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Studies on Molecules with Five-membered Rings

V. Calculation of Conformational Energies and Electron Diffraction Investigation of Gaseous Tetrahydroselenophene

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The energies calculated for various conformations of tetrahydroselenophene by the Westheimer-Hendrickson method [1–3] have been compared. Several sets of potential constants were tried. The energy minimum was always found for the conformation with C_2 symmetry; the conformation with C_s symmetry being between 3.4 and 3.9 kcal/mole less stable. These results indicate that the preference of the C_2 conformation is somewhat greater in tetrahydroselenophene than in tetrahydrothiophene.[3] Gaseous tetrahydroselenophene has also been studied by electron diffraction. In accordance with the energy calculations we found good agreement between experimental and theoretical data by assuming C_2 symmetry, while it was impossible to obtain satisfactory agreement for a C_s model. The following bond lengths, bond angles, and torsional angles were obtained for the C_2 model (standard deviations are given in parentheses): r(C—Se) = 1.975$_3$(0.003) Å, r(C—C) = 1.537$_6$(0.004) Å, r(C—H) = 1.116(0.012) Å, $\angle$CSeC = 89.1(0.5)°, $\angle$SeCC = 105.8(0.3)°, $\angle$CCC = 106.0(0.7)°, $\phi(Se_1-C_2) = 15.4(0.5)°$, $\phi(C_2-C_3) = -42.7(1.4)°$, and $\phi(C_3-C_4) = 56.9(1.7)°$.

The observed angles are in satisfactory agreement with those calculated by the Westheimer-Hendrickson method.

In our preceding investigations of five membered rings by calculation of conformational energies and by electron diffraction we found that tetrahydrofuran (THF) exhibits essentially free pseudo-rotation in the gas-phase.[1,2] The pseudo-rotation in tetrahydrothiophene (THT) is, however, restricted with a barrier of about 2 – 3 kcal/mole, the C_2 conformation being more stable than a conformation with C_s symmetry.[3] To improve our understanding of the role of hetero atoms in compounds of this type, a similar investigation of tetrahydroselenophene (THS) was undertaken. No structural investigation of this compound seems to have been reported previously.

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CALCULATION OF CONFORMATIONAL ENERGIES BY THE WESTHEIMER-HENDRICKSON METHOD

The energies of six conformations of THS ranging from C_2 symmetry (model I) to C_s symmetry (model VI) were calculated as reported in the papers on THF [1,2] and THT.[3]

The bond distances and the HCH angle applied in these calculations are given in Table 1. The values were taken from the electron diffraction investi-

Table 1. Conformational energies (in kcal/mole) and the corresponding angle parameters (in degrees) in THS.

Conformation		a	b	c	d
I (approx. C_2 symmetry)	∠CSeC	89.6	89.6	89.7	89.6
	∠SeCC	106.3	106.3	106.5	105.6
	$\phi(Se_1-C_2)$	14.0	14.1	13.7	14.9
	$\phi(Se_1-C_5)$	13.9	14.0	13.6	14.8
	E	3.92	4.78	4.97	3.33
II	∠CSeC	89.3	89.2	89.4	89.2
	∠SeCC	104.7	104.6	104.9	103.7
	$\phi(Se_1-C_2)$	25.7	26.0	25.2	27.5
	$\phi(Se_1-C_5)$	0.0[a]	0.0[a]	0.0[a]	0.0[a]
	E	4.50	5.29	5.51	3.92
III	∠CSeC	88.2	88.2	88.4	88.0
	∠SeCC	103.3	103.2	103.6	102.0
	$\phi(Se_1-C_2)$	34.4	34.6	33.5	36.9
	$\phi(Se_1-C_5)$	−13.0[a]	−13.0[a]	−12.5[a]	−14.0
	E	5.74	6.36	6.62	5.17
IV	∠CSeC	86.8	86.7	86.9	86.3
	∠SeCC	102.8	102.7	103.2	101.5
	$\phi(Se_1-C_2)$	39.6	39.9	38.8	42.6
	$\phi(Se_1-C_5)$	−24.0[a]	−24.0[a]	−24.0[a]	−26.0[a]
	E	6.88	7.33	7.74	6.27
V	∠CSeC	85.3	85.1	85.6	84.5
	∠SeCC	103.8	103.7	104.1	102.5
	$\phi(Se_1-C_2)$	41.5	42.1	40.4	44.9
	$\phi(Se_1-C_5)$	−33.5[a]	−34.0[a]	−32.5[a]	−36.5[a]
	E	7.67	8.00	8.40	6.98
VI[b]	∠CSeC	85.7	85.2	85.9	84.4
	∠SeCC	106.5	106.2	106.6	105.1
	$\phi(Se_1-C_2)$	36.2	37.8	35.5	41.1
	$\phi(Se_1-C_5)$	−36.2	−37.8	−35.5	−41.1
	E	7.84	8.16	8.58	7.15
$E(C_s)-E(C_2)$		3.92	3.38	3.61	3.82

