

amine-aniline-phosphoric acid¹¹ as well as with hydroxylamine-ferric chloride.¹² The solution was filtered, the solvent evaporated and the residue extracted with chloroform. Evaporation of the chloroform gave crystalline methyl 1,2-*O*-isopropylidene- α -D-xylofuranuronate (II) (337 mg, 68 %). After sublimation *in vacuo*, it had m.p. 104–106°C (lit.⁸ 103–104°C), and $[\alpha]_D -30^\circ$ (*c* 2, methanol) (lit.⁸ -32.8°). Strong infrared absorption was observed at 1745 cm⁻¹ (KBr), NMR signals were located at δ 1.30, 1.46, 3.74 (3 protons, singlets), 2.42 (1 proton, broad), 4.39, 4.48, 4.68, 5.95 (1 proton, doublets).

The product (20 mg) in water (3 ml) was treated with sodium borohydride (100 mg) over night. The solution was then treated with Dowex 50 W ion exchanger (H⁺), filtered and the solvent evaporated. Boric acid was removed by repeated distillations of methanol from the residue, which subsequently was hydrolyzed in 30 % acetic acid for 4 h at 100°C. Removal of the water and acetic acid under reduced pressure gave a syrup which appeared homogeneous by paper chromatography and electrophoresis, indistinguishable from authentic xylose.

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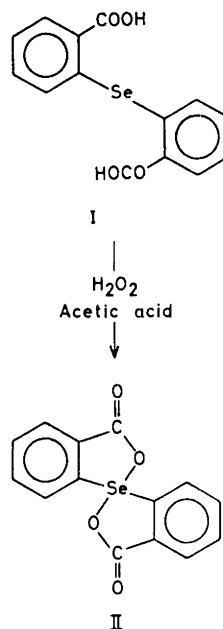
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Formation and Crystal Structure of 3,3'-Spirobi(3-selenaphthalide)

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The 3,3'-spirobi(3-selenaphthalide) (II) was first synthesized by Lesser and Weiss¹ by warming 2,2'-dicarboxy-diphenyl selenide (I) with concentrated sulphuric acid. This synthesis has now been re-investigated. Compound II has also been obtained when oxidizing I with hydrogen peroxide in acetic acid (Scheme 1). Infrared spectra and elemental analysis data of II are in good agreement with the proposed spiro-dilactone structure.



Scheme 1.

The analogous spiro-thia-dilactone has recently been synthesized and its crystal structure determined.^{2,3}

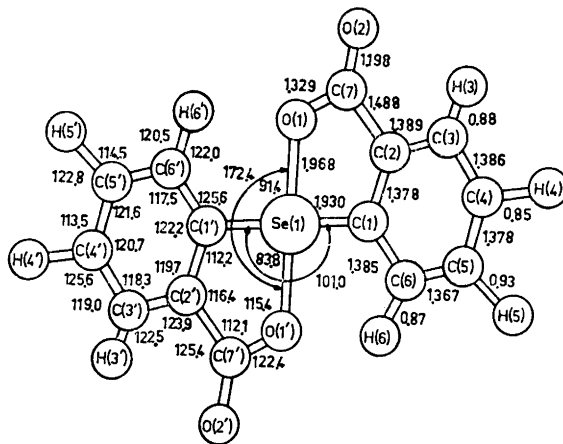


Fig. 1. Bond lengths and angles.

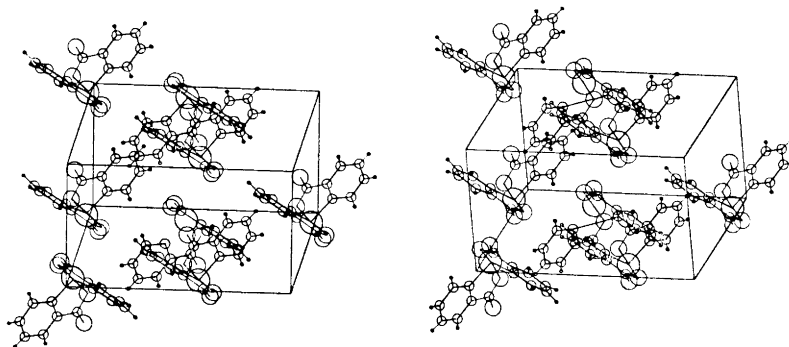


Fig. 2. Stereoscopic pair of 3,3'-spirobi(3-selenaphthalide) viewed along the c axis.

