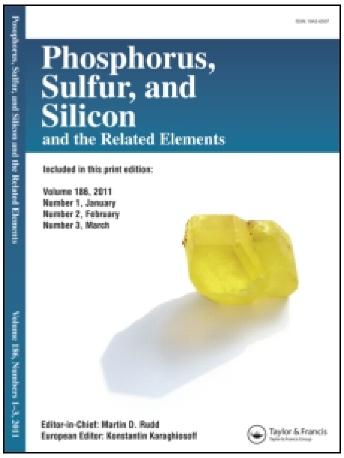

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THE FORMATION OF Se_{10} AND Se_5S_5. AN *AB INITIO* MO FEASIBILITY STUDY

RISTO S. LAITINEN, JARI TAAVITSAINEN, HELI TIAINEN and PENTTI PEKONEN
Department of Chemistry, University of Oulu, Linnanmaa, 90570 Oulu, Finland,

Ab initio MO calculations have established the structural and stability relationships of S_{10}, Se_{10}, and the three isomers of 1,2,3,4,5-Se_5S_5. The calculations imply that ten-membered selenium-containing chalcogen rings should be sufficiently stable to render their preparation possible.

Keywords: *Ab initio*, MO calculations, stability, cyclodecasulfur, cyclodecaselenium, cyclopentaselenium pentasulfide

INTRODUCTION

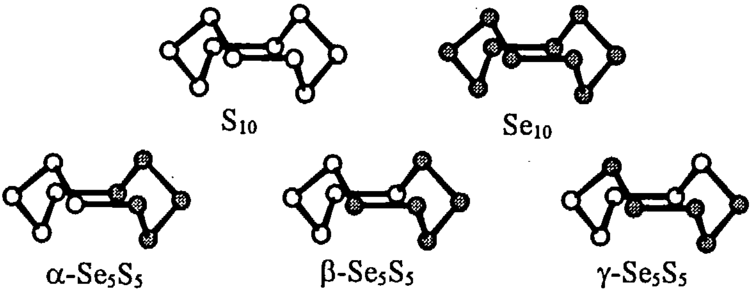
Sulfur and selenium are very similar elements forming an abundance of both homocyclic and polymeric molecular forms (for a recent review, see Ref. 1). In the case of sulfur, the crystal structures of most homocyclic molecules with the ring size 6-20 are known. In contrast, selenium has a weaker ability to form homocyclic molecules. To date, only Se_6, Se_7, and Se_8 have been structurally characterized.

The similarity of sulfur and selenium is reflected by the existence of a complicated binary system of the elements. The most stable selenium sulfides are the eight-membered heterocyclic molecules that can be prepared from the molten mixtures of the elements or by use of the different synthetic routes.[1] In addition to the eight-membered ring molecules, Se_xS_{6-x}, Se_xS_{7-x}, and Se_xS_{12-x} are also known.

The goal of the present work is to establish the plausibility of preparing cyclic selenium-containing chalcogen molecules with the ring size over eight. S_{10} and its selenium-containing analogues Se_{10} and 1,2,3,4,5-Se_5S_5 were chosen as targets, since the synthetic approaches that are well-known for S_{10} [2] can conveniently be modified for selenium-containing species.

COMPUTATIONAL DETAILS

The MO calculations were carried out for S_{10}, Se_{10}, three conformers of 1,2,3,4,5-Se_5S_5 (see Fig. 1), S_6, Se_6, S_7, S_8, SeS_7, 1,2-Se_2S_6, 1,2,3-Se_3S_5, 1,2,3,4-Se_4S_4, 1,2,3-Se_5S_3, 1,2-Se_6S_2, Se_7S, and Se_8 using Gaussian 94 [3] involving polarized MIDI-4* basis sets.[4,5] The gradient techniques were employed in the geometry optimization. A MP2 correction for electron correlation [6-8] was performed using the optimized geometries. The fundamental vibrations were calculated at the HF level of theory to establish the nature of the stationary points. The calculated wavenumbers and the zero-point energies have been scaled by 0.89 to eliminate systematic errors.[9]