[a] Not varied.

[b] Energy minimum with the restriction of C_s symmetry.

Table 1. Continued.

Structure parameters used in the calculations: $r(C-Se)=1.975$ Å, $r(C-C)=1.536$ Å, $r(C-H)=1.12$ Å, $\angle HCH=108.4°$
Below k is given in kcal mole^{-1} degree^{-2} and $V°$ in kcal mole^{-1}.

a: $\theta_{CSeC}=96°$, $\theta_{SeCC}°=\theta_{CCC}°=112°$
$k_{CSeC}=0.035$, $k_{SeCC}=k_{CCC}=0.0030$; $V_{CSe}°=1.01$, $V_{CC}°=2.9$

b: $\theta_{CSeC}°=96°$, $\theta_{SeCC}°=\theta_{CCC}°=112°$
$k_{CSeC}=0.035$, $k_{SeCC}=k_{CCC}=0.030$; $V_{CSe}°=1.50$, $V_{CC}°=2.9$

c: $\theta_{CSeC}°=96°$, $\theta_{SeCC}°=\theta_{CCC}°=112°$
$k_{CSeC}=0.041$, $k_{SeCC}=k_{CCC}=0.035$; $V_{CSe}°=1.40$, $V_{CC}°=2.9$

d: $\theta_{CSeC}°=95°$, $\theta_{SeCC}°=\theta_{CCC}°=110°$
$k_{CSeC}=0.035$, $k_{SeCC}=k_{CCC}=0.030$; $V_{CSe}°=1.40$, $V_{CC}°=2.9$

gation below. Since the calculations were carried out before all the refinements of the electron diffraction investigation were completed, the values used are not identical with the final results of the structure determination, but the differences are negligible.

The "normal" valence angles ($\theta°$)[1] are given in Table 1. The values for $\theta_{CCC}°$ and $\theta_{SeCC}°$ are the same as used previously for the corresponding angles in THF and THT, and $\theta_{CSeC}°$ was chosen to be close to the value found in dimethyl selenide (96.18°) by microwave spectroscopy.[4]

The barrier to internal rotation about a C–Se varies from compound to compound. Thus, a value of 1.50 kcal/mole was found in dimethyl selenide,[4] while the barrier is only 1.01 kcal/mole in methaneselenol.[5] Various values of $V_{CSe}°$ were therefore used. A barrier $V_{CC}°=2.9$ kcal/mole was assumed for rotation about the C–C bonds.

Siebert [6] reports a bending force constant $k_{CSeC}=0.041$ kcal mole^{-1}degree^{-2} for dimethyl selenide. For reasons discussed previously [1] a somewhat smaller value was adopted in most of the calculations. The other force constants were chosen as in the previous calculations.[1,3]

The van der Waals energy was included in the same way as discussed previously. The constants used were taken from Eliel *et al.*,[7] the values $r^*(Se)=2.0$ Å and $\varepsilon(Se\cdots H)=0.136$ kcal/mole being obtained by extrapolation. The differences in the van der Waals energy contribution for the considered models were small, as was found for THF and THT.

The conformation corresponding to minimum energy was found to have very nearly C_2 symmetry for all the sets of constants. In the models II–V one of the torsional angles was kept constant, and three angle parameters refined. The energy of model VI was calculated with the restriction of C_s symmetry.

