sired compound. Combustion analysis by the method of McCullough, Campbell and Krilanovich[9] showed a selenium content of 72.6% (calculated, 73.8). This low value would be expected to result from the method used, due to the high volatility of the compound. Appreciable amounts of diselenane vapor were carried out of the burner by the oxygen stream between the time that the flame was lit and the absorber and chimney were brought into place. A semiquantitative bromination of a 10.8-mg. sample of the compound showed that 1.91 moles of bromine was absorbed for each mole of diselenane (theor. 2.00). The resulting product, presumably 1,1,4,4-diselenane tetrabromide, melted at 149°.

The density of solid 1,4-diselenane was found by flotation in mixtures of bromoform and ethylene bromide to be 2.2. The volume of the unit cell, as determined by Marsh and McCullough,[6] was 313 Å.[3] with two molecules of diselenane per unit cell. The molecular weight of the compound as determined from these data is 206 (calcd. for $C_4H_8Se_2$, 214).

Acknowledgments.—It is a pleasure to acknowledge the assistance of Professors Theodore A. Geissman and Saul Winstein, whose suggestions proved extremely valuable in carrying out this synthesis.

Summary

1,4-Diselenane has been synthesized in 0.3% yield from β,β'-dichlorodiethyl selenide and lithium selenide in anhydrous acetone. The compound has been identified by selenium analysis, semi-quantitative bromination, and by X-ray crystallographic determination of its molecular weight and structure.

LOS ANGELES 24, CALIF.

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[9] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Ind. Eng. Chem., Anal. Ed.*, **18**, 638 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Crystal Structure of 1,4-Diselenane[1]

BY RICHARD E. MARSH AND JAMES D. MCCULLOUGH

One of the projects under investigation in this Laboratory has as its objective the synthesis of stereoisomeric cyclic selenoxides. As an intermediate in the attempted synthesis of diselenane-1,4-dioxide, Gould and McCullough[2] isolated a product which, from the method of preparation, was expected to be 1,4-diselenane. As part of the structure proof of this compound, it was thought advisable to take X-ray diffraction photographs in order to determine the size of the unit cell; this, in conjunction with the measured density of the crystals, would give the molecular weight (or a sub-multiple thereof) of the compound. Upon examination of the X-ray diffraction photographs, it was found that the space-group was advantageous for a complete structure determination. This accordingly, was undertaken.

Preparation of the Crystals.—1,4-Diselenane is a white crystalline compound with a relatively high vapor pressure at room temperature, and with a melting point of 113°. The crystals used for the diffraction photographs were prepared by slow sublimation in a small, sealed glass tube at about 40°. The crystals, which formed on the cooler end of the tube, were rather small, colorless, and lath-shaped, with elongation in the b direction. The principal faces were of the form (101). Due to the appreciable vapor pressure of the compound at room temperature, the crystals were wedged into small, thin-walled glass capillaries, which were then sealed off and mounted on a goniometer head. Two crystals of appropriate size and shape (approximately 0.05 × 0.1 × 0.2 mm.) were used, one with the b axis parallel to the axis of the capillary and the other with the b axis perpendicular to the axis of the capillary. By suitable mounting of the capillary on the goniometer head, it was possible to obtain photographs about all three monoclinic axes, as well as about the $(10\bar{1})$ zone.

X-Ray Diffraction Data.—Rotation and Weissenberg photographs about the three crystallographic axes, as well as about one oblique axis, were prepared using unfiltered copper radiation and exposure times of about 35 hours. A double film technique was used, the intensity factor for the two films being about 3. The intensities of the diffraction spots were estimated visually with the aid of a calibrated comparison strip and were corrected for Lorentz and polarization factors in the usual way. Due to the small size and fairly regular shape of the crystals, no correction for absorption was made.

Measurements made on the photographs showed a monoclinic space-group, with the following unit cell dimensions (using $\mathrm{CuK}_\alpha = 1.5418$ Å.): $a = 6.97$ Å., $b = 5.62$ Å., $c = 8.01$ Å. (all ± 0.02 Å.), $\beta = 93.6 \pm 0.1°$. Assuming two molecules of diselenane in the unit cell, the calculated density 2.27 g./cc. is obtained; the observed density from flotation measurements is 2.2 g./cc.

