DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
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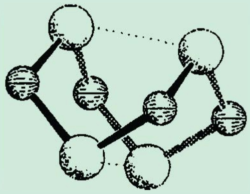
REIJO SUONTAMO



Academic Dissertation
for the Degree of
Doctor of Philosophy

Jyväskylä, Finland 1995
ISBN 951-34-0531-1
ISSN 0357-346X

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To be presented, by permission of the Faculty of Mathematics and Natural Sciencies of the University of Jyväskylä, for public examination in Auditorium S-212, on May 12th, 1995, at 12 o'clock noon

University of Jyväskylä,
Jyväskylä, Finland
ISBN 951-34-0531-1
ISSN 0357-346X

URN:ISBN:978-952-86-0303-0
ISBN 978-952-86-0303-0 (PDF)
ISSN 0357-346X

University of Jyväskylä, 2024

List of original publications

This thesis is based on the following original publications. They are referred to in the text by their Roman numerals:

I Laitinen, R.S., Pekonen, P. and Suontamo, R.J., Homo- and heteroatomic chalcogen rings, *Coord. Chem. Rev. 130* (1994) 1-62.
https://doi.org/10.1016/0010-8545(94)80002-2

II Suontamo, R.J., Laitinen, R.S. and Pakkanen, T.A., Molecular valence calculations on small sulfur clusters S_2 to S_5, *J. Mol. Struct. (Theochem.) 313* (1994) 189-197.
https://doi.org/10.1016/0166-1280(94)85001-1

III Suontamo, R.J., Laitinen, R.S. and Pakkanen, T.A., An *Ab Initio* MO Study of the Pseudorotation in Cyclohexasulfur, S_6, and Cycloheptasulfur, S_7, *Acta Chem. Scand. 45* (1991) 687-693.
https://doi.org/10.3891/acta.chem.scand.45-0687

IV Suontamo, R.J. and Laitinen, R.S, Interconversion Pathways of Chalcogen Rings. An *Ab Initio* MO Study of Model Reactions Involving Hypervalent Sulfur and Selenium Hydrides, a manuscript submitted for publication in *Main Group Chem.*
https://doi.org/10.1080/13583149612331338475

V Suontamo, R.J., Siivari, J., Laitinen, R.S. and Chivers, T., Six-membered selenium-sulfur nitrides $Se_xS_{4-x}N_2$ (x = 0-4), *Phosphorus Sulfur Silicon Relat. El., 93-94* (1994) 245-248.
https://doi.org/10.1080/10426509408021826

VI Suontamo, R.J. and Laitinen, R.S., *Ab initio* molecular orbital study of $Se_nS_{4-n}N_4$ (n = 0-4), *J. Mol. Struct. (Theochem.),* in press.
https://doi.org/10.1016/0166-1280(94)04096-B

PREFACE

This work was carried out in the Department of Chemistry, University of Jyväskylä during the years 1987 - 1994. The computer facilities of the Department of Chemistry of the University of Oulu, and of the Centre for Scientific Computing, Espoo, were used for most of the molecular orbital calculations.

I wish to warmly thank Prof. Jussi Valkonen, University of Jyväskylä, for the patience and encouragement that kept this work going during the years. I wish to express my sincere thanks to my supervisors, Prof. Risto Laitinen, University of Oulu, and Prof. Tapani Pakkanen, University of Joensuu, for their continuous support of my work and discussion of the theoretical problems.

I would like to thank my co-authors Dr. Pentti Pekonen, Dr. Jari Siivari and Prof. Tristram Chivers for their help during this work.

Special thanks goes to my very first instructor in chemistry, Prof. Paavo Lumme, for guiding my first steps through the fascinating world of theoretical chemistry.

To my many colleagues, many of whom are my former students, I wish to express my thanks for their understanding of and interest in my work, and for creating an inspiring atmosphere in our department. Frequently, informal discussions gave me an opportunity to clarify my thoughts when trying to answer their numerous questions. Especially I thank Dr. Seppo Kasa for his comments and inspiring company during these years of study and work.

I am grateful to Lecturer Michael Peacock, B.A., for revising the language.

For my wife Tuula and son Samuli, I reserve my deepest gratitude and affection, for their constant support and patience. I must also remember our dog, Nelli, for keeping me outdoors on a fairly regular basis.

I am grateful to University of Jyväskylä for financing my leave of four months in order to complete this work.

Jyväskylä, February 1995 Reijo Suontamo

I dedicate this work to Tuula and Samuli.

ABSTRACT

The bonding and allotropy of chalcogen species, and molecular orbital methods are briefly discussed.

The molecular valence method is applied to small sulfur clusters S_2 to S_5 in order to test the applicability of the method. The double zeta basis set augmented with polarization functions (DZP) is needed to reproduce the structural parameters calculated by *ab initio* all-electron MO methods or found by experiments. For a given molecular species the energy differences between isomers agree well with those obtained by the use of HF all-electron calculations at the corresponding level of theory.

Pseudorotation in *cyclo*-S_6 and *cyclo*-S_7 is studied using the *ab initio* all-electron MO method. The energetics is corrected for electron correlation at the MP2 level of theory. Hexasulfur is rigid, but heptasulfur undergoes a facile pseudorotation. Results are in agreement with the experimental findings.

The energetics of the various suggested chalcogen interconversion pathways is studied by *ab initio* MO techniques using suitable model reactions involving hypervalent chalcogen hydrides H_2EE and $H_2E(EH)_2$ as well as the radicals $HE^{\cdot}$ and $HEE^{\cdot}$ (E = S or Se). The formation of hypervalent interconversion intermediates is seen as an energetically plausible alternative to the homolytic cleavage of the chalcogen-chalcogen bonds. The present calculations provide support for the previous observations that in the case of heterocyclic selenium sulfides the interconversion proceeds with a selenium-atom transfer rather than with a sulfur-atom transfer.

Geometries, energies and fundamental frequencies of selenium-sulfur nitride six-membered ring molecules $Se_nS_{4-n}N_2$ (n = 0 – 4) and eight-membered ring molecules $Se_nS_{4-n}N_4$ (n = 0 – 4) are calculated, and the bonding and the relative stabilities of the molecules are discussed. Calculated energies show that it should be possible to synthetize all members of the both series. Calculated fundamental frequencies are in fair agreement with the observed experimental vibrational spectra where these are available. It seems reasonable to use calculated frequencies to assist the experimental characterization of those molecules that are not yet fully investigated.

CONTENTS

ABBREVIATIONS

a.u. = Atomic units

CISD = Configuration interaction with single and double excitations

DZP = Double zeta basis set augmented with polarisation functions

HF = Hartree-Fock method

HF-SCF = Hartree-Fock Self Consistent Field method

IR = Infrared

kJ = kilojoules

NMR = Nuclear magnetic resonance

MIDI-4* = A split valence basis set augmented with polarisation functions

MO = Molecular orbital

mol = mole

MPn = nth Order Møller-Plesset correction for electron correlation

MP2 = 2nd Order Møller-Plesset correction for electron correlation

MZ = A minimal basis set

NTP = Normal temperature and pressure

pm = picometers

SCF = Self Consistent Field

STO-3G = A minimal basis set

UHF = Unrestricted Hartree-Fock method

ZPE = Zero-point energy

3-21G* = A split-valence basis set augmented with polarisation functions

6-31G* = A split-valence basis set augmented with polarisation functions

1. INTRODUCTION

Sulfur is an abundant element in nature occurring in the Earth's crust both as a free element and as sulfide minerals. Crude oil contains organic sulfides, and natural gas contains hydrogen sulfide. Burning oil and coal to produce heat and electricity is a major source of pollution. Environmental legislation has required the efficient removal of the sulfur dioxide from exhaust gases, resulting in a substantial increase in world sulfur production. This increase has given impetus to research designed to find new applications for the use of sulfur and its compounds.

Sulfur, selenium and tellurium are often termed chalcogen elements. They have a strong tendency to catenate, *i.e.* to form molecular species containing cumulated homo- and heteronuclear chalcogen-chalcogen bonds. As a consequence all three chalcogen elements exhibit allotropy involving both cyclic and open chain molecular forms. For a review of the current literature, see Paper I.

The chemical and structural similarity of the three chalcogen elements has led to extensive investigations of the structures and properties of binary and ternary systems. Because of the close similarity between sulfur and selenium, the latter can be introduced into the sulfur system as a chemical label. Heterocyclic selenium sulfides can therefore serve as model compounds for the study of the structural and chemical properties of either sulfur or selenium molecules. Selenium sulfides also bridge the properties of an electrical insulator (sulfur) and a semiconductor (selenium). The heterocyclic tellurium-containing species are much sparser, and therefore very little is known about their properties.

The aim of this work was to gain information on sulfur and selenium chemistry by using quantum chemical molecular orbital methods in order to explain experimental results and to predict sulfur and selenium interconversion reaction pathways, which are difficult to study experimentally. This work is based on six original papers,[I-VI] ; one of which, Paper I, is an extensive review of cyclic chalcogen molecules.