The calculated energies and the corresponding bond and torsional angles are given in Table 1; the assumed constants are also given. The variation in the obtained angles with the choice of constants is fairly small. The difference in energy between conformation VI (C_s symmetry) and conformation I (approx. C_2 symmetry) is found to be in the range 3.38 to 3.92 kcal/mole, which is larger than the differences calculated for THT (1.96 to 3.03 kcal/mole) and THF (−0.73 to +1.25 kcal/mole).

ELECTRON DIFFRACTION INVESTIGATION

Experiment and data processing. The compound was prepared by the method devised by McCullough and Lefohn.[8] The raw product was purified by bromination followed by reduction of the resulting tetrahydroselenophene-dibromide.

The purity of the compound was established by IR spectroscopy and gas-liquid chromatography. $n_D^{20} = 1.5480$ (lit.[9] $n_D^{20} = 1.5476$).

Diffraction patterns were recorded on photographic plates using a Balzers electron diffraction apparatus.[10,11] The nozzle temperature was approximately 65°C. The electron wave length (0.0585 Å) determined from a zinc dioxide diffraction pattern, corresponds to an accelerating potential of about 42 kV. Pictures were recorded at two nozzle-to-plates distances, *i.e.* 50 cm and 25 cm giving intensity data in the s ranges 1.625 – 15.50 Å^{-1} and 4.50 – 30.50 Å^{-1}, respectively; in the final stages of the investigation these ranges were reduced to 1.625 – 15.0 Å^{-1} and 6.50 – 30.25 Å^{-1}. The intensity data were read off at intervals $\Delta s = 0.125$ Å^{-1} and $\Delta s = 0.25$ Å^{-1}. Four plates from each set were used in the investigation.

The data were processed in the same way as the data for THT.[3,12] The modified molecular intensities were calculated using the modification function [12]

$$s/(|f_C'| \cdot |f_{Se}'|)$$

The elastic scattering amplitudes were calculated by the partial wave method [12,13] using the Hartree-Fock potential [14] for C, the potential for bonded H,[15] and the potential computed by Lieberman *et al.* in the form given in Ref. 16 for Se. The inelastic scattering amplitudes were obtained from Tavard *et al.*[17] assuming that the values for bromine could be applied for selenium.

The agreement between the curves seemed satisfactory, and average intensity curves for each plate set were calculated (see Fig. 1). A composite intensity curve covering the s range 1.625 – 30.25 Å^{-1} was also calculated in the usual way.[12] The experimental radial distribution (RD) curve calculated by Fourier transformation of the composite intensity curve, is shown in Fig. 2.

The theoretical molecular intensities were calculated according to eqn. 10 of Ref. 12.

Structure analysis and refinement. In the RD curve shown in Fig. 2 the three inner peaks correspond to the C – H (near 1.11 Å), C – C (near 1.54 Å), and C – Se (near 1.97 Å) bond distances. The main contributions to the complex between 2.3 Å and 3.1 Å are from the non-bonded C···C and C···Se distances. The C···H and Se···H distances contribute between 2.2 and 4.0 Å.

Theoretical RD curves were calculated for the models I – VI using preliminary values for the bond distances and the HCH angles. The agreement with the experimental RD curve was quite good for model I (approx. C_2 symmetry), but became steadily worse in going from C_2 (model I) to C_s symmetry (model VI). Least-squares refinement of the structure was therefore carried out assuming C_2 symmetry. Further, we assumed equal length for the C – C bonds as well as for the C – H bonds. The HCH angles were also assumed equal. The planes through the CH_2 groups were taken perpendicular to the planes through XCC (X = Se or C), and were assumed to bisect the XCC angle.

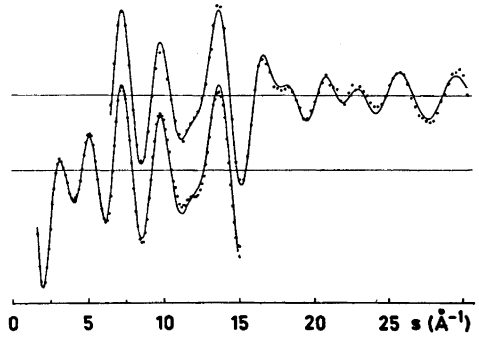

Fig. 1. Experimental (dotted) and theoretical intensity curves. The data corresponding to the two nozzle-to-plate distances are shown separately. The theoretical values have been calculated with the parameters in Table 3 assuming C_2 symmetry.