Determination of the Structure.—The systematic absences are $h0l$ with $(h + l)$ odd and $0k0$ with k odd; these absences establish uniquely the space-group $C_{2h}^5 - P2_1/n$. Since this space-group has four-fold general positions in the unit cell, the presence of only two molecules in the unit requires that the molecules be centro-symmetric. Assuming the compound to be 1,4-diselenane, $C_4H_8Se_2$, the asymmetric unit will contain one selenium atom and two carbon atoms. The positions of the four hydrogen atoms cannot be determined in this case because of their relatively low scattering power compared to that of the heavy

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[1] Based on work performed under Contract N6onr-275 between the Office of Naval Research and the University of California, Los Angeles. For detailed material supplementary to this article order Document 3032 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] E. S. Gould and J. D. McCullough, THIS JOURNAL, **73**, 1105 (1951).

selenium atom. Since the selenium atom is by far the heaviest atom, it will have most of the diffracting power, and a knowledge of its position will permit a determination of the phases of essentially all of the structure factors.

Approximate values of the *x*, *y*, and *z* parameters of the selenium atom were determined by an examination of zero-layer Weissenberg reflections of the type *h*00, 0*k*0, and 00*l*, respectively. By use of these approximate parameters, the phases of the structure factors of all of the zero-layer reflections were determined. Since the unit cell is centro-symmetric, this requires only the determination of the sign of the structure factor. Fourier projections about the three crystallographic axes were then calculated, using Patterson-Tunell strips[3] for carrying out the summations. The resulting projections were used to determine more accurate parameters for the selenium atom and also to locate the carbon atoms. By use of the revised selenium parameters and by also taking into account the contribution from the carbon atoms, the signs of the zero-layer structure factors were recalculated and final Fourier projections were carried out. It is interesting to note that the inclusion of the carbon contributions to the structure factors necessitated the reversal of only one sign out of a total of 136 observed reflections.

The final Fourier projections are shown in Figs. 1, 2 and 3. The contours are drawn at arbitrary intervals, with the contour lines about the selenium atom occurring at four times the interval of those about the carbon atoms. F(000) is not included in the summations.

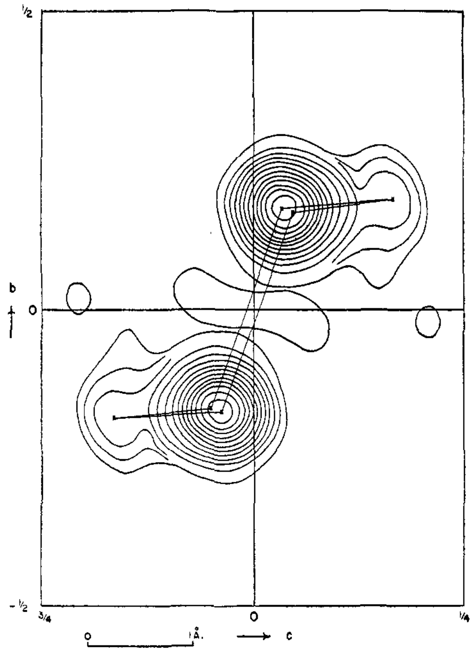

Fig. 1.—1,4-Diselenane—Fourier projection on (100).

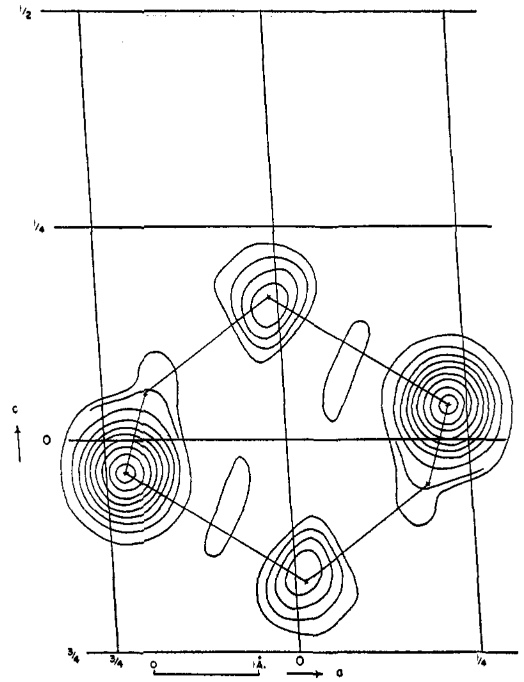

Fig. 2.—1,4-Diselenane—Fourier projection on (010).

