The Crystal Structure of Bis(o-nitrobenzeneselenenyl) Sulfide
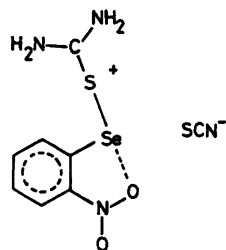
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Bis(o-nitrobenzeneselenenyl) sulfide, $C_{12}H_8N_2O_4SSe_2$ is known to occur as monoclinic and orthorhombic crystals. The modification investigated here crystallizes in the orthorhombic space group $P2_12_12$ (No. 18), with $a = 13.809(5)$ Å, $b = 12.298(4)$ Å, $c = 4.196(2)$ Å. There are two formula units per unit cell. The sulfur atom is situated on a two-fold axis. The two symmetrically related halves of the molecule are nearly planar. The divalent selenium atom of each half molecule occurs as the central atom in a practically planar three-coordinated system, with sulfur and oxygen as *trans* ligand atoms and a benzene carbon atom as the third ligand atom. The bond lengths from the selenium atom to the sulfur, oxygen, and carbon atoms are 2.202(2), 2.574(8), and 1.918(8) Å, respectively. A loose five-membred ring is thus formed by the selenium atom, two carbon atoms of the benzene ring and the nitrogen atom and one oxygen atom of the nitro group.
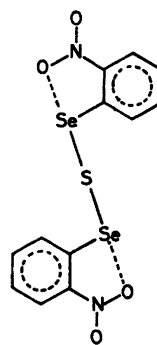
The investigated bis-(o-nitrobenzeneselenenyl) sulfide (I) was prepared by a conversion of a thiourea adduct of o-nitrobenzeneselenenyl thiocyanate (II). The structure of the latter compound has been solved,[1] and the conversion procedure described earlier.[2] The o-nitrobenzeneselenenyl-sulfur system occurs in both compounds and the present structure determination was undertaken in order to collect more information about this system, with special regard to the coordination around selenium.

EXPERIMENTAL

The space group and preliminary cell dimensions were determined from Weissenberg photographs.[2] Final cell dimensions were obtained by a least squares treatment of the θ-settings of 18 reflections on the diffractometer,

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I

II

a Siemens automatic, offline, single-crystal diffractometer (AED-1). Nb-filtered Mo$K\alpha$ radiation was used ($\lambda = 0.70926$ Å). Density was determined by flotation in a $ZnCl_2$ solution.

Crystal data.

$C_{12}H_8N_2O_4SSe_2$, molecular weight 434.19.

Cell dimensions: $a = 13.809(5)$ Å, $b = 12.298(4)$ Å, $c = 4.196(2)$ Å, $V = 712.5$ Å³.

Space group $P2_12_12$ (from systematic absences).

$Z = 2$.

Density, calc. 2.02, found 2.01 g/cm³.

$\mu = 57.45$ cm⁻¹.

Intensity values for 1049 unique reflections with $\theta < 28°$ were collected with a scintillation counter, by scanning with $\theta - 2\theta$-technique. The peaks were scanned twice between $\theta - 0.27° - 0.15°\text{tg } \theta$ and $\theta + 0.25° + 0.25°\text{tg } \theta$, starting at the Bragg angle θ. The scanning speed for each reflection was selected such that it gave all sufficiently high intensities approximately the same accuracy. The background intensity was measured on both sides of each peak, the counting time being equal to the scanning time. None of the reflections were strong enough to make attenuation necessary.

With a maximum measuring time set to 0.24 s per 0.01°, 147 of the possible reflections were coded unobserved, i.e. $I_t - I_b < 2\sqrt{I_t + I_b}$. Here I_t and I_b are the total count numbers of the scan and the background, respectively.

Two reference reflections were measured after every 50 reflections and the intervening periods thus became $2-3$ h. The intensities showed a general decrease of about 16 % during the period of data collection. A more random fluctuation was superimposed on this tendency, resulting in a maximum variation of 4 % for two subsequent reference measurements. In order to obtain the data on a common scale each intensity value was multiplied with a scale factor which was a linear function of the time between the reference measurements, and which brought all the reference intensities to the same initial value.