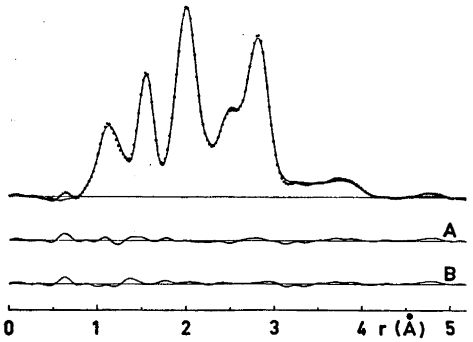

Fig. 2. The two upper curves show the experimental (dotted) and theoretical radial distribution curves. An artificial damping constant [12] $k=0.002$ Å^2 was applied. The theoretical curve corresponds to the parameters in Table 3. Curve A shows the differences between the experimental and theoretical values. Curve B illustrates in the same way the agreement obtained using the parameters in Table 2*a*. The theoretical curves were calculated for a C_2 model; reasonable agreement could not be obtained for a C_s model.

Various least-squares refinements were carried out in the same way as described for disilylmethane by Almenningen *et al.*[18] Some results obtained by using the composite intensity curve and a diagonal weight matrix are shown in Table 2, column *a*. The values in the columns *b* and *c* resulted from refinements on the data from the two plate sets simultaneously without combining them into one curve. Both diagonal weight matrices (column *b*) and weight matrices with off-diagonal elements different from zero [18,19] (column *c*) were applied. The latter matrices were of the form described in Ref. 19 with the constants (p_2 and p_3) given in the table.* The results in the various columns of Table 2 are in fairly good agreement compared to the corresponding standard deviations, though the shift in the C–C bond distance caused by the inclusion of off-diagonal elements different from zero in the weight matrix, is somewhat larger than usually found. The values given in parentheses are considerably larger in *c* than in *a* or *b*. These values should be denoted standard deviations only if the applied weight matrix is a sufficiently good approximation to the optimum weight matrix, which seems certainly not to be true for diagonal weight matrices.[18,19]

It might seem logical to give the values in Table 2*c* as our final results. However, our experience with least-squares refinements using weight matrices

* These constants were calculated from the moment matrix of the observations for this compound. The values are rather close to the constants found for intensity curves obtained with nozzle-to-plate distances of about 48 cm and 20 cm on the other Oslo apparatus.[18,19]

Table 2. Values for the most important parameters in tetrahydroselenophene obtained by least-squares refinements. The first set of results (*a*) corresponds to refinement on the composite experimental intensity curve obtained by combining the data from the two nozzle-to-plate distances.
The values in (*b*) and (*c*) were obtained by refining on the two data set simultaneously without combining them to one curve. Diagonal weight matrices were assumed in (*b*); the weight matrices used in (*c*) have been discussed previously.[18,19] ($p_2 = -0.64$, $p_3 = 0.143$ for the long nozzle-to-plate distance data, $p_2 = -0.64$, $p_3 = 0.150$ for the other data set).

	a		*b*		*c*	
	r (Å)	*u* (Å)	*r* (Å)	*u* (Å)	*r* (Å)	*u* (Å)
Se—C	1.9748 (0.0011)	0.060 (0.002)	1.9748 (0.0011)	0.060 (0.002)	1.9758 (0.0033)	0.062 (0.005)
C—C	1.5359 (0.0012)	0.038 (0.002)	1.5361 (0.0013)	0.040 (0.002)	1.5391 (0.0039)	0.0043 (0.005)
C—H	1.1090 (0.0031)	0.077 (0.003)	1.1209 (0.0032)	0.086 (0.004)	1.1112 (0.0124)	0.0087 (0.011)
	Angles (degrees)		Angles (degrees)		Angles (degrees)	
∠CSeC	89.3 (0.2)		89.2 (0.2)		89.0 (0.5)	
∠SeCC	105.7 (0.2)		105.9 (0.2)		105.7 (0.3)	
∠HCH	104.9 (2.0)		108.2 (2.0)		109.1 (5.1)	

with off-diagonal elements different from zero is limited. The final values given in Table 3 are therefore the average of the results in Table 2*b* and *c*. The standard deviations correspond to the values in Table 2*c*.