2. MOLECULAR ORBITAL METHODS

All practical molecular orbital methods that can be applied to polyatomic molecules containing heavy elements are based on an approximate evaluation of the electron structures. The general theories involved are discussed and mathematically elaborated in several standard quantum chemistry textbooks,[1-3] so only a brief review is given here. There are also many practical guides[4-8] for chemists on how to apply molecular orbital methods and use the associated computer programs.

2.1 Hartree-Fock Self-Consistent Field method

The exact wave function is known only for atoms and molecules with one electron. For systems containing more electrons, the best approach for finding a good approximate wave function involves the Hartree-Fock (HF) procedure. It uses the central field approximation in which any one electron moves in a potential that is an average of the potential due to all the other electrons. It is an iterative method, because the function to be evaluated is included in the Hartree-Fock operator.

The central potential is named as a self-consistent field, and the method is called the Hartree-Fock self-consistent field (HF-SCF) method. The HF-SCF method makes use of atomic and molecular orbitals in many-electron systems. Its rigorous mathematical formalism for the solution of the self-consistent field (SCF) equations in terms of a finite set of one-electron functions was set out by Roothaan.[9] It limited to treating only closed shells, *i.e.* molecules and atoms having only electron pairs. If all integrals are solved, *i.e.* no further approximations are made, this method is called the *ab initio* Hartree-Fock-Roothaan SCF molecular orbital method and commonly abbreviated as *ab initio* HF-SCF-MO. Later Pople and Nesbet[10] introduced the unrestricted Hartree-Fock (UHF) method, which is able to deal with unpaired electrons as well as electron pairs.

One of the drawbacks of the HF method is that even the best Hartree-Fock energy E_{HF}, is higher than the exact energy E_{exact} for the system, because the correlated movement of electrons can not be dealt with as an approximate average central potential. The difference $E_{exact} - E_{HF}$ is defined as the correlation energy.[11] A second drawback is that the bonding electron pair is inherently held together when a chemical bond is broken, *i.e.* the HF calculation leads to $AB \rightarrow A^{+} + B^{-}$ instead of the correct $AB \rightarrow A\cdot + \cdot B$.

The HF-SCF energy is often useful in itself for qualitative or semiquantitative studies, but is rarely adequate for high quantitative accuracy.

2.1.1 Pseudopotential methods

Molecules containing a high number of electrons are time-consuming to calculate with full *ab initio* methods because of the large number of basis functions and the resulting large number of integrals. To reduce the work, in the case of molecules containing atoms with atomic numbers over ten, attempts to eliminate the inner-shell electrons from the calculations has led to various pseudopotential methods.[2] They use an electronic Hamiltonian that is divided into two parts, the valence part and the core part. The valence part, *i.e.* the valence electrons, are treated as in full *ab initio* calculation, but the core part is a relatively simple potential term meant to allow for the influence of the inner-shell electrons on the valence electrons. Although such an approach is an approximation, a fair degree of success has been attained in pseudopotential calculations and they are undergoing further development.

2.2 Treatments for recovering electron correlation

The electron correlation problem is composed of two different effects. The first is the nondynamic correlation. The ground-state configuration mixes strongly with other low-energy configurations, so the single configuration HF approximation is inadequate. The nondynamic correlation is often small in closed-shell molecules near their equilibrium geometry, but it increases enormously in importance as the molecule is distorted and the bonds are formed or broken.

The second part of the correlation problem is the dynamic correlation. It arises from the $1/r_{ij}$ term in the Hamiltonian operator. Several different approaches for the treatment of the dynamic correlation have been suggested, but for the last few years one approach, the Møller-Plesset (MP) perturbation theory,[6] has been quite dominant. The energy is expanded as a perturbation series in V, the perturbation in the Hamiltonian $\hat{H} = \hat{H}_{HF} + V$. The n^{th}-order treatment is denoted MP*n*. The simplest level, MP2 (the first-order perturbation vanishes), is probably the treatment of dynamic correlation that uses less computational resources than any other treatment.

2.3 Choice of basis sets for sulfur and selenium

The sheer number of basis sets published (for recent reviews, see Refs. 12 and 13) makes the choice of basis sets a nontrivial one. It is, however, possible, if a suitable choice is made, to reach an accuracy by *ab initio* calculations that is comparable with the experimental, so called chemical, accuracy. This means reproducing the experimental internal coordinates with an accuracy of ± 1 pm for the bond lengths and ± 1° for the bond and torsion angles. Absolute energies are not so easy to reproduce, but fortunately, relative energies between absolute energies of molecular and atomic species are more important, and they can be calculated to ± 10 kJ mol^{-1}, energy differences between torsional isomers even to ± 1 kJ mol^{-1}. However, high accuracy in the relative energies of fairly large molecules requires, in many cases, very large extended basis sets, which means high computational effort and cost.[13]

The standard minimal basis sets give substantially longer calculated S-S bonds than what is found experimentally. Here the minimal STO-3G of Hehre *et al.*[14] behaves differently, giving S-S bond lengths in close agreement with the experimental bond lengths. For electron correlation calculations the smallest useful basis set is the 3-21G* of Pietro *et al.*,[15] which is a double-zeta split-valence basis set supplemented with a set of *d*-polarization functions. This basis set yields molecular properties that are uniformly close to those obtained with a much larger 6-31G* basis set representation.[16]

For selenium, the minimal basis sets behave like those of sulfur. The 3-21G* of Dobbs and Hehre[17] gives a fair agreement with experimental bond distances for both normal and hypervalent selenium compounds.

When calculating energies of molecules containing different kinds of atoms having a different number of electrons, basis sets should be tested for right performance. The quality of the basis sets for energy calculations is discussed by Sordo and Sordo.[18] Ideal basis sets should fulfil the virial theorem $-V/T = 2$ when the total HF-energy is calculated for a molecule. Well-balanced basis sets for different kinds of atoms in the same molecule should give a $-V/T$ ratio very close to 2.

2.4 Geometry optimization

The way the energy of a molecular system varies with small changes in its structure is specified by its potential energy surface. The surface has as many dimensions as there are degrees of freedom within the molecule.

Geometry optimization usually attempts to locate a minimum on the potential energy surface. The surface can be scanned by systematically varying the internal coordinates of the molecule. Each set of coordinates corresponds to a point on the search grid. The energy of the molecule is calculated at each grid point, and the calculated energies are fitted to a quadratic equation, whose variables are the varied internal coordinates. Then the first derivative of the energy function is set to zero and the corresponding geometry is evaluated for the molecule now at a stationary point on the potential energy surface. The second derivative shows whether the located stationary point is a minimum or a maximum. The systematic scan of the potential energy surface can be very time-consuming if the search grid is wide and has many points.

Automatic algorithms using the gradient techniques for geometry optimizations can substantially reduce the computational effort.[6,7] With these techniques, however, difficulties can arise when the molecular symmetry tends to change during the optimization procedure.

2.5 Calculation of fundamental frequencies

The second derivatives of the energy of the optimized molecule at a local minimum when calculated in respect to internal coordinates, give the force constants of the fundamental frequencies of the molecule. Frequency calculations can serve a number of different purposes.[7] For instance, they can be used to predict the IR and Raman spectra of molecules, and the nature of stationary points on the potential energy surface can be identified. If all calculated frequencies are real, the local minimum is a true minimum, *i.e.* it is a stable conformation. If one or more frequencies are imaginary, the stationary point corresponds to a saddle point of order n. If $n = 1$, the saddle point is a transition state. The frequency calculations also make it possible to calculate the zero-point vibrational energy (ZPE) correction to the total energy.

3. CHALCOGEN BONDING

The allotropy of sulfur is by far more extensive than is the case for any other element. The most stable allotrope of sulfur at NTP is the yellow, orthorombic α-form of *cyclo*-S_8. A great variety of molecular forms can be achieved by -S-S- catenation, and these forms can be arranged within the crystal in numerous ways. S-S bonds are very variable and flexible: interatomic distances cover the enormous range 180 - 260 pm, whilst bond angles S-S-S vary from 90° to 180° and dihedral angles S-S-S-S from 0° to 360°. Typical values for an unrestrained -S-S- bond chain are 206.6 pm for the bond length, 106° for the bond angle and 85.3° for the torsional angle.[19] Estimated S-S bond energies may be as high as 430 kJ mol^{-1}, and the unstrained -S-S- single bond energy of 265 kJ mol^{-1} is exceeded amongst homonuclear bonds only by those of H_2 (435 kJ mol^{-1}) and C-C (330 kJ mol^{-1}). On the other hand, the S-S bond is easily formed and cleaved in various chemical reactions.