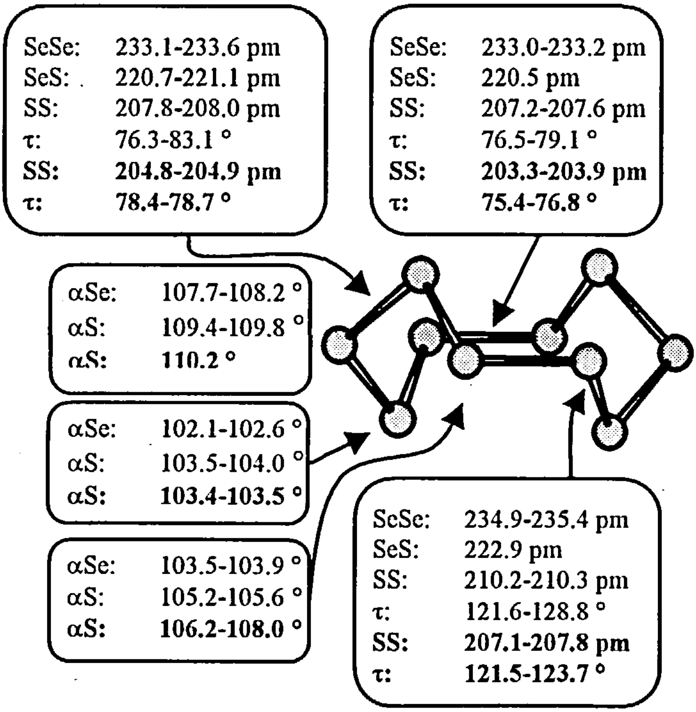

S_{10} Se_{10}

α-Se_5S_5 β-Se_5S_5 γ-Se_5S_5

FIGURE 1. S_{10}, Se_{10}, and the three isomers of 1,2,3,4,5-Se_5S_5.

RESULTS AND DISCUSSION

The HF/MIDI-4* optimized bond parameters of the ten-atomic species shown in Fig. 1 are presented in Fig. 2. The conformations of all molecules are very similar. The calculated bond parameters of S_{10} are in good agreement with the experimental data.[2] While there is no experimental information for the Se_xS_{10-x} (x = 5, 10) species, their calculated bond parameters are reasonable when compared to those of S_{10}. The calculated HF/MIDI-4* fundamental vibrations indicate that all molecules lie in the true local energy minima.



SeSe: 233.1-233.6 pm
SeS: 220.7-221.1 pm
SS: 207.8-208.0 pm
τ: 76.3-83.1 °
SS: 204.8-204.9 pm
τ: 78.4-78.7 °

SeSe: 233.0-233.2 pm
SeS: 220.5 pm
SS: 207.2-207.6 pm
τ: 76.5-79.1 °
SS: 203.3-203.9 pm
τ: 75.4-76.8 °

αSe: 107.7-108.2 °
αS: 109.4-109.8 °
αS: 110.2 °

αSe: 102.1-102.6 °
αS: 103.5-104.0 °
αS: 103.4-103.5 °

αSe: 103.5-103.9 °
αS: 105.2-105.6 °
αS: 106.2-108.0 °

SeSe: 234.9-235.4 pm
SeS: 222.9 pm
SS: 210.2-210.3 pm
τ: 121.6-128.8 °
SS: 207.1-207.8 pm
τ: 121.5-123.7 °

FIGURE 2. Optimized bond parameters of S_{10}, Se_{10}, and Se_5S_5. The experimental values from S_{10} [2] have been written in bold.

The torsional angles and the corresponding bond lengths show a marked variation throughout the rings (see Fig. 2). As discussed for S_7 [10] and demonstrated by theoretical calculations [1] the deviation of the torsional angle of the chalcogen-chalcogen bond from the ideal value of 90 ° will lengthen the bond due to increased *p*-lone pair repulsion of the two adjacent chalcogen atoms.

The optimized geometries of other molecular species calculated in this work also agree with the experimental geometry and bond parameters where available. It should be noted that these calculations reproduce the observed fluxionality of S_7. A detailed *ab initio* MO treatment of the pseudorotation and interconversion pathways of S_7 is currently in progress.[11]

The total HF/MIDI-4* and MP2/MIDI-4*//MIDI-4*energies of all molecules calculated in this work are shown in Table I. As the electron correlation plays an important role in the correct prediction of the energetics of the chalcogen molecules, the discussion on the stability of the different species is carried out at MP2 level of theory.

