Preparation and Space Group Determination of Some *o*-Substituted Benzeneselenenyl Compounds and Their Adducts with Thiourea

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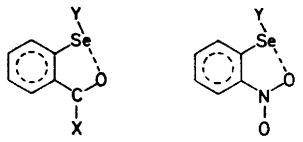
o-Substituted benzeneselenenyl compounds often exhibit properties that differ from those of corresponding compounds without *o*-substituent. Relatively high stabilities are frequently observed.[1-3]

Some benzeneselenenyl compounds with a nitro group, a chlorocarbonyl group or a methoxycarbonyl group as *o*-substituents have been prepared according to known methods.[1-4] The thiocyanate (III) is new.



I: X = Cl, Y = Cl IV: Y = Cl
II: X = OCH_3, Y = Cl V: Y = SCN
III: X = OCH_3, Y = SCN

Some of the compounds have been found to give adducts with thiourea. Equimolar quantities of the reagents were mixed in ethanol or methanol solutions. The adducts crystallized from the solutions upon evaporation, and were recrystallized once or twice from the same solvents.

The adduct (VIII) of thiourea with *o*-nitrobenzeneselenenyl thiocyanate was unstable in ethanol solution at room temperature. After some days, the compound was quantitatively converted. The product was identified as bis(*o*-nitrobenzeneselenenyl) sulphide (IX) and was contaminated only by a trace of a white impurity. An identical compound, as shown by IR spectrum and melting point, was prepared by passing hydrogen sulphide through an ethanol-benzene solution of *o*-nitrobenzeneselenenyl chloride.[5]

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Space groups and unit cell dimensions were determined from single-crystal oscillation and Weissenberg photographs. Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) was used. The cell dimensions are believed to be correct to within 0.5 %. Densities were determined by flotation.

o-Chlorocarbonylbenzeneselenenyl chloride (I). Orange needles from petrol ether, with *a* as the needle axis. M.p. 63–65° (lit.[3] 65–66°). Space group $P2_1/c$ (No. 14), from systematic absences; $a = 3.90$ Å, $b = 22.72$ Å, $c = 28.84$ Å, $\beta = 92.0°$. There are twelve formula units per unit cell, *i.e.*, three molecules in the asymmetric unit. Density, calc. 1.98, found 1.98 g/cm³.

o-Methoxycarbonylbenzeneselenenyl chloride (II). Very thin, pale yellow needles from methanol, or by sublimation at reduced pressure. The *c* axis is the needle axis. M.p. 74–75° (lit.[3] 74–75°). The crystals gave poor X-ray photographs. For the sublimated crystals, the space group $P2_12_12$ (No. 18) was indicated by the systematic absences. The unit cell dimensions are, $a = 13.66$ Å, $b = 17.70$ Å, $c = 7.66$ Å. There are eight formula units per unit cell; density, calc. 1.82, found 1.76 g/cm³.

o-Methoxycarbonylbenzeneselenenyl thiocyanate (III). 5.06 g (0.02 mol) of the chlorocarbonyl compound I was dissolved in 25 ml methanol. After a couple of minutes at room temperature, the methoxycarbonyl compound II crystallized from the solution. 1.94 g (0.02 mol) of potassium thiocyanate dissolved in 25 ml methanol was then added. The crystals redissolved. From the yellow solution, 4.4 g (81 %) of a crude product was obtained upon evaporation. Recrystallizing twice from methanol gave 3.5 g of pale yellow, monoclinic needles, elongated along the *b* axis, m.p. 106–107°. (Found: Se 28.83. Calc. for $C_9H_7NO_2SSe$: Se 28.95.) The space group is $P2_1/c$ (No. 14); $a = 10.96$ Å, $b = 4.47$ Å, $c = 21.21$ Å, $\beta = 94.1°$. With four formula units per unit cell, the calculated density is 1.74, found 1.75 g/cm³.

Recrystallization of this compound from ether gave another modification: yellow, bipyramidal crystals with the *b* axis perpendicular to the base. M.p. as above. From the systematic absences, the space group may be either $C2/c$ (No. 15) with one formula unit per asymmetric unit, or Cc (No. 9) with two formula units per asymmetric unit. The unit cell dimensions are, $a = 14.31$ Å, $b = 12.69$ Å, $c = 11.73$ Å, $\beta = 122.3°$. There are eight formula units per unit cell; density, calc. 1.73, found 1.71 g/cm³.

o-Nitrobenzeneselenenyl chloride (IV). Red crystals from petrol ether (40–60°). M.p. 66–

69° (lit.[6] 64°). Two forms were observed: long needles, and prisms with rectangular cross-section. The needles have $a=25.37$ Å, $b=7.69$ Å, $c=4.02$ Å, and there are four molecules per unit cell; density, calc. 2.00, found 2.01 g/cm³. The space group is $Pna2_1$ (No. 33) or $Pnam$ (No. 62); in the latter the molecules would lie in mirror planes.