DISCUSSION

Table 1 illustrates that the angle parameters calculated by the Westheimer-Hendrickson method do not depend critically on the set of potential constants. In Table 3 the results for one of the sets (column d) are compared to the angle parameters found by electron diffraction. The agreement is seen to be quite satisfactory. The other sets of potential constants give torsional angles of somewhat smaller absolute values.

Table 3. Final results for the interatomic distances (r_a[23]), the corresponding mean amplitudes of vibration (u), bond angles and torsional angles (ϕ). Standard deviations (see text) are given in parentheses. Calculated values for the angles (*cf.* Table 1, column d) are included for comparison.

	r (Å)	u (Å)
Se—C	1.975_3 (0.003)	0.061 (0.005)
C—C	1.537_6 (0.004)	0.042 (0.005)
C—H	1.116 (0.012)	0.087 (0.011)
$Se_1 \cdots C_3$	2.814 (0.005)	0.066 (0.008)
$C_2 \cdots C_5$	2.772 (0.013)	0.065 (0.030)
$C_2 \cdots C_4$	2.457 (0.011)	0.060 (0.011)

	Angles (degrees)	
	Experimental	Calculated
∠CSeC	89.1 (0.5)	89.6
∠SeCC	105.8 (0.3)	105.6
∠CCC	106.0 (0.7)	106.7
∠HCH	108.7 (5.1)	—
$\phi(Se_1—C_2)$	15.4 (0.5)	14.9
$\phi(C_2—C_3)$	−42.7 (1.4)	−41.7
$\phi(C_3—C_4)$	56.9 (1.7)	55.8

The agreement between the experimental and theoretical intensity and RD functions is quite good for the refined model with C_2 symmetry. The theoretical curves shown in the Figs. 1 and 2 have been calculated with the molecular parameters given in Table 3. The difference between the experimental and theoretical RD curves is shown by curve A in Fig. 2. Curve B shows similarly the difference when the theoretical curve was calculated with the parameters in Table 2*a*.

Our preliminary calculations discussed previously indicated strongly that the molecule exists predominantly in a conformation with C_2 symmetry. To

investigate this somewhat closer least-squares refinements were carried out for a model with C_s symmetry. Some of the molecular parameters refined to unreasonable values, *e.g.* ∠CSeC became 79.5°, and the agreement was far from satisfactory. It seems quite safe to conclude that THS does not have C_s symmetry. The difference in energy between the C_2 and C_s models must be considerable, though the actual barrier to pseudo-rotation cannot be obtained from the electron diffraction data. The theoretical RD curves for the models I – VI seem to indicate that the calculated increase in energy (Table 1) going from C_2 towards C_s symmetry may be essentially correct.

From an electron diffraction point of view THF is quite different from THT and THS. While the refinements based on a C_2 model converge easily to reasonable results for THT and THS, a similar procedure for THF gave very unreasonable values for some of the parameters. The electron diffraction data for THF were consistent with a mixture of several conformations including C_2 and C_s models. The barrier to pseudo-rotation seems to increase from THF (where the barrier is very low) to THS. Table 4 shows the difference in energy for the C_s and C_2 conformations calculated using (approximately) the barriers in CH_3XH and in CH_3XCH_3 for the rotation around the C – X bonds. (X = O, S, or Se). The corresponding differences in torsional and bond angle bending energies [1] are also given. The sum of these contributions gives nearly the difference in the total energies, since the van der Waals contributions are of little importance.

Table 4. Energy differences (in kcal/mole) for C_s and C_2 models of THF,[1] THT,[3] and THS. E^t is the torsional energy,[1] E^a the contribution from bond angle strain,[1] and E the sum of these two terms and the van der Waals energy.