The crystal used for data collection was prism-formed. From an arbitrarily chosen origin to the faces, the crystal had the following dimensions: to (100) and ($\bar{1}$00): 0.0405 mm, to ($\bar{1}$10) and (1$\bar{1}$0): 0.0410 mm, to (230) and ($\bar{2}\bar{3}$0): 0.0412 mm, to (001) and (00$\bar{1}$): 0.0700 mm. The observed intensities were corrected for absorption by the method of Coppens et al.[3] Subdivisions of 4, 6, and 10 Gaussian points were used along the a, b, and c axes, respectively.

The intensity values were given weights, W, according to the formula $W = (I_t - I_b)^2/[(I_t + I_b) + k^2(I_t - I_b)^2]$, were $k = 0.08$ is the estimated relative standard deviation in the time-dependent scale factor described above. These weights were used in the refinement of atomic positions and temperature factors by a full-matrix least squares procedure. The function minimized was $r - W(|F_o| - K|F_c|)^2$, where K is a scale factor. The unobserved reflections were included in the refinement when the scaled, calculated structure factors exceeded the limiting value. In such cases F_o was given a value equal to the limit.

Atomic scattering factors for all elements except hydrogen were taken from the International Tables.[4] The scattering factors for selenium and sulfur were adjusted with the real part of the anomalous dispersion correction term using the values for $\Delta f'$ given by Cromer.[5]

The scattering factors published by Stewart et al. were used for hydrogen.[6]

The calculations were carried out on an IBM 360/50 H computer, except for the plotting procedures, for which a UNIVAC 1110 was used. Both machines were at the University of Bergen. The program used for the least squares procedure was made available by the Chemical Department of X-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel, and modified for use on the IBM computer by Dr. D. Rabinowitch. The illustrations were plotted by means of the program OR TEP.[7] The remaining programs were written by K. Åse and K. Maartman-Moe of the Chemical Institute, University of Bergen.

STRUCTURE DETERMINATION

The space group $P2_12_12$ requires that the sulfur atom lies on a two-fold axis. Approximate values for the sulfur z-coordinate and the selenium coordinates were found from a Patterson synthesis. These values gave phase to 133 reflections used in a subsequent three-dimentional Fourier synthesis. This established the position of one oxygen atom. Two successive sequences of one refinement cycle of atomic positions followed by Fourier synthesis revealed the positions of all atoms except hydrogen. Refinement of these positions and isotropic temperature factors brought the reliability index $R = \sum||F_o| - |F_c||/\sum|F_o|$ down to 0.12. Introducing anisotropic temperature factors for the sulfur and selenium atoms and re-

Table 1. Fractional coordinates with standard deviations from least squares in parentheses.

	x	y	z
Se	0.13059(7)	0.02220(7)	0.0617(3)
S	0.00000	0.00000	0.3558(8)
C_1	0.1207(6)	0.1723(6)	−0.058(3)
C_2	0.1901(6)	0.2228(8)	−0.248(3)
C_3	0.1831(9)	0.3301(9)	−0.347(4)
C_4	0.1043(8)	0.3899(8)	−0.260(3)
C_5	0.3346(7)	0.3424(8)	−0.065(4)
C_6	0.0405(7)	0.2359(7)	0.016(3)
N	0.2776(6)	0.1636(7)	−0.340(2)
O_1	0.2884(5)	0.0714(6)	−0.231(2)
O_2	0.3353(6)	0.2069(7)	−0.517(3)
H_1	0.225(9)	0.355(9)	−0.49(4)
H_2	0.093(6)	0.466(8)	−0.35(2)
H_3	−0.011(7)	0.389(7)	0.00(2)
H_4	−0.004(6)	0.206(7)	0.14(2)