The level of reliability of MP2/MIDI-4*//MIDI-4*+ZPE calculations can be established by comparison of the calculated parameters with the experimental information where available.

Steudel [12] has estimated that the the ring-opening in S_7 in molten sulfur is endothermic with the enthalpy change of 127 kJ mol^{-1} ! Our MP2/MIDI-4*+ZPE calculations [11] yield the value of 142 kJ mol^{-1} for the same reaction in reasonable agreement with the experimental value. The enthalpy of formation of S_6 and S_7 from S_8 in vapour phase at 298 K have been reported as 34 and 28 kJ mol^{-1}, respectively.[12] The

MP2/MIDI-4*+ZPE values calculated from the total energies given in Table I are 39 and 29 kJ mol^{-1} in good agreement with experiment. It can be concluded that the calculated energy values have predicting power in cases where no experimental information is available.

TABLE I Total energies of some chalcogen ring molecules (a.u.)

Molecule	HF/MIDI-4*	MP2/MIDI-4*	ZPE
S_6	-2382.61002	-2383.37134	0.00932
Se_6	-14386.21889	-14386.95012	0.00511
S_7	-2779.70658	-2780.60200	0.00950
S_8	-3176.82147	-3177.84215	0.01249
SeS_7	-5177.42110	-5178.43939	0.01176
1,2-Se_2S_6	-7178.02175	-7179.03678	0.01105
1,2,3-Se_3S_5	-9178.62255	-9179.63427	0.01034
1,2,3,4-Se_4S_4	-11179.22346	-11180.23187	0.00963
1,2,3-Se_5S_3	-13179.82445	-13180.82957	0.00893
1,2-Se_6S_2	-15180.42551	-15181.42731	0.00823
Se_7S	-17181.02673	-17182.02518	0.00753
Se_8	-19181.62889	-19182.62317	0.00685
S_{10}	-3971.01730	-3972.29724	0.01391
α-Se_5S_5	-13974.02298	-13975.27833	0.01074
β-Se_5S_5	-13974.02291	-13975.27812	0.01074
γ-Se_5S_5	-13974.02300	-13975.27834	0.01074
Se_{10}	-23977.03182	-23978.26179	0.00763

TABLE II Total MP2/MIDI-4*//MIDI-4*+ZPE binding energies (E_B) and the one-atom contributions to the binding energies ($D_B = E_B/n$, where n is the number of chalcogen atoms in the molecule)

Molecule	E_B (a.u.)	D_B (a.u.)
S_6	0.48296	0.08049
Se_6	0.43995	0.07333
S_7	0.56693	0.08099
S_8	0.65600	0.08200
SeS_7	0.65113	0.08139
1,2-Se_2S_6	0.64484	0.08060
1,2,3-Se_3S_5	0.63864	0.07983
1,2,3,4-Se_4S_4	0.63256	0.07907
1,2,3-Se_5S_3	0.62656	0.07832
1,2-Se_6S_2	0.62060	0.07758
Se_7S	0.66148	0.07685
Se_8	0.60906	0.07613
S_{10}	0.81819	0.08182
α-Se_5S_5	0.78021	0.07802
β-Se_5S_5	0.78021	0.07802
γ-Se_5S_5	0.78021	0.07802
Se_{10}	0.74437	0.07444

All cyclic chalcogen molecules shown in Table I are stable relative to free atoms, as indicated by the total binding energies shown in Table II. The one-atom contribution to the total binding energy provides a qualitative estimate of the relative stability of the molecules.

It can be seen from Table II that the binding energies establish a stability trend that can experimentally be deduced from the reactivity of sulfur rings with respect to nucleophilic attack [13] (Calculated stability:

$S_8 > S_{10} > S_7 > S_6$; the rate constants of the nucleophilic attack: $S_6 > S_7 > S_8$). The stability relationship of the homocyclic selenium molecules follows the same trend in terms of the ring size as sulfur ($Se_8 > Se_{10} > Se_6$).