Compound	Barrier around C – X bonds	$E^t(C_s) - E^t(C_2)$	$E^a(C_s) - E^a(C_2)$	$E(C_s) - E(C_2)$
THF [1]	1.07 (CH_3OH)	2.51	−1.33	1.25
	2.70 (CH_3OCH_3)	−0.26	−0.57	−0.73
THT [3]	1.27 (CH_3SH)	2.90	0.09	3.03
	2.18 (CH_3SCH_3)	1.39	0.56	1.96
THS	1.01 (CH_3SeH)	3.37	0.52	3.92
	1.50 (CH_3SeCH_3)	2.57	0.79	3.38

These results show clearly that the calculated barriers to pseudorotation become rather different even if the barriers to rotation around the C – X bonds are assumed to be roughly equal. In THT and THS the torsional energies are very likely lower in the C_2 than in the C_s conformations, and this may very well be the case in THF also. However, the bond angle strain energy is probably favourable in the C_s model of THF, and most likely in the C_2 models of THT and THS. The difference between THF on one hand and THT and THS on the other is thus probably caused by differences both in torsional

energies (mainly because of changes in the C–X barrier) and in angle bending energies.

The bond angles are several degrees smaller in THF, THT, and THS than in the corresponding unstrained molecules. The CXC angles are 106.4–109.7° in THF (the lowest value is for the C_s, the highest for the C_2 conformation), 93.4° in THT and 89.1° in THS. The corresponding angles in dimethyl ether,[21,22] dimethyl sulfide,[20] and dimethyl selenide[4] are 111.5°, 99.0°, and 96.2°, respectively.

The C–C and C–H bond lengths given in Table 3 are close to usual values for these bonds. The C–Se bond is 0.032 Å longer than the bond length found by microwave spectroscopy in dimethyl selenide.* The difference between the C–S bond lengths found in THT[3] and dimethyl sulfide[20] was 0.037 Å. These differences seem consistent with the smaller values of the CXC bond angles and of the torsional angles around the C–X bonds in the ring compounds compared to the dimethyl compounds.

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REFERENCES

1. Seip, H. M. *Acta Chem. Scand.* **23** (1969) 2741.
2. Almenningen, A., Seip, H. M. and Willadsen, T. *Acta Chem. Scand.* **23** (1969) 2748.
3. Náhlovská, Z., Náhlovský, B. and Seip, H. M. *Acta Chem. Scand.* **23** (1969) 3534.
4. Beecher, J. F. *J. Mol. Spectry.* **21** (1966) 424.
5. Thomas, C. H. *Bull. Am. Phys. Soc. Ser. II* **11** (1966) 235.
6. Siebert, H. *Z. anorg. allgem. Chem.* **271** (1952) 65.
7. Eliel, E. L., Allinger, N. L., Angyal, S. J. and Morrison, G. A. *Conformational Analysis*, Interscience 1965.
8. McCullough, J. D. and Lefohn, A. *Inorg. Chem.* **5** (1966) 150.
9. Milazzo, G. *Rend. Ist. Super. Sanita* **22** (1959) 479.
10. Zeil, W., Haase, J. and Wegmann, L. *Z. Instrumentenk.* **74** (1966) 84.
11. Bastiansen, O., Graber, R. and Wegmann, L. *Balzers High Vacuum Report* **1969** 1.
12. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* **23** (1969) 3224.
13. Peacher, J. and Wills, J. C. *J. Chem. Phys.* **46** (1967) 4809.
14. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* **40** (1964) 1686.
15. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
16. Cox, H. L. and Bonham, R. A. *J. Chem. Phys.* **47** (1967) 2599.
17. Tavard, C., Nicolas, D. and Rouault, M. *J. Chim. Phys.* **64** (1967) 541.
18. Almenningen, A., Seip, H. M. and Seip, R. *Acta Chem. Scand.* **24** (1970) 1697.
19. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Letters* **3** (1969) 617.
20. Pierce, L. and Hayashi, M. *J. Chem. Phys.* **35** (1961) 479.
21. Kimura, K. and Kubo, M. *J. Chem. Phys.* **30** (1959) 151.
22. Kasai, P. H. and Myers, R. J. *J. Chem. Phys.* **30** (1959) 1096.
23. Kuchitsu, K. *Bull Chem. Soc. Japan* **40** (1967) 498.
24. Goldish, E., Hedberg, K., Marsh, R. E. and Schomaker, V. *J. Am. Chem. Soc.* **77** (1955) 2948.

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* However, an older electron diffraction investigation[24] gave about the same bond length in dimethyl selenide as found in THS.