The prism-shaped crystals were poorly developed. They appeared to be orthorhombic, with axes 3.96 Å and 7.04 Å, and the third axis a multiple of 7.1 Å.

o-*Nitrobenzeneselenenyl thiocyanate* (V). Yellow plates and prisms from carbon tetrachloride. The prisms are extended along the *a* axis. M.p. 110–111° (lit.[4] 113.5°). The space group is $P2_1/c$ (No. 14); $a=8.02$ Å, $b=7.98$ Å, $c=12.74$ Å, $\beta=90.3°$. There are four formula units per unit cell; density, calc. 2.10, found 2.09 g/cm³.

Adduct of thiourea with o-*methoxycarbonylbenzeneselenenyl chloride* (VI). 1.97 g (0.0076 mol) of II and 0.59 g (0.0077 mol) of thiourea gave 2.26 g (89 %) of the adduct. The compound crystallized from methanol as pale yellow prisms, and melted with decomposition at approx. 180°. (Found: Se 23.68. Calc. for $C_9H_{11}ClN_2O_2SSe$: Se 23.64.)

From the systematic absences, the space group may be either $Pbc2_1$ (No. 29) with two formula units per asymmetric unit or $Pbcm$ (No. 57) with one formula unit per asymmetric unit. The unit cell dimensions are, $a=8.20$ Å, $b=14.70$ Å, $c=20.80$ Å. With eight formula units per unit cell, the calculated density is 1.77, found 1.75 g/cm³.

Reaction of thiourea with o-*methoxycarbonylbenzeneselenenyl thiocyanate*. The compound III did react with thiourea in several solvents. In contrast to the rest of the compounds reported here, this particular product was white. Attempts to crystallize it satisfactorily were unsuccessful. The crude product melted with decomposition at approx. 125–130°.

Adduct of thiourea with o-*nitrobenzeneselenenyl chloride* (VII). 2.4 g (0.01 mol) of IV and 0.76 g (0.01 mol) of thiourea gave 2.86 g (88 %) of the adduct (VII). It crystallized from methanol as short, yellow prisms {110}. The compound melts with decomposition at approx. 175°. (Found: Se 25.29. Calc. for $C_7H_8ClN_3O_2SSe$: Se 25.26.) The space group is $P2_1/c$ (No. 14); $a=8.27$ Å, $b=9.20$ Å, $c=15.26$ Å, $\beta=93.2°$. There are four formula units per unit cell; density, calc. 1.79, found 1.74 g/cm³.

Adduct of thiourea with o-*nitrobenzeneselenenyl thiocyanate* (VIII). 3.0 g (0.116 mol) of the selenenyl compound and 0.87 g (0.116 mol) of thiourea gave 1.8 g (47 %) of the adduct (VIII). Yellow laths, elongated along the *b* axis, were obtained on evaporation of an ethanol solution. The compound decomposes at approx. 150°. The space group is $C2/c$ (No. 15); $a=36.36$ Å, $b=5.091$ Å, $c=14.59$ Å, $\beta=98.44°$. The structure of this compound has been solved.[7]

Bis(o-*nitrobenzeneselenenyl*) *sulphide* (IX). The conversion product from an ethanol solution of VIII crystallized from this solution as needles or prisms extended along the *c* axis. The compound melts with decomposition at approx. 160°. Systematic absences determine the space group as $P2_12_12$ (No. 18); $a=13.81$ Å, $b=12.30$ Å, $c=4.19$ Å. There are two molecules per unit cell, which indicates that the molecules lie on twofold axes of symmetry. Density, calc. 2.02, found 2.01 g/cm³. The determination of the structure of this compound is in progress.

The same compound, when prepared from IV and hydrogen sulphide in benzene-ethanol-mixture,[5] formed yellow, irregularly shaped crystals. Recrystallization from benzene of the $P2_12_12$ modification converted it into this latter one. It melts at 169–170° (lit.[6] 169–170°). The space group may be either $C2$ (No. 5), Cm (No. 8), both with one molecule per asymmetric unit, or $C2/m$ (No. 12) with half a molecule per asymmetric unit. The unit cell dimensions are, $a=13.27$ Å, $b=7.85$ Å, $c=12.60$ Å, $\beta=110.0°$. With four molecules per unit cell, the calculated density is 2.06, found 2.02 g/cm³.

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Received February 7, 1972.