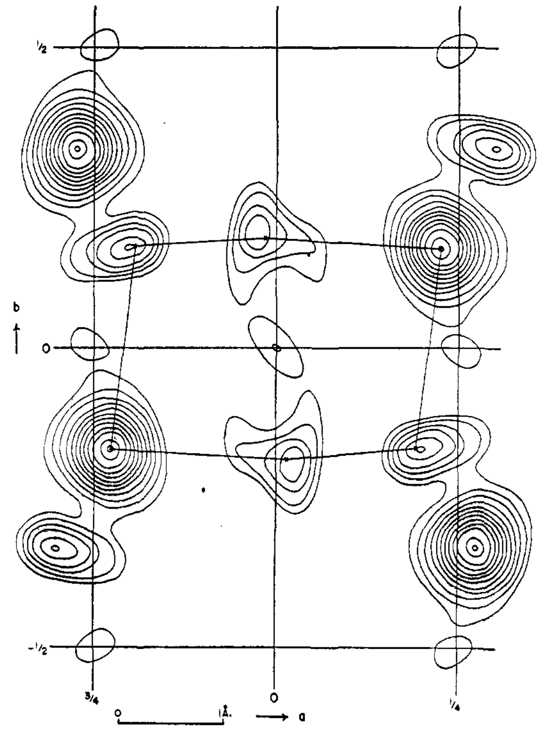

Fig. 3.—1,4-Diselenane—Fourier projection on (001).

Since one carbon atom (C_2) is obscured by the selenium atom in the projections on (010) and (100), Weissenberg photographs about the $10\bar{1}$ zone were also prepared, and a Fourier projection on the $10\bar{1}$ face was calculated. This projection is shown in Fig. 4. It shows good resolution of C_2, but in this case C_1 is partially obscured by the selenium atom.

For the final parameters of the atoms, values were used which gave the best over-all agreement with the four projections. Since only 28 reflections of the type *hkh* were observed, the projection on ($10\bar{1}$) was given less weight than the other projections. The final parameters are given in Table I. The probable errors are estimated to be 0.001

[3] A. L. Patterson and G. Tunell, *Am. Min.*, **27**, 655 (1942).

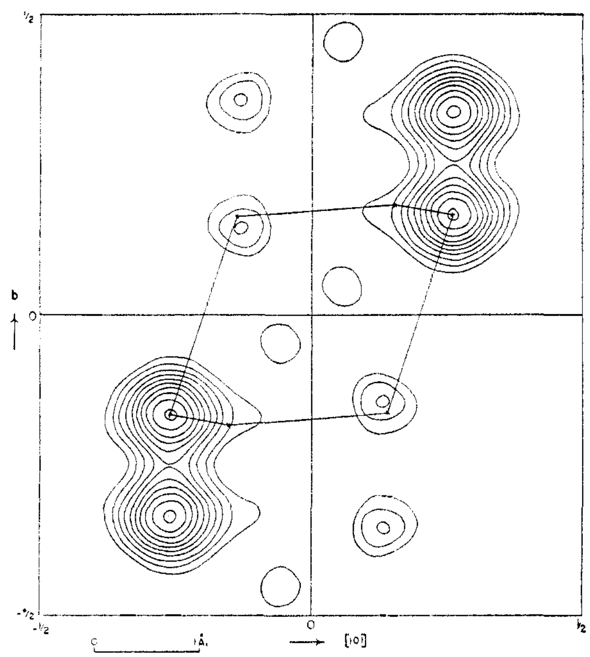

Fig. 4.—1,4-Diselenane—Fourier projection on (101).

for the selenium parameters and 0.004 for the carbon parameters. Positions corresponding to these parameters are indicated by means of crosses on the projections.

TABLE I

PARAMETER VALUES FOR 1,4-DISELENANE

	Se	C_1	C_2
x	0.225	0.987	0.192
y	.167	.183	.835
z	.038	.167	.947

The final parameters were used to calculate structure factors for zero-layer reflections about the four axes that were photographed. In order to obtain satisfactory agreement with observed intensities of reflections at large angles, it was necessary to apply an empirical temperature correction. This correction is of the form

$$F_{\text{cal.}} = K_f F(e^{-1.35 \sin^2\theta})$$

where F is the sum of the contributions from the four selenium atoms and eight carbon atoms in the unit cell, and K_f is a film constant. A comparison of $F_{\text{cal.}}$ and $F_{\text{obs.}}$ for all reflections used in the structure determination leads to a value of 0.123 for the correlation factor R,

$$\left| \frac{\sum^{N} |F_{\text{obs.}}| - |F_{\text{cal.}}|}{\sum^{N} |F_{\text{obs.}}|} \right|$$

for the 164 observed reflections. This correlation factor is nearly constant for reflections about all four axes, being 0.130, 0.129, 0.099 and 0.123 for photographs about the a, b, c, and $(10\bar{1})$ axes, respectively.

