The Molecular Structure of 4,4'-Spirobi(4-selena-4-butanolide)

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The synthesis of 4,4'-spirobi(4-selena-4-butanolide) (I) has been published earlier,[1] but to obtain unequivocal proof for the structure of (I) we have now studied it by X-ray crystallography.

Different types of tetracoordinate selenium and sulfur compounds containing selenium-oxygen and sulfur-oxygen bonds respectively, have recently been studied,[2-7] and the title compound is another contribution to the study of this type of molecule.

The final atomic coordinates for (I) are given in Table 1. Bond lengths and angles are shown in Fig. 1 which also shows the atomic numbering. The selenium atom is located on the 4-fold screw-axis and the two halves of the molecule are related by 2-fold symmetry. The configuration around the selenium atom is a trigonal bipyramid (Fig. 2), with the two oxygen atoms at apical positions and the C(3)-carbons occupying two of the equatorial positions; the third one is considered to be occupied by the unshared pair of electrons.

The $O-Se-O$ angle is 172.4°, with the oxygens bending away from the lone pair of electrons. The same angle was observed in 3,3'-spirobi(3-selenaphtalide)[2,3] (SSP). The $C-Se-C$ angle is 101.5°, which agrees within the estimated standard devia-
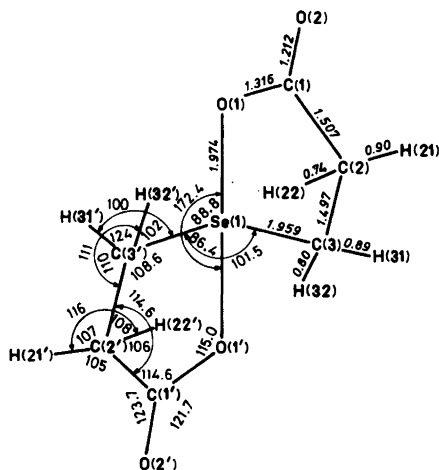

Fig. 1. Bond distances and angles. The estimated standard deviations are 0.003 – 0.006 Å for bonds involving non-hydrogen atoms and 0.04 – 0.05 Å for bonds involving hydrogens. The esd's for the angles are 0.1 – 0.3 and 3 – 5°, respectively.

tion with the one found in SSP (101.0°). The corresponding $C-S-C$ angle for the analogous spirocyclic sulfur compounds[5,7] is around 108° which is in agreement with the rule given by Bent[8] that the $C-Se-C$ angle should be smaller than the $C-S-C$ angle. It is also consistent with the statement given by Paul, Martin and Perozzi[6] that the more electro-negative the ligands at the apical positions the smaller the $C-Se-C$ angle since this angle is 106.5° for $(p-CH_3C_6H_4)_2SeCl_2$[9] and 108° for $(p-CH_3C_6H_4)_2SeBr_2$.[9]

The $Se(1)-C(3)$, $C(3)-C(2)$ and $C(1)-C(2)$ bonds are all longer than the corresponding bonds in SSP,

Table 1. Fractional atomic coordinates and thermal parameters with standard deviations. The anisotropic temperature factors are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se(1)	0.25(−)	0.75(−)	0.2857(1)	0.0261(4)	0.0296(4)	0.0399(5)	0(−)	0(−)	0.0007(2)
O(1)	0.0958(3)	0.9161(3)	0.2986(3)	0.0300(14)	0.0313(14)	0.0569(12)	0.0110(12)	0.0041(11)	0.0046(11)
O(2)	−0.1375(3)	0.9672(3)	0.3734(3)	0.0384(14)	0.0467(16)	0.0636(18)	0.0059(14)	0.0077(13)	0.0135(13)
C(1)	−0.0273(4)	0.8819(4)	0.3688(4)	0.0307(17)	0.0369(19)	0.0440(20)	0.0001(16)	−0.0010(16)	−0.0001(15)
C(2)	−0.0172(5)	0.7322(5)	0.4436(5)	0.0369(21)	0.0420(24)	0.0498(27)	0.0085(20)	0.0052(19)	−0.0010(8)
C(3)	0.1188(4)	0.6347(4)	0.4086(4)	0.0314(19)	0.0346(19)	0.0450(22)	0.0084(18)	−0.0034(18)	−0.0039(15)

