

The Structure of 6a-Selenathiophthene

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The results from an X-ray structure study of 6a-thiathiophthene (I) based on film data have been reported.¹ A reinvestigation of I by diffractometer methods has recently been carried out,² and molecular dimensions from that study are given in Fig. 1. Furthermore, in Fig. 1, bond lengths

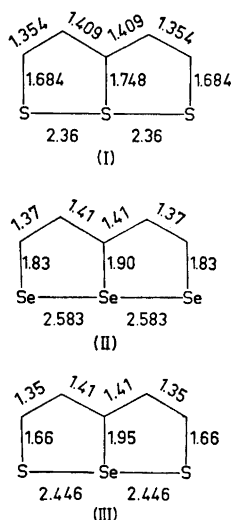


Fig. 1. Comparison of bond lengths (Å) in 6a-selenathiophthene (III) with bond lengths in 6a-thiathiophthene (I) and 6a-selenaselenophthene (II).

in 6a-selenaselenophthene (II)³ are given. The latter are averages of the lengths of corresponding bonds in the two halves of the molecule. There were no significant differences between the lengths of corresponding bonds in the two halves.³

We have now carried out a structure study of 6a-selenathiophthene (III), and the molecular dimensions of III, *cf.* Fig. 1, may be compared with those of I and II.

The selenium-sulphur bonds in III, 2.446(5) Å, are 10.1 % longer than the sum of the covalent radii of selenium and sulphur, 2.22 Å,^{4,5} the selenium-selenium bonds in II, 2.583(3) Å, are 10.7 % longer than a selenium-selenium single bond, 2.34 Å,⁴ and the sulphur-sulphur bonds in I, 2.363(1) Å, are 12.4 % longer than the sulphur-sulphur single bond, 2.10 Å, in a *cis* planar disulphide group.⁵ It should be mentioned that the bond lengths given for 6a-thiathiophthene (I) have been corrected for rigid-body libration, while those given for 6a-selenaselenophthene (II) and 6a-selenathiophthene (III) have not been corrected. The thermal parameters of the carbon atoms in II and III are inaccurate, and rigid-body analyses are therefore hardly warranted. The uncorrected S-S bond length in I, 2.350 Å, is 11.8 % longer than an S-S single bond.

The length of the sulphur-carbon bonds in III, 1.66(2) Å, agrees with the length of the terminal S-C bonds in I, 1.684(3) Å, and the length of the selenium-carbon bond in III, 1.95(2) Å, is not significantly different from the length of the central Se-C bond in II, 1.90(2) Å. The lengths of the central and terminal C-C bonds in the three structures agree closely; they are 1.354(3) and 1.409(3) Å in I, 1.37(3) and 1.41(3) Å in II, and 1.35(3) and 1.41(3) in III.

The S-S-S angle in I is 177.93(8)°, the Se-Se-Se angle in II is 173.8(3)°, and the S-Se-S angle in III is 169.6(5)°.

A sample of 6a-selenathiophthene was generously supplied by Reid.⁶ The crystals are red and belong to the orthorhombic space group *Pnma*. The unit cell dimensions were determined from high order reflections on *hk0* and *0kl* Weissberg photographs where sodium chloride powder lines had been superimposed for reference ($a_{\text{NaCl}} = 5.6396$ Å). A least squares procedure on 30 measured 2θ -values gave $a = 7.896(8)$ Å, $b = 15.990(5)$ Å, and $c = 5.454(5)$ Å. There are four molecules per unit cell; density, calc. 1.997 g/cm³, found 2.02 g/cm³. The crystals are isomorphous with those of 6a-thiathiophthene.^{1,2}

The structure analysis is based on photographic data collected by the equi-inclination Weissberg technique (CuK α radiation). The intensities of the 619 observed *0kl*-*6kl* reflections were estimated visually. Lp corrections, corrections for extended spots on upper layer Weissberg films, and absorption correc-

tions were applied. The absorption corrections were carried out according to a procedure by Coppens, Leiserowitz and Rabinovich.⁷ The dimensions of the intensity crystal were $0.39 \times 0.04 \times 0.04$ mm in the three axial directions. A grid of $32 \times 4 \times 4$ points was used.

The atomic parameters were refined by a full-matrix least squares procedure, and the final *R* factor is 0.12. Anisotropic temperature factors were applied to selenium, sulphur, and carbon, and isotropic to hydrogen. The hydrogen positions were not refined.

Final atomic coordinates from the least squares refinement are listed in Table 1.

Table 1. Atomic coordinates in fractions of corresponding cell edges. The standard deviations given in parentheses refer to the last digits of the respective values.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Se	0.05316(28)	0.25000	0.2248(3)
S	0.06777(72)	0.09766(32)	0.1904(12)
C(1)	0.1850(23)	0.0993(12)	-0.0622(42)
C(2)	0.2364(26)	0.1715(12)	-0.1661(32)
C(3)	0.1956(26)	0.2500	-0.0661(39)
H(1)	0.2096	0.0499	-0.1267
H(2)	0.2920	0.1746	-0.2996

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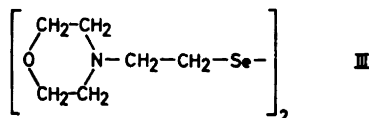
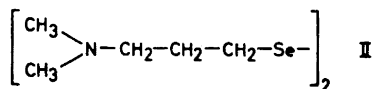
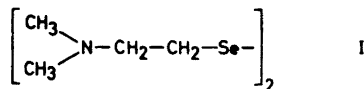
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Diseleno Derivatives of Some Amines

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The diselenides I–III and some related compounds have been prepared in order to test their activity in preventing dietary liver necrosis in rats (factor-3-effect).¹ This effect is found in various organoselenium compounds and many diselenides show good potency.^{2,3} Compounds with tertiary amino groups like those in I–III are often



pharmacologically active and it was therefore of interest to study the influence of such amino groups upon the factor-3-activity of diselenides. It turned out, however, that the potency of the compounds was remarkably low, even compared to that of inorganic selenites.

Synthesis in the ordinary way from chlorosubstituted amines and alkali diselenide solutions gave rather impure products, obviously contaminated with mono- and/or triselenides. Such complications have been observed in other cases. In addition, decomposition during the purification is not uncommon and even rearrangements have been reported.⁴ It seems that the amino group makes the diselenide less stable. Attempts to oxidise the amines to aminoseleninic acids led to cleavage of the C–Se bond, yielding selenous acid.