Table 2. Thermal parameters (Å^2) with their standard deviations in parentheses. Anisotropic temperature factors are given by the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots\cdots+2U_{12}hka^*b^*+\cdots\cdots)]$ and isotropic temperature factors by the form $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. The parameters for non-hydrogen atoms are multiplied by 10^3, those for hydrogen atoms by 10^2.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Se	42.4(5)	34.3(4)	54.4(6)	3.1(4)	1.8(5)	4.8(5)
S	58(2)	45(2)	40(2)	−9(2)	—	—
C_1	31(4)	35(4)	52(6)	−3(4)	−7(5)	0(6)
C_2	30(5)	40(5)	62(7)	−3(4)	−10(6)	−6(5)
C_3	55(7)	44(6)	66(10)	−19(5)	−8(6)	10(6)
C_4	60(7)	33(5)	80(9)	1(5)	3(6)	−9(7)
C_5	47(6)	40(5)	71(8)	8(5)	−6(7)	11(6)
C_6	37(5)	40(5)	57(8)	−2(4)	−1(6)	−1(5)
N	35(5)	64(6)	60(7)	0(5)	−13(6)	10(5)
O_1	50(4)	56(4)	94(6)	12(4)	−7(5)	5(5)
O_2	52(5)	109(7)	151(12)	−1(5)	26(9)	50(6)

	U		U		U		U
H_1	10(5)	H_2	7(3)	H_3	6(3)	H_4	4(3)

fining one cycle resulted in an R-value of 0.085. Anisotropic temperature factors were then assigned to the remaining non-hydrogen atoms, and $R=0.079$ was obtained.

The average calculated $C-C$ bond distance of the benzene ring was 1.418 Å at this stage.

This high value was assumed to be the result of refinement of the carbon atoms to positions a little too close to the neighbouring hydrogen atoms, since these were at this stage not included in the calculations. However, the positions of the latter were clearly revealed
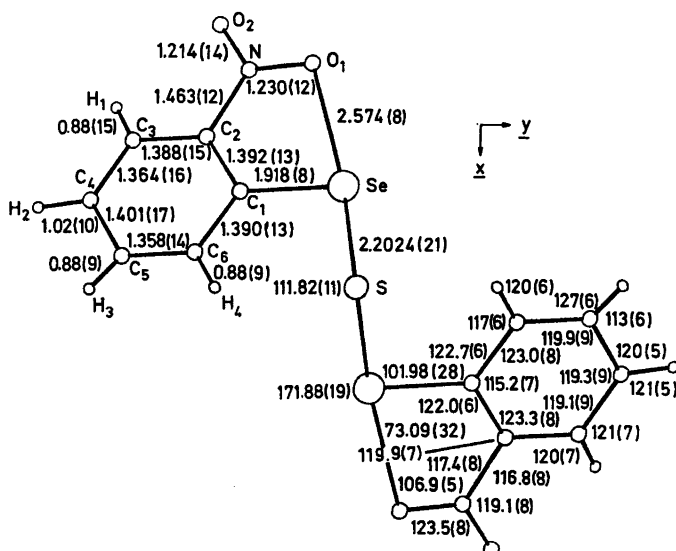

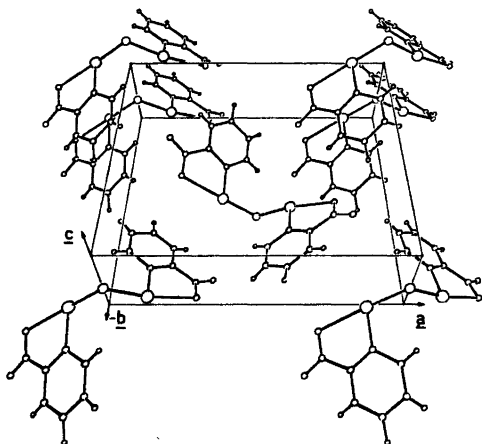*Fig. 1.* Bond lengths and angles. The molecule is shown in (001) projection.

Fig. 2. Perspective drawing of molecular packing as viewed perpendicular to the *x*-axis.

in a difference map. Mainly to improve the apparent dimensions of the benzene ring, the four hydrogen atoms were now included in the refinement. Although their final calculated isotropic temperature factors were high, and the accuracy of their positions low, their inclusion seems justified by the obtained average $C-C$ bond length of 1.382 Å. The final R-value was 0.051.

