The Crystal Structure of Selenium Dibenzenesulphinate

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The crystal structure of sulphur dibenzenesulphinate $S(SO_2C_6H_5)_2$ (bisphenylsulphonyl sulphide) was determined by Mathieson and Robertson in 1949[1]. Foss has since then prepared the analogous selenium compound [2], $Se(SO_2C_6H_5)_2$, and has also shown that the two compounds are isomorphous [3]. We thought it worth while to determine the exact atomic positions also in the selenium compound, as relatively little is known about the stereochemistry of substances of this type. Thus no direct determinations of the covalent bond distance Se—S and the angle S—Se—S have been reported in the literature. The need for more structural information on selenium compounds has recently been stressed [4].

THE STRUCTURE DETERMINATION

The unit cell and space group was determined by Foss [3], and we have confirmed his results. The crystals are monoclinic, elongated along b, with $\{10\bar{1}\}$ predominant, and with the following cell dimensions: $a = 16.14$ Å, $b = 5.60$ Å, $c = 15.84$ Å, and $\beta = 112°$ (all $\pm$ 0.5 %). Cu$K\alpha$ radiation ($\lambda = 1.542$ Å) was used throughout the investigation.

The systematic absences in the X-ray reflexions are consistent with the space groups $A2/a$ and Aa. The structure determination of the isomorphous compound (cell dimensions $a = 15.88$ Å, $b = 5.52$ Å, $c = 15.88$ Å, and $\beta = 112.9°$) shows that the former ($A2/a$) is the correct one. The density was found to be 1.79_5 g cm^{-3} (flotation method), corresponding to four (calc. 3.97) molecules in the unit cell. The selenium atoms occupy consequently fourfold positions, and the molecule must have a twofold axis of symmetry. The origin and the axes are chosen as in Mathieson and Robertson's paper.

For the structure determination Weissenberg diagrams were taken about the b and c axes, using crystals of cross-sections about 0.1×0.1 mm. To correlate the strong and weak reflexions, three diagrams were taken of each zone, and intensities were obtained over a range of about 6 500 to 3. The intensities were estimated visually and corrected for the Lorentz polarization factor. They were converted to an approximately absolute scale later by comparison of observed and calculated structure factors.

The signs of most of the structure factors were derived from the data given on the isomorphous compound [1], making allowance for the effect of replacing
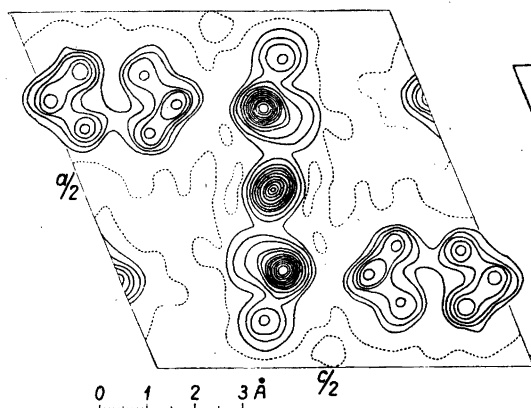
Fig. 1. Fourier projection in direction of b axis. Contours at intervals of 5 eÅ⁻² for Se, 2 eÅ⁻² for S and O, and 1 eÅ⁻² for C. The first contour line corresponds to 3 eÅ⁻². The one-electron line is dotted.
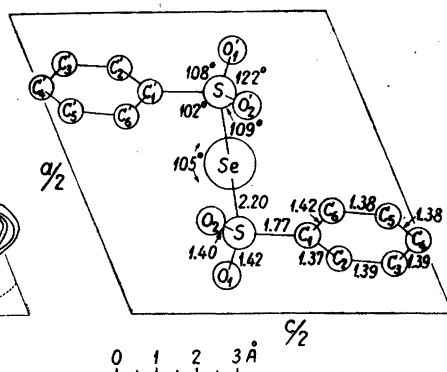
Fig. 2. Bond lengths and bond angles in Se (SO₂C₆H₅)₂.

the central sulphur atom by selenium. The electron density maps corresponding to projections along the b and c axes could now be calculated, and from these more accurate atomic positions were derived. After a number of refinements, the final electron density maps given in Figs. 1 and 3 were obtained. In the Fourier projection along the b axis (Fig. 1) all the atoms are well resolved with the exception of O_2, and fairly reliable values of the x and z coordinates of the atoms can be derived directly from the map. The interpretation of Fig. 1 is obvious from a comparison with Fig. 2, which shows the corresponding projection of the molecule. In the c projection (Fig. 3) bad overlapping occurs, and only very approximate y coordinates can therefore be obtained, except for the selenium and sulphur atoms. The former is well resolved, and the y coordinate of the latter could be determined by applying a graphical
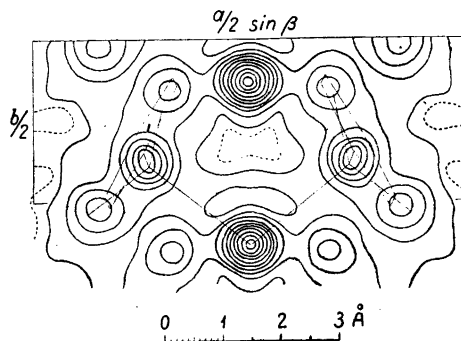

Fig. 3. Fourier projection in direction of c axis. Contours at intervals of 5 eÅ⁻², starting at 3 eÅ⁻². The one-electron line is dotted.

correction for the óverlapping effect from the atoms C_1 and C_4. In Table 1 the atomic coordinates are given.