The allotropy of selenium and tellurium is simpler than that of sulfur. Though the molecular structures of selenium- and tellurium-containing species are often similar to those of the analogous sulfur compounds, there are also pronounced differences among the three chalcogen elements. For instance, selenium and tellurium have weaker ability to form homocyclic molecules than sulfur. In fact, the polymeric trigonal chains of selenium and tellurium are the most stable forms of the two elements. However, Se_6, Se_7 and Se_8 ring molecules are known for selenium and have molecular structures similar to those of analogous sulfur species. The existence of Te_8 has been suggested but not confirmed.[I]

The structural and electronic features of the different chalcogen-chalcogen bonds are rather similar.[20,21] The valence orbitals seem to be rather insensitive to the substitution of sulfur by selenium or *vice versa*. The calculated energy change involved in the formation of two S-Se bonds from one S-S and one Se-Se bond is very small,[20,21] in agreement with the enthalpy of mixing liquid sulfur and selenium,[22] or with the enthalpy change in the reaction of gaseous S_2 and Se_2 to form gaseous SeS.[23]

Chalcogen bonding has been subject to many theoretical calculations. These are reviewed in Paper I, and a more detailed discussion for small sulfur molecules S_2 to S_5 is given in Paper II. In particular, S_4 has turned out to be a difficult case, and sixteen different isomers have previously been studied. Six of them have been suggested as likely candidates for the ground state.[II]

4. MOLECULAR VALENCE CALCULATIONS OF SMALL SULFUR MOLECULES

The present calculations[II] were carried out for the selected isomers of small sulfur clusters S_2 - S_5 using the molecular valence method of Pakkanen *et al.*[24] Although small sulfur and selenium species have been observed in the vapour, there is little experimental evidence on their structure. There is, however, an abundance of theoretical studies[I] that together with the experimental data provide a good environment to test the theoretical model, with the ultimate goal of applying it to other chalcogen systems where experimental information is not so readily available. The method has previously been applied to the homocyclic sulfur molecules S_6 to S_8 using minimal basis sets (MZ) for valence orbitals,[25] but here the method is tested with species whose ground state conformations have been the subject of considerable debate.

The present molecular valence method[24] calculates the valence part of the electronic structure with an *ab initio* HF algorithm. The core part is frozen in a pseudopotential manner. The principal approximations involve the freezing of the atomic core orbitals, the description of the core-valence interactions using density matrix expansion techniques, and the enforcement of the core-valence orthogonality by means of auxiliary bases and the projection operator method. The approximations are executed in a stepwise manner and thus each step can be separately relaxed and tested for reliability. The approximations can be chosen for each case depending on the accuracy demands of the problem. As the core expansions are generated from the extended basis atomic calculations, the same core can be used when the valence description is of either minimal or double zeta quality. Polarization functions can also be included.

A full geometry optimization using both minimal (MZ) and polarised double zeta (DZP) basis sets was carried out numerically, using basis sets the construction of which has been described in detail elsewhere.[24] Only single-point calculations of the grid point geometries of the potential energy surface scan were carried out at the HF level of theory.

When the minimal basis MZ is used, the present method overestimates bond lengths for all species studied.[II] For cyclic S_6, S_7 and S_8 the same basis gave bond lengths that were overestimated by *ca.* 10 % when compared[25] with the experimental bond lengths. The relative energies between the isomers of S_3 were high, and for S_4, only the square (D_{4h}) and the cis chain (C_{2v}) isomers of the studied species were at local minima. On the other hand, energy differences were calculated to be rather small between the different isomers of S_5. These results again point out the importance of using more flexible basis sets than MZ when calculating the properties of sulfur compounds.

The calculation with the present polarised double zeta (DZP) basis set results in a bond length for S_2 that is in excellent agreement with the experiment.

The calculated species S_3 to S_5 are shown in Fig. 4.1 together with the DZP relative energies in kJ mol^{-1}. The DZP basis gave structural parameters that are in agreement with other single-configuration HF all-electron calculations. For example, Quelch *et al.*[26] optimised S_4 at its rectangular ring (D_{2h}) conformation with CISD and found the bond lengths to be 254.2 and 188.9 pm. Our calculation gave the same geometry, 254.4 and 188.4 pm, respectively.[II]

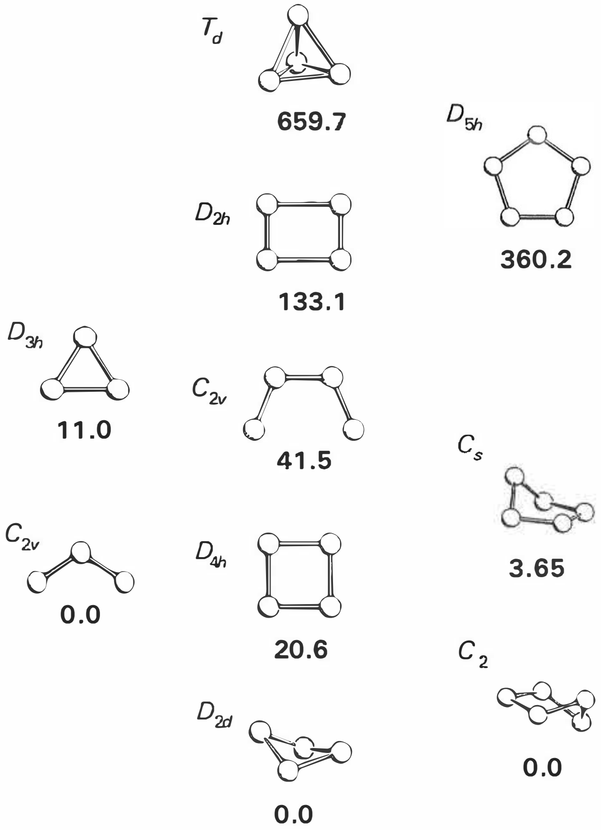


Figure 4.1 Relative energies (kJ mol^{-1}) of the species S_3 to S_5 calculated by the molecular valence method using the DZP basis set. (not to scale).[II]

5. PSEUDOROTATION OF HOMOCYCLIC S_6 AND S_7

The most stable conformation of cyclohexasulfur S_6 is the chair conformation of D_{3d} symmetry as shown in the present MO study.[III] It seems to be relatively rigid, in fact no boat conformation of C_{2v} symmetry has ever been observed to the neutral molecule. In theory, two possible pathways can be envisaged for the change of conformation of the six-membered sulfur ring from the chair to the boat conformation. The first possibility involves a direct inversion through an intermediate semi-plane conformation of C_s symmetry. In this study the semi-plane conformation was calculated to be 136.9 kJ mol^{-1} higher in energy than the chair conformation and 73.6 kJ mol^{-1} above the boat conformation at the MP2 level of theory. The semi-plane conformation was shown to be a transition state. The second possible route of inversion is via pseudorotation about any of the six equivalent bonds of the molecule in its chair form ground state. This pseudorotation scheme is presented in Fig. 5.1.

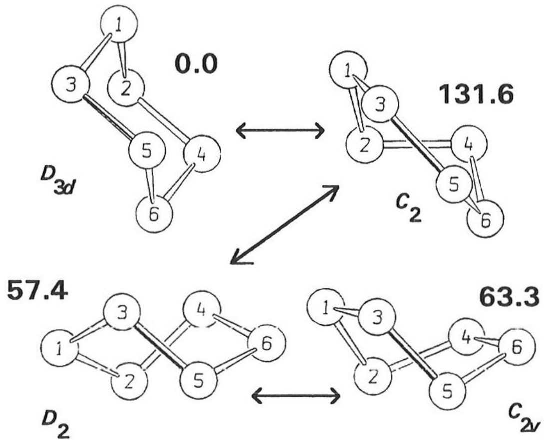


Figure 5.1 The pseudorotation about the bond between atoms 3 and 5 in S_6 leading to the inversion of the chair conformation to a boat conformation. Relative energies (in kJ mol^{-1}) are given at the MP2 level of theory.[III]

A twist conformation with C_2 molecular symmetry is the first intermediate formed during the pseudorotation. This transition state lies 131.6 kJ mol^{-1} above the ground state and represents the energy barrier for this pathway. Upon continued pseudorotation another twist conformation with D_2 molecular symmetry is formed. This can be viewed as a distorted boat and it lies 57.4 kJ mol^{-1} above the energy of the chair conformation. The boat conformation is easily reached from the D_2 twist and has a relative energy of 63.3 kJ mol^{-1} with respect to the chair conformation.

Since both above-mentioned pathways for inversion in S_6 have very high energy barriers, interconversion from the chair conformation to the boat conformation or *vice versa* is very unlikely. These high barriers explain why the boat conformation has not been observed for the neutral cyclic six-membered chalcogen molecules. They also indicate, however, that the boat conformation, if formed, should also be relatively stable against inversion to the chair conformation.

The pseudorotation scheme for cycloheptasulfur is shown in Fig. 5.2.