The calculated atomic parameters are given in Tables $1-2$.

Observed and calculated structure factors can be obtained from the author upon request.

RESULTS AND DISCUSSION

The bond lengths and angles are given in Fig. 1. The arrangement of the molecules in the unit cell is illustrated by Figs. 2 and 3.
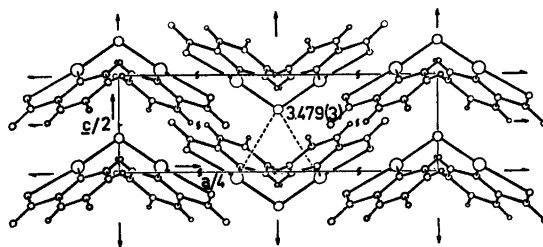

Fig. 3. Packing of the molecules shown in (010) projection. The intermolecular contact between a sulfur atom of one molecule and the two selenium atoms of another is indicated. (Distance in Å).

Table 3. Least squares planes and dihedral angles. The plane equation refer to orthorombic coordinates X, Y and Z in Å.

Plane through all atoms, except hydrogen, of one half molecule:
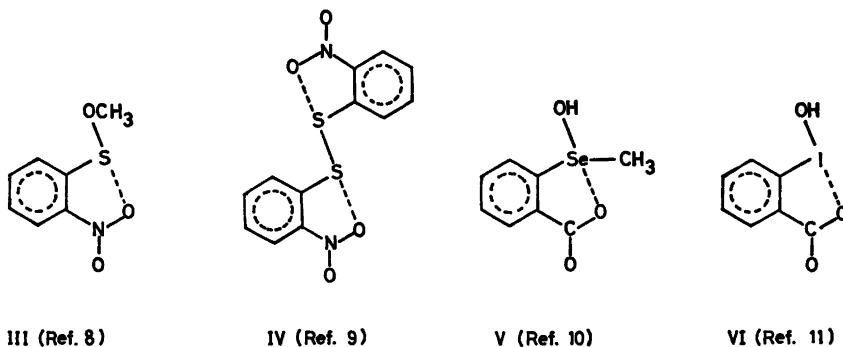
$6.5026\ X + 3.7285\ Y + 3.4765\ Z - 1.2227 = 0$
Distances (Å) of atoms from this plane:

S	Se	O_1	O_2	N	C_1
0.014	-0.076	0.115	-0.069	0.011	0.003

C_2	C_3	C_4	C_5	C_6
-0.016	-0.009	0.007	0.045	-0.024

Angle between this plane and the corresponding plane of the other half molecule, related by the two-fold axis: 68.12°
Dihedral angle $C_1SeSSe' = 79.67°$
Se' is related to Se by the two-fold axis.

III (Ref. 8)   IV (Ref. 9)   V (Ref. 10)   VI (Ref. 11)

Both the present compound (I) and its precursor (II) contain the o-nitrobenzeneselenenyl sulfur system in approximately the same linear arrangement. A five-membered ring is formed by the loose interaction between an oxygen atom of the nitro group and the selenium atom in the *ortho* position. In both compounds the selenium atom is further linked to a benzene carbon atom and a sulfur atom which is *trans* to the loosely bonded oxygen atom.

The planarity of the o-nitrobenzeneselenenyl sulfur system in the diselenenyl sulfide (I) is illustrated in Table 3. The largest distance of a relevant non-hydrogen atom from a least squares plane through one of the symmetrically related halves of the molecules is 0.115 Å. The angle between the least squares planes of the two molecular halves is 68.1°.

A ring closure by *ortho* substituents of benzene similar to the present case, and II, is characteristic of several compounds (III – VI) investigated by X-ray crystallography.[8–11] The compounds all contain an approximately linear sequence of three atoms, corresponding to the sequence O⋯Se – S of the present compound. The central atoms are either sulfur. selenium, or iodine, and the loosely connected atoms are oxygen atoms of carbonyl or nitro groups.