Discussion of the Results.—Since the 1,4-diselenane molecule must possess a center of symmetry in order to satisfy space-group requirements, it was apparent at the start that the molecule must exist in the chair rather than the boat form. This would also be predicted from a calculation of bond distances. Using Pauling's normal single-bond covalent radii[4] and tetrahedral bond angles for the selenium and carbon atoms, the selenium atoms in the chair form would be separated by 3.4 Å., and by 3.1 Å. in the boat form; this compares with a distance of 4.0 Å. calculated from Pauling's van der Waals radii.[5] One would thus expect the chair form to be the more stable of the two.

The bond distances and angles calculated from the observed parameters are given in Table II.

TABLE II

BOND DISTANCES AND BOND ANGLES IN 1,4-DISELENANE

	Distances, Å.		Angles
Se-C_1	2.01 ± 0.03	C_1-Se-C_2	98.6 ± 2.0°
Se-C_2	2.01 ± 0.03	Se-C_1-C_2	111.4 ± 1.0°
C_1-C_2	1.50 ± 0.05	Se-C_2-C_1	110.8 ± 1.0°
Se-Se	3.67 ± 0.01 (non-bonded)		

The observed Se-C bonded separation of 2.01 Å. is unexpectedly long, being 0.07 Å. longer than the sum of Pauling's single-bond covalent radii for selenium (1.17) and carbon (0.77). The only other observed Se-C bonded distances appearing in the literature are 1.96 Å. in selenanthrene[6] and 1.94 Å. in the di-*p*-tolylselenium dihalides.[7] In both of these cases the carbon atoms bonded to selenium are involved in aromatic ring systems so that the bond distances may not be truly representative of a normal, covalent Se–C single-bond. The discrepancy between the observed distance in 1,4-diselenane and the sum of the accepted radii is definitely beyond the experimental error of the present study and accordingly appears to be real. Further studies of aliphatic organoselenium compounds are to be desired in order to clarify this point.

Although the observed C–C bond distance of 1.50 Å. is somewhat short, the experimental error in this case may be large so that there is not necessarily anything unusual here. The C–Se–C and Se–C–C bond angles are in almost exact agreement with the corresponding angles in one of the structures (chair form) proposed for 1,4-dithiane as a result of an electron diffraction study of that substance.[8] The second structure proposed as a possibility for 1,4-dithiane vapor possesses the molecular symmetry D_2-222 and is inconsistent with the centro-symmetric molecular structure required by the space-group of crystalline 1,4-diselenane.

The packing of the molecules within the unit cell, as shown in Fig. 5, is essentially a body-centered arrangement. The packing is determined by selenium-carbon or selenium-hydrogen contact, each selenium atom being surrounded by three carbon atoms at distances of 3.68, 4.05 and 4.07 Å., respectively. Consideration of a model of the structure shows that the shortest selenium–carbon distance is in such a direction that there is no hydrogen atom between the two; while the longer

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(4) L. Pauling, "Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., p. 164.

(5) Ref. 4, p. 189.

(6) R. G. Wood and G. Williams, *Nature*, **150**, 321 (1942).

(7) J. D. McCullough and R. E. Marsh, *Acta Cryst.*, **3**, 41 (1950).

(8) O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947).

distances are approximately in the direction of hydrogen atoms attached to the carbon. The closest intermolecular selenium–selenium distance is 4.42 A.—well beyond the predicted van der Waals separation of 4.0 Å.

ADDED IN PROOF.—As a check on the unexpectedly long selenium–carbon distances, the observed and calculated structure factors of the type *hk*0, *h*0*l*, and 0*kl* were used in a least-squares refinement of parameters. The 135 observational equations, appropriately weighted, were reduced to 9 normal equations in the usual manner.[9] Since the normal equations were essentially diagonal, the solutions were straightforward. The resulting best parameters, together with the probable errors as evaluated from the residuals, were as follows

	Se	C_1	C_2
x	0.2234 ± 0.0004	0.986 ± 0.005	0.189 ± 0.004
y	.1675 ± .0009	.190 ± .009	.827 ± .010
z	.0383 ± .0003	.162 ± .004	.956 ± .003

The corresponding bond distances and angles are

Se-C_1	1.99 ± 0.04 Å.	C_1-Se-C_2	97.6 ± 3.5°
Se-C_2	2.04 ± .06 Å.	Se-C_1-C_2	108.5 ± 3.0°
C_1-C_2	1.54 ± .04 Å.	Se-C_2-C_1	107.8 ± 4.0°
Se-Se	3.66 ± .02 Å.		