Table 1. Atomic coordinates as fractions of the corresponding cell edge.

Atom	x	y	z
Se	0.250	0.871	0.250
S	0.134	0.110	0.219
O_1	0.062	0.959	0.167
O_2	0.153	0.323	0.183
C_1	0.130	0.158	0.327
C_2	0.090	0.980	0.358
C_3	0.083	0.008	0.443
C_4	0.120	0.209	0.495
C_5	0.162	0.388	0.466
C_6	0.168	0.360	0.382

The agreement between observed and calculated structure factors is satisfactory, the reliability factor $R = \Sigma \| F_{obs.} \| - \| F_{calc.} \| / \| \Sigma F_{obs.} \|$ being 0.17 for both projections. For the non-observed reflexions half the lowest observable value of F_{obs} was used in the calculation of R. The contribution from the hydrogen atoms was neglected. The atomic scattering curves of the *International Tables* were employed, with a temperature factor of $B = 3.7$ Å². A list of observed and calculated structure factors can be supplied by the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

From the coordinates in Table 1 the bond lengths and bond angles given in Table 2 were calculated. They are also shown in Fig. 2. For comparison, the values reported for the sulphur compound are included in the table.

Table 2. Bond lengths (in Å units) and bond angles.

Bond	$Se(SO_2C_6H_5)_2$	$S(SO_2C_6H_5)_2$	
Se—S	2.20	2.07	(S—S)
S—O_1	1.42	1.41	
S—O_2	1.40	1.41	
S—C_1	1.77	1.76	
C—C	1.37—1.42	1.39	(average)

Bond angles.

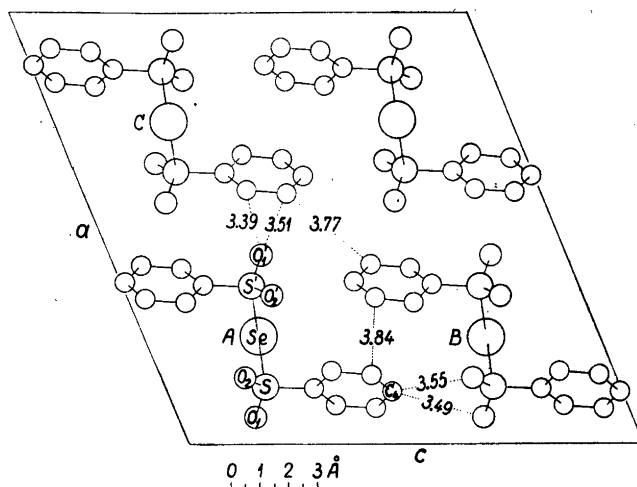| $Se(SO_2C_6H_5)_2$		$S(SO_2C_6H_5)_2$	
S—Se—S'	105.1°	S_2—S_1—S_2'	106.5°
Se—S—O_1	102°	S_1—S_2—O_1	104.2°
Se—S—O_2	109°	S_1—S_2—O_2	111.9°
Se—S—C_1	102°	S_1—S_2—C_1	101.7°
O_1—S—O_2	122°	O_1—S_2—O_2	117.2°
O_1—S—C_1	108°	O_1—S_2—C_1	107.5°
O_2—S—C_1	111°	O_2—S_2—C_1	115.9°

Fig. 4. The b *projection of the structure, showing the packing of the molecules and some of the intermolecular distances.*

The non-bonded intramolecular distance S—S′ is 3.49 Å, whereas the corresponding distance in the sulphur compound is 3.32 Å.

It is believed that the error in the Se—S distance is less than 0.03 Å and in the S—Se—S′ angle less than about 2°. The errors in the other distances and angles may be considerably greater due to the overlapping of atoms and the distorting effect of the heavy atoms, but it is seen that the values in general agree well with those reported for the sulphur compound.

The Se—S distance is found to be 2.20 Å, corresponding closely to the sum of the covalent radii for selenium and sulphur (1.17 Å and 1.04 Å respectively) derived from crystal structure investigations of the elements. The angle S—Se—S′ is slightly smaller than the corresponding angle S—S—S in the isomorphous compound, the values being 105° and 106.5°. As selenium and sulphur are supposed to form p-bonds, the ideal bond angle would be 90°. It is therefore to be expected that the angle is somewhat smaller in the selenium compound, as the repulsive forces between the non-bonded sulphur atoms are probably weaker in this case.

Table 3. Intermolecular distances (in Å units).

	$Se(SO_2C_6H_5)_2$	$S(SO_2C_6H_5)_2$
$C_4(A) - O_1(B)$	3.49	3.43
$C_4(A) - O_2(B)$	3.55	3.43
$C_3'(B) - C_3(C)$	3.77	3.7
$O_1'(A) - C_2(C)$	3.39	3.31
$O_1'(A) - C_3(C)$	3.51	3.58

The shortest intermolecular distances are given in Table 3 and Fig. 4. They are in general greater than those reported for the sulphur compound, where certain intermolecular attractions are indicated [1], and correspond roughly to normal van der Waals separations. The packing of the molecules is shown in Fig. 4.

SUMMARY

The crystal structure of selenium dibenzenesulphinate is determined with the aid of the known structure of the isomorphous sulphur compound. The Se—S bond distance is found to be 2.20 ± 0.03 Å and the S—Se—S' angle to be $105° \pm 2°$.

REFERENCES

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3. Foss, O. *Acta Chem. Scand.* **6** (1952) 508.
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