Referring to the three-center four-electron model of linear three-atoms systems, one would be inclined to expect that a reduction of one bond length should be accompanied by a lengthening of the bond in the *trans* position.[12–13] In contrast, the present molecule shows slightly increased bond lengths for both the O⋯Se and Se – S bonds relative to the corresponding

bonds in the thiourea adduct (II). The O⋯Se bond lengths are 2.574(8) and 2.505(8) Å, and the Se – S bond lengths are 2.202(2) and 2.188(3) Å, respectively. However, these variations seem reasonable when regarding the different charge distributions of the two compounds. In the thiourea adduct (II) the o-nitrobenzeneselenenyl sulfur system is part of a cation with the charge formally located on the thiourea group, whereas the dieselenenyl sulfide (I) is a neutral molecule. The positive charge in II must be expected to reduce the electron density on the selenium atom to some extent, and thus facilitate the approach of the oxygen donor atom in the formation of a co-ordinate O⋯Se bond. Also the same positive charge may affect the π-electron system that probably has some importance for the bonds of the selenium atom. The course of this influence is hard to predict, but the nearly insignificant increase of the Se – C distance of II relative to I seems to be consistent with a higher π-bond order of the Se – S bond in II.

The O⋯Se bond length of 2.378(3) Å reported for o-carboxybenzene methyl selenium oxide (V) is considerably shorter than those of I and II. This is consistent with the charge distribution of V. When disregarding the O⋯Se interaction, the selenium atom formally carries one unit positive charge and the neighbouring carboxyl group one unit negative charge. Both with respect to charge separation and to O⋯Se bond length, the thiourea adduct (II) represents a situation between I and V.

The structures of bis(o-nitrobenzene) disulfide[14] and its *ortho* isomer (IV)[9] reported by Ricci and Bernal seem to indicate a small *trans*-bond lengthening effect by one oxygen atom

of the nitro group on the S−S bond in IV. The S−S bond lengths of the *ortho* and *para* isomers are 2.045(3) and 2.019(5) Å, respectively. *trans*-Bond lengthening effects of a similar magnitude can hardly be excluded for the analogous O···Se interactions on the basis of the available observations.

Besides the bond distances discussed so far, there are no significant differences between corresponding values of I and II. Among the pairs of corresponding bond angles there is a significant difference only for the $S-Se-C_1$ angle, which is 102.0(3)° in I and 99.9(3)° in II.

The closest intermolecular contact of the present compound exists between the selenium atoms of one molecule and the sulfur atom of another, related to the first by one unit cell translation along z; see Fig. 3. The distance is 3.479(3) Å, which is approximately the sum of the van der Waals radii. The compound II has a hydrogen bond in a direction roughly corresponding to this van der Waals contact.

REFERENCES

1. Eriksen, R. and Hauge, S. *Acta Chem. Scand.* 26 (1972) 3153.
2. Eriksen, R. *Acta Chem. Scand.* 26 (1972) 1274.
3. Coppens, P.,Leiserowitz, L. and Rabinovich, D. *Acta Crystallogr.* 18 (1965) 1035.
4. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, Table 3.3.1.
5. Cromer, D. T. *Acta Crystallogr.* 18 (1965) 17.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
7. Johnson, C. K. *ORTEP: A Fortran Thermal-Ellipsoid Plot Program For Crystal Structure Illustrations*, 2nd Revision, Oak Ridge National Laboratory, Oak Ridge 1970.
8. Hamilton, W. C. and La Plaza, S. *J. Amer. Chem. Soc.* 86 (1964) 2289.
9. Ricci, J. S. and Bernal, I. *J. Chem. Soc. B* (1970) 806.
10. Dahlén, B. *Acta Crystallogr. B* 29 (1973) 595.
11. Shefter, E. and Wolf, W. *J. Pharm. Sci.* 54 (1965) 104.
12. Foss, O. *Acta Chem. Scand.* 16 (1962) 779.
13. Foss, O. In Andersen, P., Bastiansen, O. and Furberg, S. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 145.
14. Ricci, J. S. and Bernal, I. *J. Amer. Chem. Soc.* 91 (1969) 4078.