crystal rotation and oscillation photographs.

The cell dimensions were measured from zero-layer precession photographs and intensities were estimated visually from $\text{Cu-K}\alpha$ Weissenberg photographs of reciprocal lattice layers $h0-l$, giving 489 independent structure amplitudes. The structure was solved by the heavy-atom method and full-matrix least-squares refinement of atomic positions with isotropic temperature factors converged to $R = 14.0\%$. Further refinement with allowance for anisotropic temperature factors and with the weighting

scheme $w = 1/(10 + |F_o| + 0.01|F_o|^2 + 0.012|F_o|^3)$ converged to $R = 11.7\%$. The hydrogen atoms were then included in calculated positions and refined with isotropic temperature factors fixed at $U = 0.05$ Å² giving a residual of 11.4% .

The final atomic co-ordinates and their estimated standard deviations are given in Table 1 and the vibration tensor

TABLE 1
Fractional co-ordinates of 1,4-diselenocyanatobenzene with estimated standard deviations in parentheses

	x/a	y/b	z/c
Se	0.3400(2)	0.2479(6)	0.0716(1)
C(1)	0.1429(20)	0.4012(66)	0.0341(14)
C(2)	0.1147(23)	0.5729(71)	−0.0654(9)
C(3)	0.0297(23)	0.3203(62)	0.0990(17)
C(4)	0.3454(22)	0.3601(67)	0.2221(19)
N	0.3521(21)	0.3902(95)	0.3189(14)
H(2)	0.1970(231)	0.6287(596)	−0.1118(197)
H(3)	0.0373(267)	0.2161(546)	0.1518(228)

components are given in Table 2. The observed and calculated structure factors are listed in Supplementary Publication No. SUP 20011 (3 pp., 1 microfiche).*

Refinement of the Structure of $\text{Se}(\text{SeCN})_2$.—The need to compare the intermolecular contacts in 1,4-diselenocyanatobenzene (see next section) with those in other selenocyanates prompted us to refine further the structure of $\text{Se}(\text{SeCN})_2$ determined by Aksnes and Foss.⁴ Crystals of $\text{Se}(\text{SeCN})_2$ are orthorhombic, with $a = 10.07$, $b = 13.35$, and $c = 4.48$ Å, $Z = 4$. Space group $Pnma$ (D_{2h}^{10} , No. 62). The analysis of Aksnes and Foss used a total of 152 structure factors for the three axial projections. We used their observations in a full-matrix least-squares refinement of positional parameters and isotropic temperature factors. The final R value was 10.0% , and the results of the refinement are given in Table 3. The weighting scheme used was $w = 1/(10 + |F_o| + 0.01|F_o|^2 + 0.001|F_o|^3)$. The revised dimensions show a lengthening of the Se-C bond from 1.83 to 1.92 ± 0.05 Å and a shortening of the C-N bond from 1.05 to 1.01 ± 0.05 Å. This C-N bond length appears to be abnormally short although it is just within 3σ of the expected value of 1.15 Å.

Molecular Dimensions.—The molecular dimensions are given in Table 4. The bond length from selenium to the carbon atom of the benzene ring, 1.92 Å, agrees with

* See note about Supplementary Publications in Notice to Authors, *J. Chem. Soc. (A)*, Issue No. 11.

¹ E. Goldish, K. Hedberg, R. E. Marsh, and V. Schomaker, *J. Amer. Chem. Soc.*, 1955, **77**, 2948.

² R. E. Marsh and J. D. McCullough, *J. Amer. Chem. Soc.*, 1951, **73**, 1106; W. R. Blackmore and S. C. Abrahams, *Acta Cryst.*, 1955, **8**, 323.

³ S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 430.

⁴ O. Aksnes and O. Foss, *Acta Chem. Scand.*, 1954, **8**, 1787.

⁵ F. Challenger and A. T. Peters, *J. Chem. Soc.*, 1928, 1364.

the single-bond value given by Pauling,⁶ and with the lengths found in diphenyl diselenide⁷ and in di-*p*-tolyl selenide⁸ although it is a little shorter than the value estimated by Abrahams (1.97 Å).³ The Se-C(N) distance of 1.84 Å suggests some double-bond character, but the standard deviation of 0.02 Å does not allow a firm conclusion on this point. The C-N distance (1.15 Å) is normal and the C-Se-C angle of 94.4° lies within the range of values given by Abrahams.³ The selenocyanate group seems to deviate from linearity (Se-C-N = 172°) and the deviation is probably significant since a similar departure from

Figures 2 shows a projection of the Se(SeCN)₂ structure, and similar Se...N intermolecular contacts occur here and are indicated in the Figure. In the Se(SeCN)₂ structure the intermolecular distances are 3.07 and 3.27 Å for one selenium, and two symmetry-equivalent distances of 3.16 Å for the other.