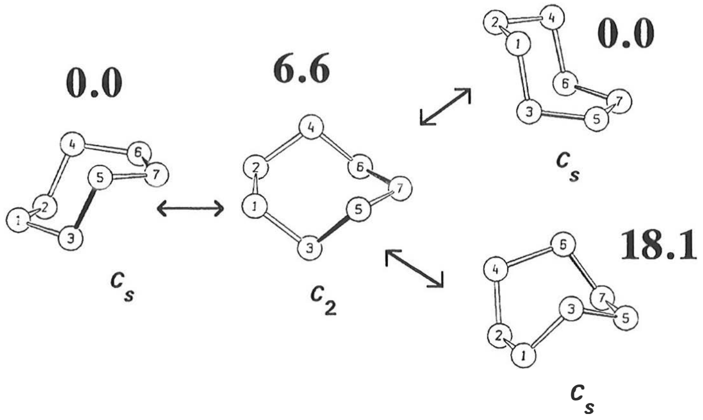


Figure 5.2 The pseudorotation in S_7. Relative energies (in kJ mol^{-1}) are given at the MP2 level of theory.[III]

The S_7 molecule has a ground state symmetry of C_s in the chair conformation consistent with the crystal structure information.[27] The pseudorotation of 90° about the unique bond (the bond between atoms 6 and 7 in Fig. 5.2) in C_s symmetry, with subsequent adjustment of all bond lengths and angles to accommodate the changed chemical environment of all sulfur atoms, creates a different, but identical S_7 molecule. It is easily seen that all S-S bonds have been shifted from their original positions. An intermediate transition state with C_2 symmetry is obtained upon the pseudorotation of 45°. From this intermediate an alternative pathway can also be conceived. It involves pseudorotation about the bond between atoms 1 and 2, which is unique in C_2 symmetry. This creates a molecule in the boat conformation with C_s molecular symmetry. As the pseudorotation process is repeated, it can be understood that all seven S-that all seven S-S bonds can exist in any position in every conformation. This concept of facile pseudorotation in the seven-membered chalcogen-containing ring molecules is consistent with the ^{77}Se NMR spectroscopic study of selenium sulfide 1,2,3,4,5-Se_5S_2.[28]

At the MP2 level of theory the C_2 intermediate lies only 6.6 kJ mol^{-1} above the ground state chair conformation. The difference in energies of the boat and chair conformations is only 18.1 kJ mol^{-1}. These values are in excellent agreement with the predicted barrier of pseudorotation, which from vapour-phase thermodynamic data[29] was estimated to be $\leq$ 24 kJ mol^{-1}.

6. PATHWAYS FOR INTERCONVERSION REACTIONS BETWEEN SULFUR AND SELENIUM RINGS

Many compounds containing cumulated S-S bonds undergo facile interconversion reactions in solution and in the molten state. Similar interconversion reactions have also been observed for selenium. The complicated mixtures of selenium sulfides formed with most preparative routes are most likely to result from the interconversion reactions.

Several pathways have been suggested for sulfur ring interconversion reactions.[30,31] Lack of rigorous experimental evidence renders all of them speculative. However, there is evidence that supports two possible mechanisms. The first, the formation of free radicals as primary intermediates, was favoured by the early workers.[32,33] However, radicals have not been detected for sulfur in organic solvents or in the molten state below the polymerisation threshold at *ca* 160 °C.[34,35] The second mechanism, shown in Fig. 6.1 and involving the hypervalent species (**I**) and (**II**) as intermediates, has been suggested by Steudel.[30] Although compounds containing the structural units (**I**) or (**II**) are unknown, a number of related species have been prepared or identified spectroscopically.

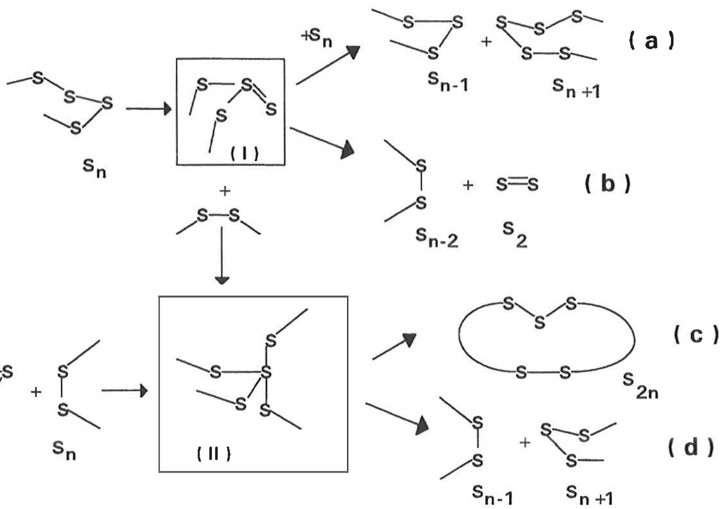


Figure 6.1 Suggested chalcogen ring interconversion pathways involving hypervalent intermediates (**I**) and (**II**).

It seems probable that there are several competing mechanisms, depending on the reaction conditions.[36] The unstable intermediate (**II**) can undergo pseudorotation at the central sulfur atom and dissociate in the two different fashions. Reaction (**d**) is in effect a "sulfur atom transfer" from one molecule to another and could therefore explain the formation of S_7 from S_8 and *vice versa*. This atom transfer can also be explained by reaction (**a**) from the intermediate (**I**).

In view of the similarity of the electronic structures of the S-S, S-Se and Se-Se bonds[20,21] it is possible that the interconversion reactions involving sulfur and selenium rings proceed in a manner similar to that described above. Reaction type (**d**) with the intermediate (**II**) was proposed for the formation of SeS_5 and 1,2,3-Se_3S_5 from 1,2-Se_2S_5 in CS_2-solution at 25 °C. [37]

Ab initio MO calculations were performed with the goal of estimating the energies of formation of the intermediates from the unbranched sulfur and selenium species. As calculations with the existing homocyclic and heterocyclic molecules containing selenium and sulfur or organic chain-like polysulfanes or polyselanes would be very time consuming, model reactions between sulfanes HS_nH ($n = 1,2$ or 4), selanes HSe_nH ($n = 1,2$ or 4) and selenosulfanes HS_nSe_mH ($n = 1\text{-}3$; $m = 1\text{-}3$; $n+m = 4$) have been studied.[IV]

As a starting point, HSH, HSeH, HSSH, HSeSeH, HS· and HSe· were fully optimised and their energies were calculated using the basis sets STO-3G,[14] 3-21G*,[16,17] and MIDI-4* of Huzinaga.[38,39] Using Huzinaga's notation, which gives the number of the primitive gaussians for each subshell in the form (*s/p/d/f*), these basis sets are compared (see Table 6.1).

Table 6.1 Composition of the basis sets STO-3G, 3-21G* and MIDI-4* using Huzinaga's[38] notation.

Basis set	Huzinaga's notation Sulfur	(*s/p/d/f*) Selenium
STO-3G	(333/33)	(333/33/3)
3-21G*	(3321/321) $+d_{\mathrm{pol}}$	(33321/3321/3) $+ d_{\mathrm{pol}}$
MIDI-4*	(4321/421) $+ d_{\mathrm{pol}}$	(43321/4321/4) $+ d_{\mathrm{pol}}$
El. config.	$1s^22s^22p^63s^23p^4$	$1s^22s^22p^63s^23p^63d^{10}4s^24p^4$

The MIDI-4* differs from 3-21G* by having four primitive gaussians instead of three for 1*s*, 2*p* and 3*d* orbitals. The split valence part is similar in both basis sets. The MIDI-4* uses different orbital exponents for *s* and *p* orbitals. The other two sets both use same exponents for *s* and *p* orbitals. So the MIDI-4* is more flexible leading to a better description of the single HF configuration.

The calculated internal coordinates for HSH, HSeH, HSSH, HSeSH, HSeSeH, HS· and HSe· are shown in Table 6.2.

As can be seen from Table 6.2, all three basis sets studied here can reproduce the internal coordinates of calculated molecules quite well. The energies of calculated species are given in Table 6.3, and the energies of chalcogen-chalcogen bond dissociation reactions calculated from them are given in Table 6.4.

The general trend in the experimental S-S and Se-Se bond strengths is that the Se-Se bond is weaker than the S-S bond. For example, D_0(S-S) = 268 kJ mol^{-1} in S_8 and D_0(Se-Se) = 172 kJ mol^{-1} in Se_6.[46] Another example is the measured bond strength for dichalcogen molecules,[29] $D_0(S_2)$ = 421.29 kJ mol^{-1}, D_0(SSe) = 367 kJ mol^{-1} and $D_0(Se_2)$ = 329.1 kJ mol^{-1}. In the present work, the order of the bond energies of S-S and Se-Se bonds when calculated using the STO-3G and 3-21G* basis sets was found to disagree with the experimental trend, and the Se-Se bond was the strongest; see Table 6.4. The MIDI-4* basis sets were able to give the right order for the stability of the chalcogen-chalcogen bonds considered here.