A number of papers dealing with similar problems have been published recently. An aliphatic spiro-selena-dilactone has been isolated by oxidizing 3,3'-selenodipropionic acid.⁴ The 2-carboxyphenyl methyl sulphoxide and selenoxide systems have been studied by one of us with reference to different interactions between the carboxy group and the sulphinyl and seleninyl groups, respectively.⁵ Interactions have also been found in 2-nitrobenzene-seleninyl compounds between the selenium atom and an oxygen atom of the nitro group.⁶

The interatomic distances and angles of II are given in Fig. 1. The molecular packing is shown by a stereoscopic drawing in Fig. 2. The standard deviations of the

bond lengths and angles involving non-hydrogen atoms are approximately 0.01 Å and 0.06° respectively.

The two identical halves of the molecule are related by a twofold axis with the selenium atom located on the axis. The configuration around the selenium atom is a trigonal bipyramid very similar to that found in the sulphur analogue.² The dihedral angle between the best planes through the two benzene rings is 102.7°. The corresponding angle in the sulphur analogue is 106.7°.

The O-Se-O angle is 172.4° and the value obtained in the sulphur compound is 178.5°. These values are in good agreement with other values reported for O-Se-O,⁵ O-S-O,^{3,5,6} and S-Se-O⁷

angles which are all close to 180°. The configuration around the selenium atom is also similar to that found in 2-carboxyphenyl methyl selenoxide⁵ where a ring closure has taken place by migration of the hydrogen atom from the carboxyl group to the selenoxide oxygen.

The Se—C distance is 1.930(7) Å which is normal for Se—C single bonds.^{5,8} The Se—O bond is 1.968 Å which is considerably longer than the Se—O 'normal' single bond of 1.774 Å found in 2-carboxyphenyl methyl selenoxide but it is much shorter than the corresponding Se—O bond of 2.378 Å in the latter compound. The shorter Se—O bond in this structure has led to a substantial decrease of the valence angles in the five-membered ring.

The Se—O bond can not extend due to the short intramolecular contact between O(1) and H(6') of 2.46 Å. The O(1)···C(6') distance is 2.914 Å which is much shorter than the sum of the van der Waals radii which is approximately 3.2 Å⁹ and this close C—H···O interaction may indicate a hydrogen bond.

Experimental. The selenium analyses were performed by a microanalytical method developed by Bengtsson¹⁰ and very similar to that of Gould.¹¹ The melting points are uncorrected.

2,2'-Dicarboxy-diphenyl selenide (I). Sodium formaldehydesulphoxylate 4.2 g (0.027 mol) was added to a solution of 9.6 g (0.024 mol) unpurified 2,2'-dicarboxy-diphenyl diselenide^{12,13} in 60 ml 2 M ammonia. The solution was discoloured upon the addition. 2-Iodobenzoic acid 12 g (0.048 mol) was dissolved in 30 ml 2 M ammonia and added to the discoloured solution. The mixture was heated together with 0.5 g of copper powder in a glass vessel immersed in an autoclave for 5–6 h at 160–180°C, then filtered and acidified. Yield 10 g (65 %). M.p. 210–217°C (d). The product can be recrystallized from acetic acid.

3,3'-Spirobi(3-selenaphthalide) (II). Hydrogen peroxide (30 %), 0.6 g (0.0053 mol), was added dropwise with cooling and stirring to a suspension of 1.6 g (0.005 mol) unpurified 2,2'-dicarboxy-diphenyl selenide (I) in 20 ml of acetic acid. After the addition the temperature of the reaction mixture was allowed to rise to room temperature standing over night. The product was filtered and dried. Yield 1.4 g (88 %). M.p. 310–322°C. The product was purified by dissolving in warm diluted sodium hydroxide and slowly aci-

difying the warm solution with diluted sulphuric acid. (Found: Se 24.65. C₁₄H₈O₄Se requires: Se 24.73).

Crystal data. The compound crystallizes in the monoclinic spacegroup *C2/c* with 4 molecules in the unit cell. The cell dimensions are $a = 13.646(2)$, $b = 8.639(3)$, $c = 10.034(2)$ Å, and $\beta = 96.64(2)^\circ$; $D_c = 1.804$ g cm⁻³ and $D_m = 1.803$ g cm⁻³. Intensity data were collected on a Picker FACS I automatic diffractometer using the Vanderbilt disc oriented diffractometer system by Dr. P. G. Lenhert. The reflexions were measured by step scanning using 8 steps of 2 sec with a step size of 0.3°. 891 intensities recorded were more than 2 σ above background and used in the calculations. The structure was solved by the heavy atom method and refined by full matrix least-squares treatment. The final *R*-value is 0.043. Full details of the X-ray investigation will be published elsewhere.

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