The crystal structure of the isomorphous selenium dithiocyanate has also been reported,⁹ but our attempt at full-matrix least-squares refinement of the positional coordinates was unsuccessful because of insufficient data. Published co-ordinates were therefore used to calculate

TABLE 2

Vibration tensor components * of 1,4-diselenocyanatobenzene with estimated standard deviations in parentheses (Å²)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Se	0.029(1)	0.032(1)	0.035(1)	-0.009(2)	-0.007(1)	0.016(2)
C(1)	0.041(10)	0.031(12)	0.036(9)	0.019(20)	-0.027(16)	0.012(20)
C(2)	0.043(11)	0.038(15)	0.063(13)	0.000(28)	0.034(19)	0.039(26)
C(3)	0.041(10)	0.057(20)	0.033(9)	0.018(18)	-0.004(15)	0.040(19)
C(4)	0.036(10)	0.059(18)	0.048(11)	0.031(21)	-0.001(17)	0.016(20)
N	0.053(12)	0.149(23)	0.037(10)	-0.025(26)	-0.012(17)	0.059(28)

* Where the temperature factor = $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{23}kbl^{*}c^{*} + 2U_{13}hla^{*}c^{*})]$.

the linearity is found in Se(SeCN)₂ (next section). The selenocyanate group is rotated out of the plane of the benzene ring by an angle of 45.3°.

Intermolecular Bonding.—Figure 1 shows a *b*-axis projection of the structure of 1,4-diselenocyanatobenzene.

TABLE 3

Refined atomic parameters of selenium diselenocyanate

	x/a	y/b	z/c
Se(1)	0.5358(6)	0.2500	0.4927(23)
Se(2)	0.4418(4)	0.1149(3)	0.2535(22)
C	0.2903(38)	0.1091(30)	0.5136(121)
N	0.2007(34)	0.1000(29)	0.6084(98)

Bond lengths (Å) and angles (deg.) with estimated standard deviations in parentheses

Se-Se	2.301(8)	Se-Se-Se	103.2(0.4)
Se-C	1.921(45)	Se-Se-C	94.3(1.4)
C-N	1.005(54)	Se-C-N	167.0(5.0)

Se-Se-Se-/Se-Se-C dihedral angle 88.2°.

TABLE 4

1,4-Diselenocyanatobenzene bond lengths (Å) and angles (deg.) with estimated standard deviations in parentheses

Se-C(1)	1.916(19)	C(1)-Se-C(4)	94.4(9)
Se-C(4)	1.837(23)	Se-C(1)-C(3)	121.7(1.6)
C(1)-C(2)	1.376(32)	Se-C(1)-C(2)	117.3(1.4)
C(1)-C(3)	1.388(28)	C(1)-C(2)-C(3')	119.5(1.9)
C(3)-C(21)	1.407(31)	Se-C(4)-N	171.8(3.0)
C(4)-N	1.149(28)	C(1)-C(2)-H(2)	120(13)
C(2)-H(2)	1.00(22)	C(1)-C(3)-H(3)	125(18)
C(3)-H(3)	0.78(26)		

There are two intermolecular Se...N contacts which are appreciably less than the sum of the van der Waals radii, which Pauling⁶ gives as 3.5 Å, although this should probably be reduced slightly because of the chemical environment of the nitrogen atom in a SeCN group. The Se...N distance which is almost co-linear with the SeCN group is 3.06 Å, and the other Se...N distance is 3.32 Å. These intermolecular bonds are shown as dotted lines in Figure 1.

⁶ L. Pauling, 'Nature of the Chemical Bond,' Cornell U.P., New York, 1960.

⁷ R. Marsh, *Acta Cryst.*, 1952, **5**, 458.

⁸ W. R. Blackmore and S. C. Abrahams, *Acta Cryst.*, 1955, **8**, 323.

the symmetrical intermolecular Se...N distances of 2.98 Å. The S...N distances, however (3.03 and 3.32 Å), deviate less from expected van der Waals contact distances (3.3 Å). In all the compounds considered the selenium atoms are approximately co-planar with their four nearest neighbours while this is certainly not the case for the sulphur