Table 6.2 STO-3G, 3-21G* and MIDI-4* optimised geometries of HSH, HSeH, HSSH, HSeSH, HSeSeH, HS· and HSe· [a]

		value			
Molecule	parameter	STO-3G	3-21G*	MIDI-4*	exptl.
HSH	r_{HS}	132.9	132.6	134.4	133.56 [b]
	α_{HSH}	92.5	94.2	93.8	92.11
HSeH	r_{HSe}	144.0	146.4	146.3	146.0 [c]
	α_{HSeH}	92.5	92.1	92.6	90.6
HSSH	r_{SS}	206.4	205.7	208.9	206.1 [d]
	r_{HS}	133.4	132.7	134.6	134.2
	α_{HSS}	96.5	99.0	98.3	97.5
	τ_{HSSH}	92.6	89.8	90.0	90.8
HSeSH	r_{SeS}	220.2	219.4	221.4	
	r_{HSe}	144.4	146.6	146.7	
	r_{HS}	133.4	132.7	134.5	
	α_{HSeS}	96.2	96.6	97.0	
	α_{HSSe}	96.4	99.0	98.0	
	τ_{HSeSH}	93.7	89.7	89.9	
HSeSeH	r_{SeSe}	233.2	231.4	233.7	
	r_{HSe}	144.4	146.6	146.6	
	α_{HSeSe}	95.7	97.0	96.8	
	τ_{HSeSeH}	94.6	89.7	89.8	
HS·	r_{HS}	133.7	133.0	134.9	134.5 [e]
HSe·	r_{HSe}	144.6	146.9	146.9	146.4 [f]

[a] Bond lengths are in pm and angles in deg. [b] Ref. 40. [c] Refs. 41 and 42. [d] Ref. 43. [e] Ref. 44. [f] Ref. 45.

Table 6.3 STO-3G, 3-21G* and MIDI-4* total energies (in a.u.) of HSSH, HSeSH, HSeSeH, HS· and HSe·.

Molecule	STO-3G	3-21G*			MIDI-4*		
	HF	HF	MP2	ZPE	HF	MP2	ZPE
HSSH	−787.49104	−792.48318	−792.72544	0.02013	−795.35293	−795.60039	0.01965
HSeSH	−2767.88232	−2785.51393	−2785.76010	0.01865	−2795.94423	−2796.18858	0.01831
HSeSeH	−4748.27330	−4778.54521	−4778.79538	0.01729	−4796.53659	−4796.77698	0.01699
HS·	−393.71028	−396.21804	−396.31832	0.00655	−397.65257	−397.75433	0.00643
HSe·	−2374.09959	−2389.24329	−2389.34831	0.00584	−2398.24740	−2398.34752	0.00580

Table 6.4 Energetics of the formation of the radical chalcogen hydrides (in kJ mol^{-1}) using STO-3G, 3-21G* and MIDI-4* basis sets.

Reaction	STO-3G	3-21G*			MIDI-4*			exptl.[a]
	HF	HF	MP2	MP2+ZPE	HF	MP2	MP2+ZPE	
HSSH → 2 HS·	185	124	233	215	126	241	223	276
HSeSH → HSe· + HS·	190	138	245	229	116	228	212	
HSeSeH → 2 HSe·	195	154	259	245	110	215	201	

[a] Ref. 48.

As can be seen from Table 6.5, the MIDI-4* basis sets fulfil the virial theorem quite well, and they are better balanced than 3-21G* basis sets.[18] Thus MIDI-4* basis sets were used in this work when selenium was present in the calculated species.[IV-VI]

Table 6.5. Values of the virial theorem –*V*/T for selected basis sets and species.

Species	STO-3G	3-21G*	MIDI-4*
S	2.0100	2.0077	2.0028
Se	2.0001	2.0016	2.0012
HSSH	2.0117	2.0075	2.0029
HSeSH	2.0020	2.0026	2.0015
HSeSeH	2.0003	2.0019	2.0013
HS·	2.0110	2.0076	2.0029
HSe·	2.0002	2.0017	2.0012

The MIDI-4* energetics of formation of radical hydrides and hypervalent chalcogen hydrides is summarised in Table 6.6.

The present calculations[IV] indicate that the formation of hypervalent intermediates of type **(I)** or **(II)**, Fig. 6.1, is energetically more favoured than the formation of free radicals. Model reactions involving intermediates of type **(I)** need less energy than other model reactions considered in this study. For insertion of the sulfur atom into the chalcogen-chalcogen bond, type **(I)** model reactions are more favourable energetically. For insertion of the selenium atom into the chalcogen-chalcogen bond, this study found that both type **(I)** and **(II)** model reactions involved comparable energy change. These results also provide support for the previous observations that in the case of heterocyclic selenium sulfides, interconversion involves a selenium-atom transfer rather than a sulfur-atom transfer.[47] The chain contraction of HSeSH into H_2SSe requires less energy than that into H_2SeS. At the same time bond, lengths and the atomic charges indicate that the chalcogen-chalcogen bond is somewhat weaker for H_2SSe; rendering the terminal selenium a better leaving group.

Table 6.6 Energetics of formation of hypervalent chalcogen hydrides (kJ mol^{-1}) IV

Reaction	HF	MP2	MP2+ZPE	Exptl.
Radical formation reactions:				
HSSH → 2 HS·	125.5	241.0	223.0	276.1 [a]
HSeSH → HSe· + HS·	116.3	227.6	217.6	
HSeSeH → 2 HSe·	109.6	215.1	200.8	
HSSSSH → 2 HSS·	64.7	172.0	162.5	146.4 [b]
HSeSSSH → HSeS· + HSS·	65.0	173.1	164.0	
HSSeSSH → HSSe· + HSS·	65.7	172.8	164.4	
HSeSeSSH → HSeSe· + HSS·	63.8	171.7	163.7	
HSeSSeSH → HSeS· + HSSe·	65.9	173.6	165.7	
HSeSSSeH → 2 HSeS·	64.7	173.7	165.1	
HSSeSeSH → 2 HSSe·	68.9	173.3	166.1	
HSeSeSeSH → HSeSe· + HSSe·	67.7	172.9	166.1	
HSeSeSSeH → HSeSe· + HSeS·	64.6	173.3	165.8	
HSeSeSeSeH → 2 HSeSe·	66.4	172.4	166.1	
Type (**I**) model reactions:				
HSSH → H_2SS	132.2	131.7	134.5	
HSeSH → H_2SeS	143.3	137.7	138.5	
HSeSH → H_2SSe	110.2	119.3	124.0	
HSeSeH → H_2SeSe	122.6	125.7	128.5	
Type (**II**) model reactions:				
HSH + HSSH → $H_2S(SH)_2$	242.7	163.8	174.9	
HSeH + HSSH → $H_2Se(SH)_2$	189.4	119.3	128.6	
HSH + HSeSH → $H_2S(SeH)SH$	244.3	166.4	177.6	
HSeH + HSeSH → $H_2Se(SeH)SH$	192.0	124.6	134.1	
HSH + HSeSeH → $H_2S(SeH)_2$	246.9	167.3	178.5	
HSeH + HSeSeH → $H_2Se(SeH)_2$	196.0	128.7	138.3	

[a] Ref. 48. [b] Ref. 49.

7. SELENIUM SULFUR NITRIDE RING MOLECULES

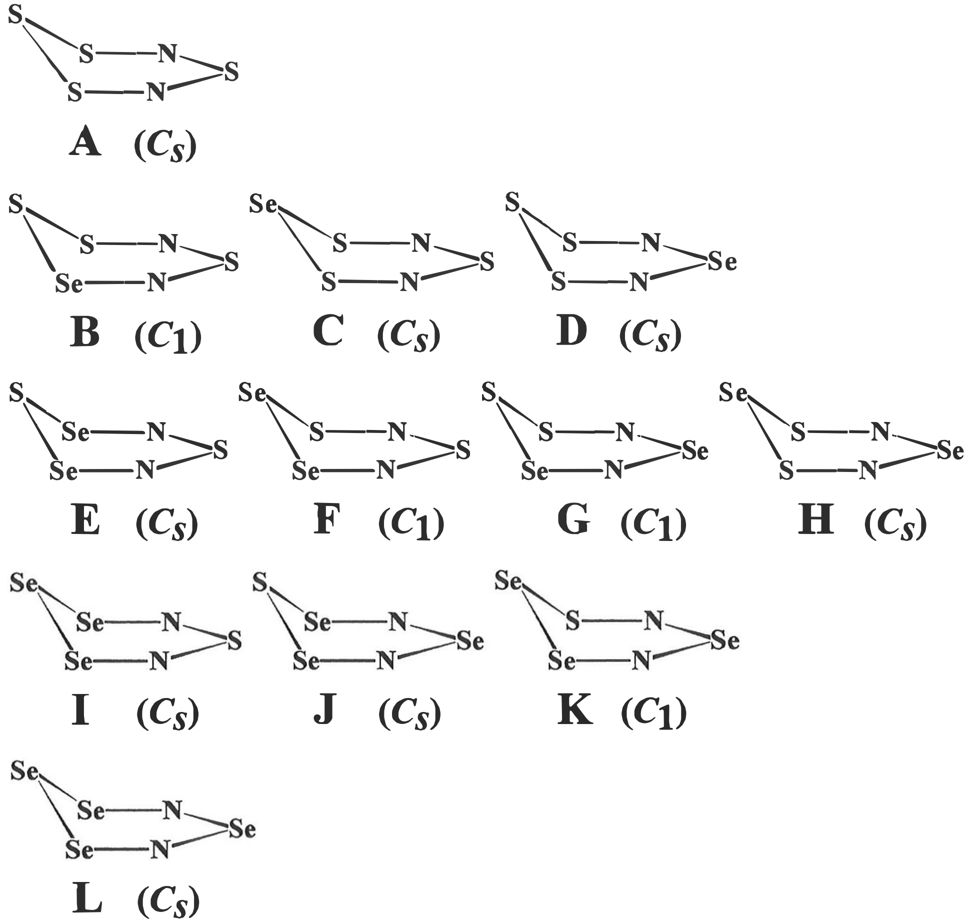
Sulfur and nitrogen form an extensive series of binary compounds,[50] most of which are cyclic. They are formed in a variety of reactions. Tetrasulfur tetranitride S_4N_4 is a molecular cage which has inspired many theoretical studies seeking to explain sulfur-nitrogen bonding.[50] The isostructural tetraselenium tetranitride Se_4N_4, was for long the only known selenium nitride, the other being the radical SeN.[51]