Since in only one case (the *z* parameter of C_2) was the shift in atomic parameter as indicated by the least-squares treatment significantly greater than the probable error in that parameter, it is not felt that the parameters obtained from the Fourier analysis should be revised. However, the least-squares treatment has resulted in a confirmation of the various interatomic distances and angles in general, and in particular has lent further weight to the observation of the unpredictedly long selenium–carbon bond.

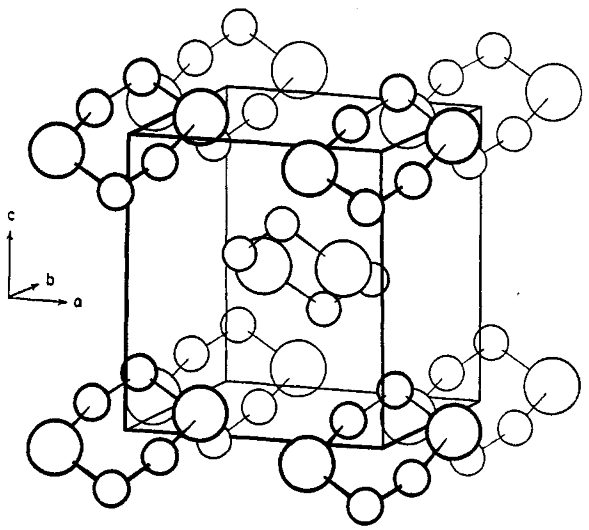

Fig. 5.—The structure of 1,4-diselenane.

Summary

The crystal structure of 1,4-diselenane ($C_4H_8Se_2$) has been determined by X-ray diffraction analysis. The crystals are monoclinic with space-group C_{2h}^5-$P2_1/n$ and with two molecules in the unit cell. The molecule is in the chair form, the only unanticipated feature being an unexpectedly long Se–C bonded separation of 2.01 ± 0.03 Å. which is 0.07 Å. longer than the sum of the single-bond covalent radii for selenium and carbon.

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[9] For example, see E. T. Whittaker and G. Robinson, "The Calculus of Observation," Blackie and Son, Ltd., London and Glasgow, 2nd edition, p. 209 ff.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Dissociation Constants of Some Monosubstituted Benzeneseleninic Acids. II. A New Synthesis of Diaryl Diselenides[1]

BY EDWIN S. GOULD AND JAMES D. MCCULLOUGH

In work described in an earlier communication,[2] thirteen benzeneseleninic acids were prepared and the logarithms of their ionization constants were found to be a linear function of Hammett's σ values.[3] In a continuation of this work, five additional seleninic acids have been synthesized and their dissociation constants measured. This extension is of interest chiefly because the preparation of certain of these acids involved two reactions which, to our knowledge, have not been described in the literature. We have found that treatment of an aryllithium compound with elementary selenium, followed by hydrolysis of the product, yields appreciable amounts of the corresponding selenophenol which may be easily oxidized by air to a symmetrically substituted diaryl diselenide

$$ArLi + Se = ArSeLi$$
$$ArSeLi + H_2O = ArSeH + Li^+OH^-$$
$$2ArSeH + (O) = ArSeSeAr + H_2O$$

The diaryl diselenides may be further oxidized, with or without purification, to the desired seleninic acids, using concentrated hydrogen peroxide. This series of steps was carried out using *p*-bromobiphenyl, *p*-bromodiphenyl ether and *m*-bromobiphenyl as starting materials for preparation of the corresponding aryllithium derivatives. The overall yields of the seleninic acids (based on the original aryl bromides) were, respectively, 24, 2 and 5%. Although these yields are poor, the method may possibly prove to be an improvement over that of Taboury[4] which would ordinarily be the method of choice in syntheses of this kind. In the latter reaction a selenophenol is prepared by treatment of an aryl Grignard reagent with selenium. For purposes of comparison, we attempted to apply Taboury's method to the synthesis of *p*-biphenylseleninic acid and to *p*-phenoxybenzeneseleninic acid. The yield of the biphenyl acid was 15%, while Taboury's method proved inapplicable to the synthesis of the phenoxy acid since *p*-bromodiphenyl ether would not form a Grignard reagent under the conditions used.

Although our synthesis has been applied to only

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[1] Based on research carried out under Task Order I of Contract N6onr-275, between the Office of Naval Research and the University of California, Los Angeles.

[2] J. D. McCullough and E. S. Gould, THIS JOURNAL, **71**, 674 (1949).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[4] M. F. Taboury, *Bull. soc. chim.*, **35**, 668 (1906).