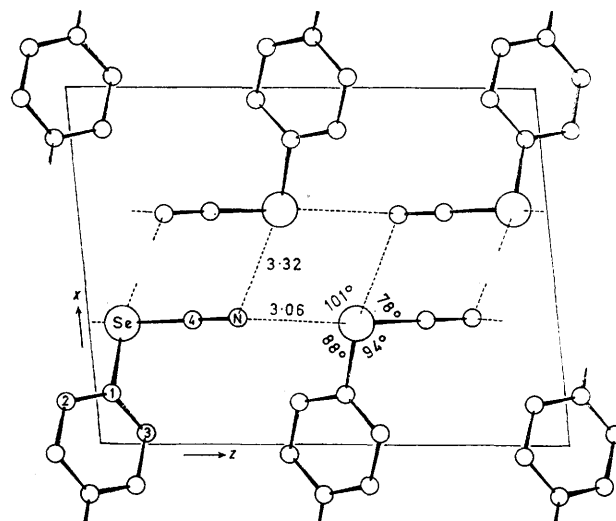


FIGURE 1 The crystal structure of C₆H₄(SeCN)₂ viewed along the *b*-axis

atoms in Se(SCN)₂ (see Table 5 which gives the distances of neighbours from the central atom and the deviations from the mean plane passing through these central atoms).

This close approach between the selenium and the nitrogen atoms of neighbouring molecules in each of the three compounds agrees with Krebs' predictions which have been applied to tellurium compounds by Foss.^{10,11} The

⁹ S. M. Odberg and P. A. Vaughan, *J. Amer. Chem. Soc.*, 1954, **76**, 2649.

¹⁰ O. Foss, *Acta Chem. Scand.*, 1962, **16**, 779.

¹¹ K. Fosheim, O. Foss, A. Scheie, and S. Solheimsnes, *Acta Chem. Scand.*, 1965, **19**, 2336; O. Foss and S. Hague, *ibid.*, 1965, **19**, 2395; O. Foss, K. Johnson, K. Maartmann-Moe, and K. Marøy, *ibid.*, 1966, **20**, 113; O. Foss and K. Marøy, *ibid.*, 1966, **20**, 123.

nitrogen atoms are approximately co-linear with the selenium σ bonds of normal type and with internuclear

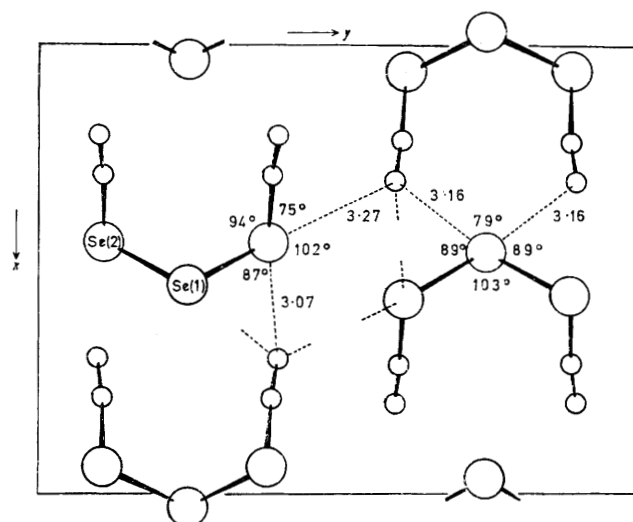


FIGURE 2 The crystal structure of $\text{Se}(\text{SeCN})_2$ viewed along the c -axis

distances (described by Krebs as 'half p -bonds') *ca.* 0.4 Å less than the expected non-bonding distances, assuming van der Waals radii given by Pauling. The non-bonding distances given by Foss¹⁰ were taken from contact distances in monoclinic selenium where limited interaction is thought likely. Presumably the selenium(II) in a pseudo-planar

TABLE 5

Selenium co-ordination: deviations from planarity (Å)

Compound	Atoms defining plane (see Figures 1 and 2)	Distance from central atom	Deviation from plane
$\text{C}_6\text{H}_4(\text{SeCN})_2$	Se	0	0
	C(1)	1.92	-0.28
	C(4)	1.84	0.18
	N'	3.06	0.07
$\text{Se}(\text{SeCN})_2$	N''	3.32	-0.18
	Se(1)	0	0
	Se(2)	2.30	0.03
	Se(3)	2.30	0.03
	N'	3.16	0.02
	N''	3.16	0.02
	Se(2)	0	0
	Se(1)	2.30	-0.06
$\text{Se}(\text{SCN})_2$	C	1.92	-0.20
	N'	3.08	-0.29
	N''	3.27	-0.23
	Se	0	0
	S(1)	2.21	-0.13
	S(2)	2.21	-0.13
	N'	2.98	-0.12
	N''	2.98	-0.12
	S(1)	0	0
	Se	2.21	-0.76
	C(1)	1.69	-1.23
	N'	3.03	-0.57
	N''	3.32	-0.63

environment is acting as a weak Lewis acceptor to electrons of the nitrogen atom. It therefore seems possible that regular square-planar selenium(II) complexes, analogous to the thiourea complexes of tellurium,¹¹ could exist.

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