7.1 Six-membered ring molecules

The six-membered heterocyclic S_4N_2 is well known.[52] The existence of analogous selenium-containing heterocycles has been a matter of debate. Dehnicke *et. al.*[53] have reported the preparation of Se_4N_2, but reinvestigation showed the product to be violently unstable $Se_3N_2Cl_2$.[54,55]

All twelve members of the heterocyclic $Se_xS_{4-x}N_2$ (x = 0-4, see Fig. 7.1) species were fully optimized at the *ab initio* HF/MIDI-4* level of theory and a MP2 correction for electron correlation was performed using the optimized geometries. All molecules are remarkably similar and exhibit an optimum geometry with an approximate half-chair conformation that is well established experimentally for S_4N_2.[56-58] The fundamental vibrations were calculated at the HF/MIDI-4* level of theory. This serves to establish the nature of the stationary points. The numbering of the atoms and bonds is given in Fig. 7.2.

The optimized *ab initio* bond parameters are given in Table 7.1. The calculated bond parameters of S_4N_2 are in good agreement with the experimental ones. While there is no experimental information for other $Se_xS_{4-x}N_2$ species, their calculated bond parameters are reasonable when compared to those of S_4N_2. The chalcogen-chalcogen bonds in the NEEEN fragments (E = S, Se) show parameters expected for single bonds. The nitrogen-chalcogen bonds in this fragment also approach those of the single bonds. The bonds in the NEN units, on the other hand, are clearly shorter; indicating their double-bond character.



A (C_s) **B** (C_1) **C** (C_s) **D** (C_s) **E** (C_s) **F** (C_1) **G** (C_1) **H** (C_s) **I** (C_s) **J** (C_s) **K** (C_1) **L** (C_s)

Figure 7.1 The calculated heterocyclic $Se_xS_{4-x}N_2$ (x = 0 – 4) molecules, their molecular symmetries and the abbreviated notation.

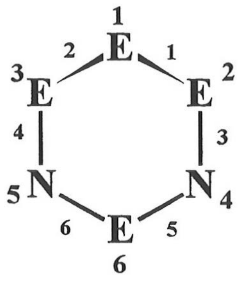


Figure 7.2 Numbering of the bonds and atoms in the $Se_xS_{4-x}N_2$ (x = 0 – 4) ring molecules.

Table 7.1 Optimized bond parameters of $Se_xS_{4-x}N_2$ (x = 0-4).[a]

Parameter	A calc.	A exptl.[b]	B	C	D	E	F	G	H	I	J	K	L
r_1 (pm)	208.5	206.1	208.6	221.2	208.7	221.3	221.4	221.4	208.6	233.7	221.4	221.6	233.9
r_2 (pm)	208.5	206.1	221.2	221.2	208.7	221.3	233.4	221.4	221.5	233.7	221.4	233.7	233.9
r_3 (pm)	171.7	167.5	171.7	171.8	170.8	184.5	171.7	170.9	170.6	184.6	183.7	170.7	183.7
r_4 (pm)	171.7	167.5	184.6	171.8	170.8	184.5	184.7	170.9	183.8	184.6	183.7	183.9	183.7
r_5 (pm)	154.8	156.1	154.8	154.8	168.2	154.3	154.8	168.2	168.1	154.3	167.6	168.2	167.6
r_6 (pm)	154.8	156.1	154.3	154.8	168.2	154.3	154.2	168.2	167.7	154.3	167.6	167.7	167.6
a_1 (deg)	99.8	102.9	99.8	96.0	101.4	99.7	96.0	97.6	101.4	96.0	101.3	97.7	97.7
a_2 (deg)	102.9	103.4	104.1	102.9	104.1	101.0	104.0	104.1	105.2	101.1	102.0	105.1	102.1
a_3 (deg)	102.9	103.4	104.1	102.9	104.1	101.0	99.7	104.1	100.8	101.1	102.0	100.9	102.1
a_4 (deg)	126.0	126.7	127.3	127.0	125.1	127.6	128.1	126.1	127.0	128.6	126.7	127.7	127.7
a_5 (deg)	126.0	126.7	126.3	127.0	125.1	127.6	127.5	126.1	124.8	128.6	126.7	126.2	127.7
a_6 (deg)	123.4	122.9	120.1	124.2	120.1	124.7	124.8	121.0	121.0	125.4	121.7	121.8	122.5
t_1 (deg)	−60.8	−57.5	−61.5	−59.9	−62.8	−59.4	−60.9	−61.8	−62.5	−58.7	−61.5	−62.2	−60.6
t_2 (deg)	60.8	57.5	59.0	59.9	62.8	59.4	58.0	61.8	61.9	58.7	61.5	60.4	60.6
t_3 (deg)	37.2	34.9	38.5	38.8	37.4	37.0	40.5	39.1	37.0	38.5	37.1	39.6	38.6
t_4 (deg)	−37.2	−34.9	−35.8	−38.8	−37.4	−37.0	−36.9	−39.1	−37.7	−38.5	−37.1	−38.2	−38.6
t_5 (deg)	−5.5	−5.9	−5.5	−6.1	−5.9	−5.6	−6.2	−6.7	−5.1	−6.0	−5.9	−6.2	−6.4
t_6 (deg)	5.5	5.9	5.7	6.1	5.9	5.6	5.8	6.7	7.2	6.0	5.9	7.1	6.4

[a] For the notation of the different isomers, see Figure 7.1. For the numbering of atoms and bonds, see Figure 7.2. [b] Ref. 57.

The calculated HF/MIDI-4* fundamental vibrations are given in Table 7.2 and they indicate that all molecules lie in the true local energy minima. For S_4N_2 the calculated fundamental vibrations are in fair agreement with the experimental IR spectrum.[57] For Se_4N_2 the vibrations found in the present study are in fair agreement with those calculated with 3-21G* basis sets by Dehnicke *et al.*[53] For other molecules in the series studied in this work, the calculated fundamental vibrations show differences between different isomers. It is reasonable to predict that these vibrations can be of use in assisting the assignment of experimental IR and Raman spectra of these compounds in the future.

The total energies and binding energies are given in Table 7.3. All calculated species are stable when compared to free atoms.

Table 7.3 Total energies of free atoms and $Se_xS_{4-x}N_2$ (x = 0-4) ring molecules (in a.u.).

Species [a]		Total Energy			Binding energy
		HF/MIDI-4*	MP2/MIDI-4* //HF/MIDI-4*	ZPE	MP2+ZPE
N		−54.29070	−54.36283		
S		−397.06579	−397.14651		
Se		−2397.67269	−2397.75314		
S_4N_2	**A**	−1696.94461	−1697.81210	0.01570	0.48470
SeS_3N_2	**B**	−3697.54189	−3698.40796	0.01485	0.47478
	C	−3697.54158	−3698.40753	0.01490	0.47430
	D	−3697.51439	−3698.39987	0.01403	0.46751
$Se_2S_2N_2$	**E**	−5698.13969	−5699.00411	0.01400	0.46515
	F	−5698.14006	−5699.00357	0.01407	0.46454
	G	−5698.11146	−5698.99527	0.01323	0.45708
	H	−5698.11143	−5698.99519	0.01320	0.45703
Se_3SN_2	**I**	−7698.73902	−7699.60001	0.01323	0.45519
	J	−7698.70891	−7699.59071	0.01236	0.44676
	K	−7698.70945	−7699.59042	0.01241	0.44642
Se_4N_2	**L**	−9699.30830	−9700.18670	0.01160	0.44642

[a] For the notation of the different isomers, see Figure 7.1.

Table 7.2 Fundamental vibrations of the $Se_xS_{4-x}N_2$ (x = 0-4) isomers (in cm^{-1}).