In the case of heterocyclic selenium sulfides the increasing selenium content within the given ring size decreases the binding energy and thus the stability of the molecule. When there are several isomers, those with all selenium and sulfur atoms adjacent to each other seem to be the most stable. This is in agreement with the density functional calculations of Jones and Hohl [14] and is consistent with the ^{77}Se NMR spectroscopic observation that these isomers are the most abundant in any mixture containing several molecular species in equilibrium.[15]

It can be concluded from Table II that the Se_xS_{10-x} rings should be sufficiently stable to render their preparation possible. Our preliminary calculations further indicate that the ten-membered chalcogen ring might be fluxional undergoing pseudorotation in an analogous fashion to the seven-membered ring molecules.[1] A more detailed study to establish the existence of fluxionality in ten-atomic chalcogen rings is currently in progress.

In addition to the deduction of the nature of the stationary point in the wave function, the calculated fundamental vibrations can be used in the identification of any ten-membered species that might be formed. This is exemplified by the HF/MIDI-4* calculated frequencies and Raman intensities of S_{10} and Se_{10} that are listed in Table III and compared with the observed Raman wavenumbers of S_{10}. It can be

TABLE III The calculated HF/MIDI-4* fundamental vibrations and Raman intensities of S_{10} and Se_{10}. Comparison with observed Raman wavenumbers

S_{10}			Se_{10}		
Calc.(cm^{-1})	Int.	Raman (cm^{-1}) [2]	Calc. (cm^{-1})	Int.	Raman (cm^{-1})
493 b_3	10	495 w	279 b_3	23	
493 b_1	8		278 b_1	9	
493 a	21	487 m	278 b_2	11	
491 b_2	34	481 sh	278 a	34	303 m
486 b_3	1		276 b_3	0	
479 b_1	0		274 b_1	0	
475 a	5	469 s	268 a	6	
459 b_2	0		261 b_3	4	260 s
456 b_3	6	466 sh	259 b_2	1	
449 a	100	425 m	255 a	100	241 m
241 a	11	255 w	122 a	10	156 m
235 b_2	3	246 sh	118 b_2	2	
228 b_1	16	243 m	117 b_1	13	126 s
218 b_2	1	231 vw	111 b_2	1	
212 b_3	1		109 b_3	0	
209 b_1	1		106 b_1	1	
160 a	16	178 s	82 a	14	96 s
134 b_3	2	131 m	67 b_3	2	
118 b_2	3	100 m	60 b_2	3	
87 b_3	4	85 s	44 a	7	
87 a	9	73 vs	42 b_3	4	
69 b_1	4		35 b_1	3	
54 a	7	39 s	26 a	7	
35 b_1	0	29 m	17 b_1	0	

seen that the calculated wavenumbers make a reasonable prediction of the Raman spectrum of S_{10}.

We have made a tentative attempt to produce Se_{10} from $[TiCp_2Se_5]$ and SO_2Cl_2 modifying the analogous preparation of S_{10}.[2]

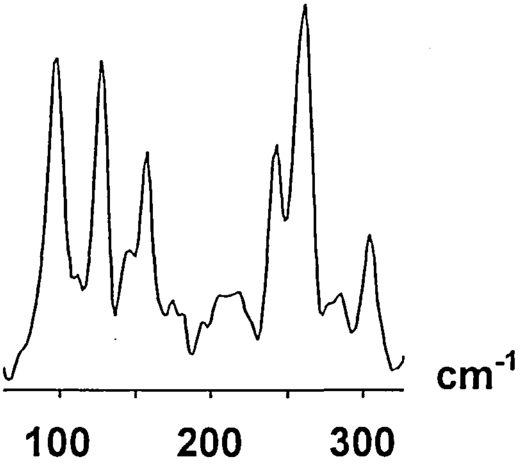


FIGURE 3. Raman spectrum of the reaction product from $[TiCp_2Se_5]$ and SO_2Cl_2.

$$[TiCp_2Se_5] + SO_2Cl_2 \rightarrow \tfrac{1}{2}\, Se_{10} + SO_2 + [TiCp_2Cl_2]$$

A red, slightly soluble material was obtained. Its 12 eV EI mass spectrum showed the Se_n^+ (n = 1-9) fragments. The FT Raman lines (see Fig. 3) can tentatively be assigned with the help of the calculated HF/MIDI-4* wavenumbers of Se_{10} (see Table III). This preliminary data imply that Se_{10} indeed might be formed in the reaction. Further work to confirm the identification and characterization of the product is currently in progress.

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