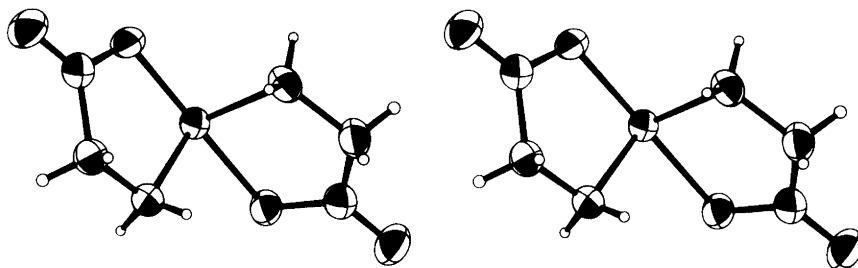|	x	y	z	U
H(21)	−0.102(6)	0.679(5)	0.421(4)	0.047(12)
H(22)	−0.011(5)	0.753(6)	0.515(5)	0.037(14)
H(31)	0.089(4)	0.557(5)	0.356(4)	0.029(10)
H(32)	0.175(5)	0.625(5)	0.472(4)	0.033(11)

Fig. 2. A stereo view of the molecule.

since, in the latter compound, the counterpart of C(2) – C(3) belongs also to a benzene ring. All other bonds are equal within their standard deviations.

The small bond angle differences between SSP and the title compound (I) are due to the influence of the benzene ring in SSP, where the valence angles in the five-membered ring are rather distorted. In the title compound the angles are also somewhat distorted to get a ring closure. The valence angle at O(1) – C(1) – C(2) (sp^2-carbon atom) has decreased to 114.6° and the C(1) – C(2) – C(3) angle (sp^3-carbon atom) has increased to the same value.

The two symmetrical halves of the molecule are planar within 0.07 Å and form a diheral angle of 127.1°. The corresponding angle between the planes of the benzene rings in SSP is 102.7°.

The molecular packing is shown in Fig. 3. There is a Se – O contact of 3.09 Å, which is shorter than the sum of the van der Waals radii (3.4 Å).[10] Even shorter non-bonding distances have, however, been observed (2.91 Å).[11] All other contacts are normal van der Waals distances.

Experimental. The melting points are uncorrected.

4,4′-Spirobi(4-selena-4-butanolide) (I). A solution of 1.12 g (0.005 mol) of 3,3′-seleno-dipropionic acid (analytically pure)[12] in 250 ml acetic acid was prepared. The solution was cooled on ice and 0.61 g (0.0055 mol) of 30.7 % hydrogen peroxide was added dropwise with stirring. The reaction mixture was
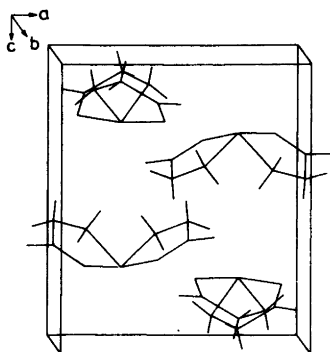

Fig. 3. The molecular packing seen along the *b*-axis.

left at room temperature and after 2 h 250 ml of light petroleum was added. The mixture was left in the refrigerator for a few days. Yield: 0.9 g of well-developed crystals. M.p. 152.5 – 153.5 °C (160 – 151 °C[1]). The difference in the melting points may be due to different crystal forms, as the IR-spectra were identical. (Found: C 32.32; H 3.62; Se 34.79. Calc. for $C_6H_8O_4Se$: C 32.30; H 3.62; Se 35.39).

Crystal data. The compound crystallizes in the tetragonal space group $P4_2/n$ (86) with 4 molecules in the unit cell. Cell dimensions are $a = 8.690(5)$ Å, $c = 10.034(7)$ Å. The cell volume is 761.5 Å^3, the molecular weight 223.10 and the calculated density 1.95 g cm^{-1}. The crystal dimensions were 0.18 × 0.20 × 0.20 mm ($\mu = 72.29$ cm^{-1}). Intensity data were recorded on a PW 1100 diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). Reflexions with $\theta < 67°$ were measured at a scan rate of 0.04 °/$_s$ and with a scan width of 1.8°. Stationary background counts were taken on both sides of the peak. A total of 676 unique reflexions were measured. 55 of these were less than 2.5 $\sigma(I)$ and considered as unobserved. Corrections were made for the Lorentz and polarization factors and for absorption and isotropic extinction.

The structure was solved by heavy atom methods. Full matrix least-squares refinement was applied using anisotropic temperature factors for the heavier atoms and isotropic temperature factors for the hydrogen atoms. The structure refined to a final *R*-value of 0.033.* The shift/standard deviation was then less than 0.01 for all parameters. The weighting scheme used during the final stage of the refinement was $w = 7.55(\sigma^2(F) + 0.00014\ F^2)$.

Scattering factors for Se were taken from International Tables, Vol. IV,[13] for C and O from Cromer and Mann[14] and for H from Stewart, Davidson and Simpson.[15] All calculations were performed on an IBM 360/75 computer using the SHELX program system[16] except the Lp and absorption correction which were made by DATAPU.[17]

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* List of structure factor tables may be obtained from the Dept. of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden.

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