S_4N_2		SeS_3N_2			$Se_2S_2N_2$				Se_3SN_2			Se_4N_2	
A		**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	
MIDI-4*	Obs [a]	MIDI-4*			MIDI-4*				MIDI-4*			MIDI-4*	3-21G* [b]
1116 *a"*	1034	1115	1116 *a"*		1115 *a"*	1115			1114 *a"*				
1014 *a'*	918	1020	1013 *a'*		1025 *a'*	1020			1025 *a'*				
				973 *a"*			946 *a"*	940		932 *a"*	939	931 *a"*	951 *a"*
				910 *a'*			901 *a'*	902		909 *a'*	903	910 *a'*	939 *a'*
647 *a'*	635	632	637 *a'*			624							
628 *a"*	628				608 *a'*		602 *a'*		600 *a'*				
		593	626 *a"*	585 *a'*		587		593			590	547 *a'*	509 *a'*
				566 *a"*			578 *a"*						
546 *a'*	561		539 *a'*		534 *a"*			538	531 *a"*	557 *a'*	531		
481 *a'*		480								500 *a"*		495 *a"*	
464 *a"*	469	470		453 *a'*		473		464					458 *a"*
				428 *a'*	435 *a'*		432 *a'*		431 *a'*				
			406 *a'*			389		394			404		
		382			380 *a"*		383 *a'*			375 *a"*			
365 *a'*			370 *a"*		379 *a'*			371		374 *a'*			
		353	347 *a'*				359 *a"*				366		
305 *a"*	322				339 *a'*	339			336 *a'*	330 *a'*		324 *a'*	326 *a'*
				288 *a"*									
		272	281 *a"*	282 *a'*		275	280 *a'*	282	276 *a'*		276	277 *a'*	277 *a"*
262 *a'*	266						264 *a"*		269 *a"*	267 *a'*	266	264 *a"*	258 *a'*
				223 *a"*	235 *a"*	252		239	225 *a"*		227	256 *a'*	258 *a'*
		215	211 *a'*	195 *a'*	183 *a'*	180	191 *a'*	197		211 *a"*		203 *a"*	212 *a"*
171 *a'*		151		153 *a'*					152 *a'*	164 *a'*	165		
			138 *a'*									138 *a'*	138 *a'*
134 *a"*			136 *a"*		125 *a'*	126	118 *a'*	135					
		118		103 *a"*	109 *a"*	116	114 *a"*	109	112 *a"*	117 *a'*	103		107 *a"*
									99 *a'*	91 *a"*	98	95 *a"*	
												89 *a'*	85 *a'*

[a] Ref. 57 [b] Ref. 53.

The total binding energy of each isomer is shown in Fig. 7.3.

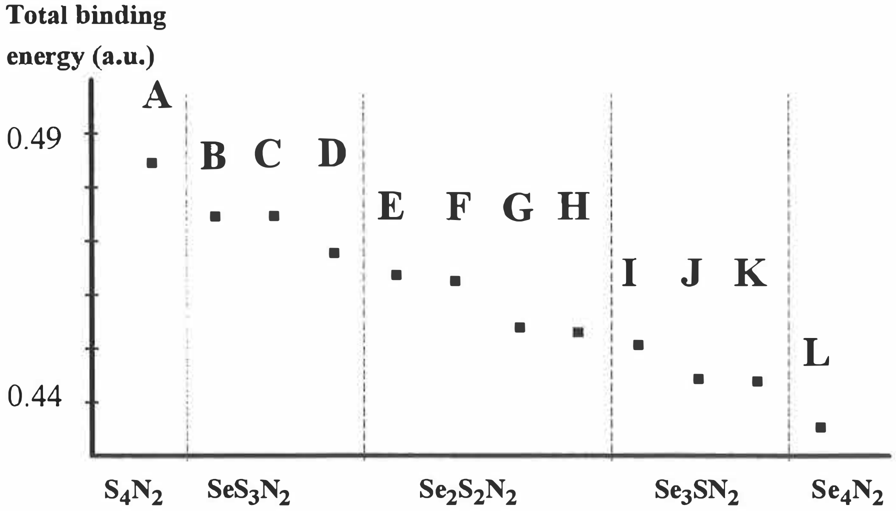


Figure 7.3. Total binding energies of $Se_xS_{4-x}N_2$ (x = 0-4). For the notation of the different isomers, see Fig. 7.1.

The total binding energy diminishes as the selenium content of the molecule increases. Within a given composition isomers containing a NSeN unit show less binding than those containing a NSN unit. This is shown in Fig. 7.4. From the energy values it can be seen that the NSeN unit is *ca.* 20 kJ mol^{-1} less stable than the NSN unit. The selenium atoms are therefore preferably located in the NEEEN unit (E = S, Se). The relative energies of the isomers seem to be virtually independent of the distribution of sulfur and selenium atoms within this fragment.[V]

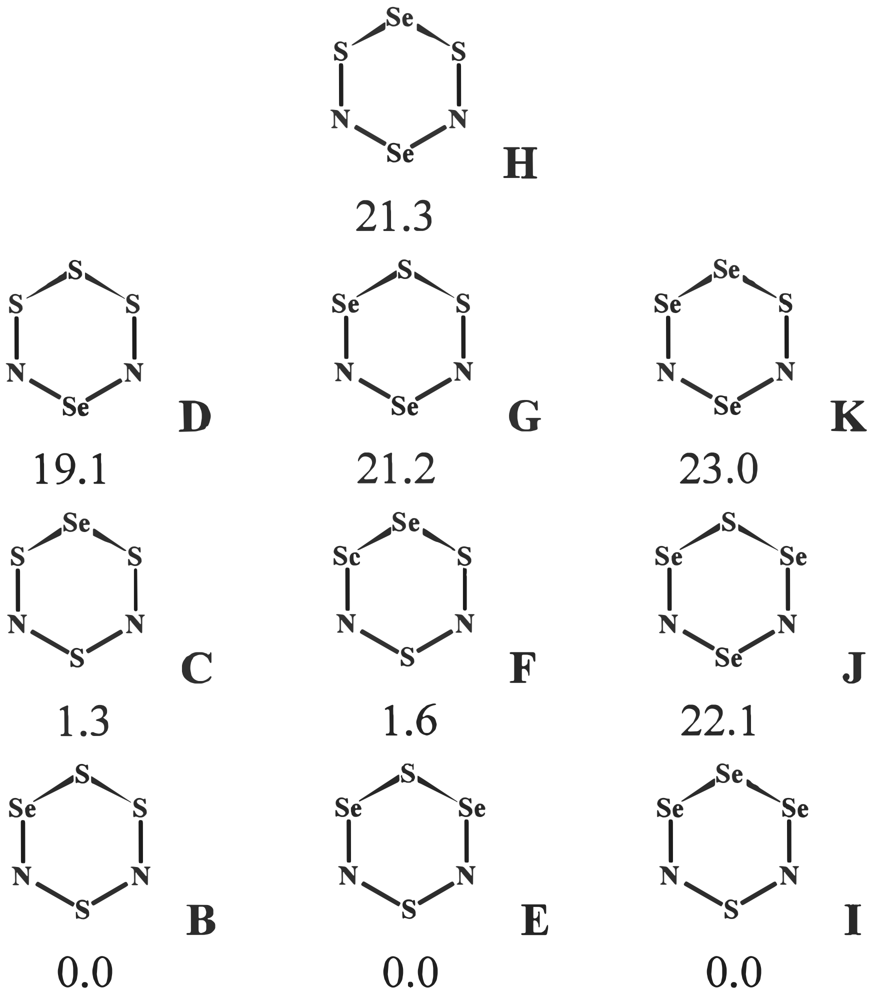


Figure 7.4 Relative energies (kJ mol^{-1}) of the different isomers of SeS_3N_2, $Se_2S_2N_2$, and Se_3SN_2 calculated at the MP2/MIDI-4*//HF/MIDI-4* + ZPE level of theory.

7.2 Eight-membered rings

The crystal structure of S_4N_4 has shown that the molecule has a cage-structure with unusual cross-ring sulfur-sulfur bonding interaction.[59,60] Se_4N_4 exists in two crystalline modifications.[61-65] Both modifications have a molecular structure and intramolecular bonding similar to those observed for S_4N_4, but the most stable polymorph is not isostructural with S_4N_4; reflecting the differences in molecular packing. When

Se_4N_4 is recrystallized in liquid ammonia at 70 °C, a metastable phase isostructural with S_4N_4 is obtained.

There is very little experimental information on the existence of analogous mixed sulfur-selenium tetranitrides $Se_nS_{4-n}N_4$. Due to the similarity in bonding and molecular structures of S_4N_4 and Se_4N_4 it is reasonable to expect that the mixed species also show a similar cage.

We have performed an *ab initio* MO study [VI] on the complete series of $Se_nS_{4-n}N_4$ (n = 0-4) using the same procedures as were employed in the study of the six-membered $Se_xS_{4-x}N_2$ molecules.[V] The general conformation of all $Se_nS_{4-n}N_4$ (n = 0-4) species is fairly similar and is shown in Fig. 7.5 with the ranges of optimized bond parameters. More detailed parameters for each molecule are given in Table 7.3.

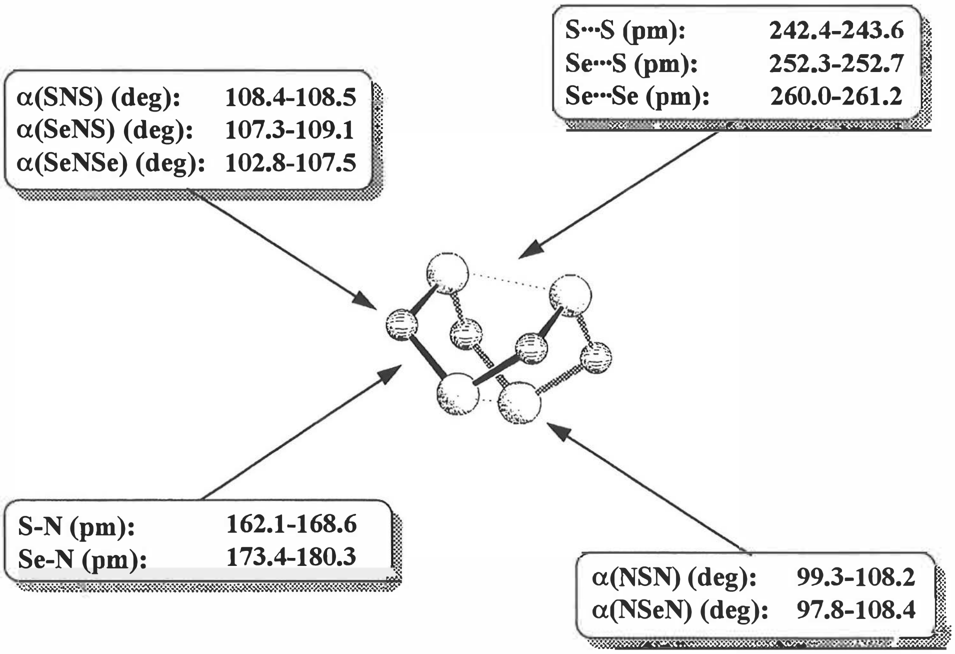


Figure 7.5 The geometry of the $Se_nS_{4-n}N_4$ (n = 0-4) molecules.[VI] The range of the optimized HF/MIDI-4* parameters is indicated in the figure. For more detailed information on the individual molecules, see Table 7.3.

Table 7.3. Optimized bond parameters of $Se_nS_{4-n}N_4$ (n = 0-4) molecules [distances in pm, angles in deg.].

Molecule	Point group	Parameter	Calc.	Exptl.[a]	Molecule	Point group	Parameter	Calc.	Exptl.[b]
S_4N_4	D_{2d}	r(SN)	164.6	162.6	$Se_2S_2N_4$	C_{2v}	r(SN)	164.9	
		r(S...S)	243.0	259.3			r(SeN)	177.2	
		a(SNS)	107.6	112.7			r(S...S)	242.4	
		a(NSN)	103.7	104.5			r(Se...Se)	260.0	
							a(SeNS)	107.9	
SeS_3N_4	C_s	r(SN)	162.1, 167.7, 168.				a(NSN)	108.2	
		r(SeN)	173.4				a(NSeN)	97.8	
		r(S...S)	243.6						
		r(Se...S)	252.3		Se_3SN_4	C_s	r(SN)	168.5	
		a(SNS)	108.5				r(SeN)	173.9, 174.6, 180.3	
		a(SeNS)	107.3				r(Se...S)	252.7	
		a(NSN)	99.3, 106.1				r(Se...Se)	261.2	
		a(NSeN)	102.3				a(SeNS)	109.1	
							a(SeNSe)	107.5	
$Se_2S_2N_4$	C_2	r(SN)	165.1, 166.0				a(NSN)	104.0	
		r(SeN)	175.9, 176.8				a(NSeN)	100.5, 107.2	
		r(Se...S)	252.6						
		a(SNS)	108.4		Se_4N_4	D_{2d}	r(SeN)	177.3	176.9-180.0
		a(SeNS)	108.1				r(Se...Se)	261.2	274.7
		a(SeNSe)	103.4				a(SeNSe)	102.8	102.0-102.3
		a(NSN)	103.1				a(NSeN)	108.4	110.7-113.7
		a(NSeN)	107.9						

[a] Ref. 59. [b] Ref. 63.

The calculated bond parameters are well predicted in the case of S_4N_4 and Se_4N_4, for which experimental information is available. It is therefore conceivable that the present method can also be used to predict reliably the geometries of the mixed tetrachalcogen tetranitrides.

The total binding energies are given in Table 7.4.[VI] The trends in binding are reproduced by our calculations, that explain *ca.* 75 % of the experimental binding energy that is reasonable for the basis sets used in this work.[66]

Table 7.4 Total binding energies of $Se_nS_{4-n}N_4$ (n = 0-4) molecules (in kJ mol^{-1}). Energies corrected with zero point energies are given in parentheses. [a]

Molecule	HF/MIDI-4*	MP2/MIDI-4* //HF/MIDI-4*	Exptl. [b]
S_4N_4	109 (50)	1817 (1758)	2408
SeS_3N_4	55 (-1)	1740 (1684)	
$Se_2S_2N_4$	23 (-31)	1676 (1621)	
	21 (-32)	1680 (1626)	
Se_3SN_4	-27 (-77)	1603 (1552)	
Se_4N_4	-55 (-103)	1542 (1494)	1976

[a] The total binding energy of a molecule has been defined as a difference of its total energy and that of the free atoms constituting the molecule. [b] Refs. 67 and 68.

With a few notable exceptions, the calculated vibrations presented in Table 7.5 show fair agreement with the observed frequencies of both S_4N_4 and Se_4N_4. The calculated frequencies may therefore be used to assist the interpretation of the vibrational spectra of the $Se_nS_{4-n}N_4$ molecules, and thus IR and Raman spectroscopy can prove to be useful tools for the identification of the hitherto unknown mixed species.

Our calculations indicate that it should be possible to synthesise mixed $Se_nS_{4-n}N_4$ (n = 0-4) molecules possessing a cage-structure similar to that found in S_4N_4 and Se_4N_4.

Table 7.5 Fundamental vibrations of $\mathrm{Se}_n\mathrm{S}_{4-n}\mathrm{N}_4$ (n = 0-4) (in cm^{-1}).[VI]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
S_4N_4																		
D_{2d}	214	256	285		346	368	532		545	569		703	715		724	728	740	882
Raman [a]	201	218	*i*		344	224	550		524	558		701	*i*		925	720	-	765
	b_2	a_1	a_2		e	b_1	b_2		e	a_1		e	a_2		e	a_1	b_1	b_2
SeS_3N_4																		
C_s	188	229	261	332	337	350	412	506	530	545	627	642	662	676	713	757	765	874
	a'	a'	a''	a''	a'	a''	a'	a'	a''	a'	a''	a''	a'	a'	a''	a'	a''	a'
$Se_2S_2N_4$																		
C_{2v}	169	229	237	300	320	350	358	435	503	508	630	639	665	676	677	727	739	836
	a_1	a_2	a_1	a_2	a_2	b_1	b_2	a_1	a_1	b_1	b_1	a_2	b_2	a_1	b_1	a_2	b_2	a_1
C_2	183	202	248	286	318	339	355	432	490	542	626	655	672	673	688	704	718	837
	b	a	a	a	b	a	a	b	b	a	a	b	a	b	a	b	a	b
Se_3SN_4																		
C_s	163	191	223	263	292	319	348	351	443	484	591	595	634	635	694	701	713	815
	a'	a'	a''	a''	a''	a'	a'	a''	a'	a'	a''	a'	a'	a''	a''	a'	a''	a'
Se_4N_4																		
D_{2d}	161	172	217	227		283		334	341	427		606	616	634	659		669	785
Raman [b]	-	154	*i*	-		261		-	381	-		-	-	621	*i*		787	-
	b_2	a_1	a_2	b_1		e		e	a_1	b_2		e	b_1	a_1	a_2		e	b_2

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[a] Ref. 69. [b] Ref. 70.

8. CONCLUSIONS

Molecular orbital calculations, at the level of theory presented in this study, can be used to explain and predict chalcogen chemistry in fair agreement with experimental findings, where these are available.

The findings of this study can be summarised as follows:

Molecular valence calculations using pseudopotential can be used for sulfur molecules. In this study the method was shown to reproduce the corresponding geometries and energetics of small sulfur molecules S_2 – S_5 established using the full *ab initio* calculations reported in the literature. The present method was even able to recover some of the electron correlation via the inner core pseudopotential.

The comparison of the energies between different isomers of the same sulfur molecule can be made in reasonable semiquantitative fashion when using *ab initio* HF-SCF optimised geometries followed by MP2 correction to the energies. For S_6 and S_7, calculated results agree with experimental findings when studying pseudorotation effects in these cyclic molecules.

Ab initio MO calculations, even at the present level of theory (MP2/MIDI-4*//HF/MIDI-4* + ZPE), can give support for the study of reaction pathways, which are often difficult to study experimentally. Two possible model reaction pathways (**I**) and (**II**) suggested in the literature involving hypervalent chalcogen intermediates are both favourable for selenium insertion into the E–E bond (E = S, Se), but the insertion of sulfur is more likely to proceed via type (**I**) model reaction pathways.

Ab initio MO calculations were shown to be useful as assisting the experimental work in predicting the relative stabilities and geometries of different isomers of cyclic sulfur and selenium nitrides. Assignment of experimental vibrational spectra should be possible using calculated fundamental frequencies and geometries.

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