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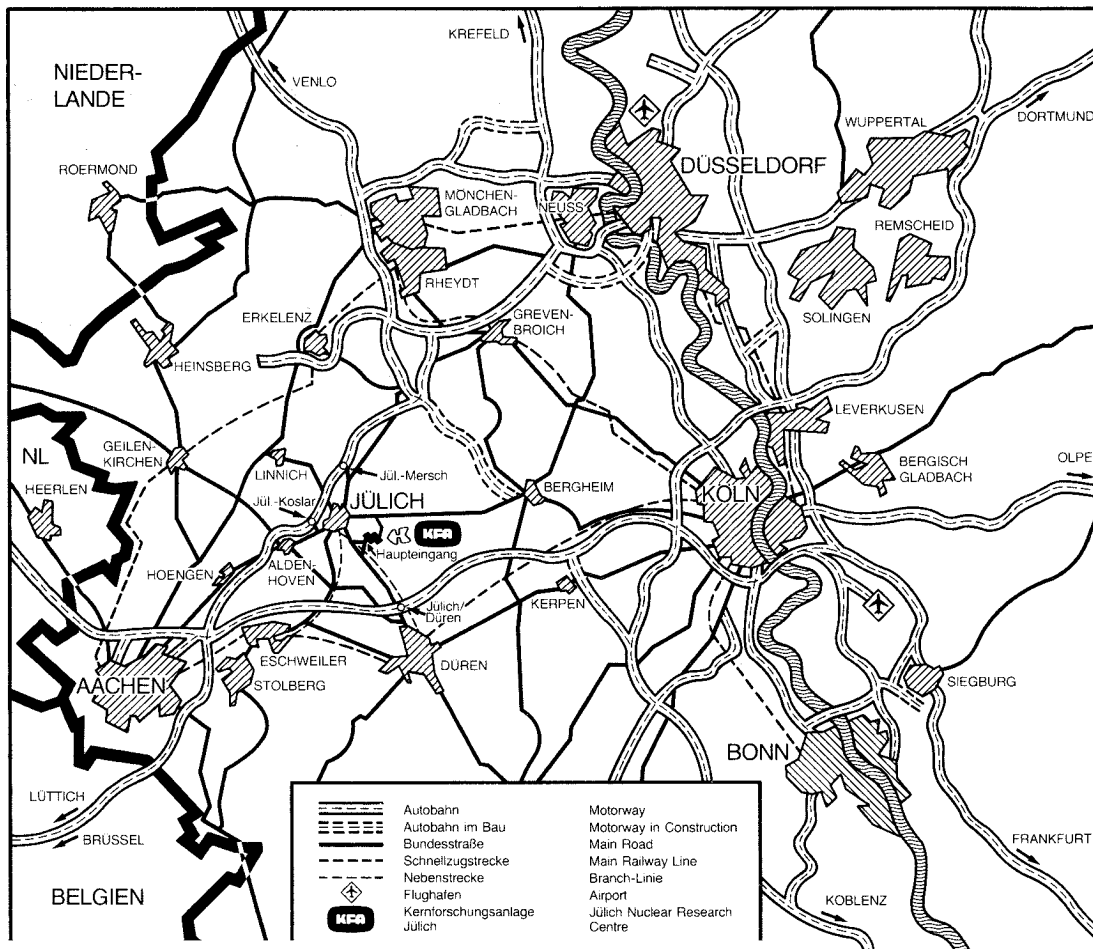
**Unified Molecular Dynamics and
Density Functional Calculations
for Group VIA Clusters**

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1. INTRODUCTION

The determination of ground state structures and other properties of clusters and molecules is an important goal in molecular physics and chemistry, and the associated problems fall into two main categories: (i) finding a reliable method for calculating the total energy E for fixed atomic positions $\{\mathbf{R}_I\}$, (ii) minimizing E with respect to variations in $\{\mathbf{R}_I\}$. While the difficulties in calculating E are well known, systematic procedures to locate global minima in configuration space – $\min_{\{\mathbf{R}_I\}} E[\{\mathbf{R}_I\}]$ – have received less attention. Assuming N atoms in a cluster, the total number of internal coordinates is $3N - 6$, since the energy of the (non-linear) cluster is invariant to rotations and translations. In a 10-atom cluster, for example, there are 24 independent interatomic degrees of freedom and the magnitude of the problem is apparent: (1) Finding the energy minimum by calculating the energy for all possible geometries is obviously impracticable, since 10 calculations per coordinate would lead to 10^{24} calculations in a cluster where *one* seems already to be very difficult. (2) If one takes any particular geometry and locates the *next* local minimum, there is still little prospect of success. As we now show, the number of local minima in the energy surface can be very large.

Tab. 1: Number M of local minima in clusters of N particles interacting with a Lennard-Jones potential (Hoare and McInnes).

N	M
6	2
7	4
8	8
9	18
10	57
11	145
12	366
13	988

Hoare and McInnes¹ have studied clusters where the atoms interact with each

other with a simple, pairwise Lennard-Jones potential:

$$V_{\text{Lennard-Jones}} = 4\epsilon_0 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

For small clusters it is possible to locate all the minima, and the results are shown for clusters of different sizes in Tab. 1. The number of minima increases rapidly with increasing N , showing signs that the increase is exponential. For clusters of identical atoms interacting with a pairwise potential, Wille and Vennik² have shown, in fact, that there is no known algorithm that grows with time as power of N and with which one can determine the ground state energy and structure. Such problems are classified as “ $NP - hard$ ”³ (non-polynomial) and are considered “intractable”. For sufficiently small clusters, the global minimum can still be determined by locating and enumerating *all* the local minima. However, the search is confined in practice to small parts of configuration space based on intuition, experimental information and/or symmetry restrictions.

In systems where the ground state is unknown or where there are many local minima, it is necessary to develop alternative methods for finding solutions which are near to optimal. Kirkpatrick *et al.*⁴ noted the connection between statistical physics and the minimization of a function of many variables, and suggested “simulated annealing” based on a Monte Carlo sampling as a generally applicable way of finding such solutions. It has been shown recently⁵ that simulated annealing can lead to *nearly* optimal solutions of special NP-complete problems in polynomial average time.

Molecular dynamics (MD) provides an alternative to the Monte Carlo approach, and Car and Parrinello⁶ showed that it could be combined with the density functional (DF) scheme for calculating total energies. The result is a parameter-free method for calculating electronic properties which makes no assumptions about ground state geometries. Finite temperature MD techniques allow an efficient sampling of the potential energy surface, and the DF method,^{7,8} with the local spin density (LSD) approximation for the exchange-correlation energy, does not require the parametrization of the interatomic forces common in MD schemes.⁹ In the context of group VIA molecules, the DF approach has been applied with success to triatomic molecules¹⁰ and to helical chains of sulphur and selenium.¹¹ Calculated geometries agree well with experimental values where available, and the *systematic* overestimate of bond strengths [by ~ 1 eV per bond] means that bonding trends are given reliably.

The group VIA elements (O, S, Se, Te, Po) show a range of structures unmatched

in the periodic table.¹² Sulphur, in particular, has the largest number of allotropes of any element, with many comprising cyclic molecules, S_n , with $n \geq 6$.^{12,13} Sulphur clusters are present in the vapour phase (the main constituents up to ~ 800 K are S_6 , S_7 and S_8 ,¹³ and all clusters up to S_{56} have been identified¹⁴), in crystals (S_{6-13} , S_{18} , S_{20}), and in the liquid.¹⁵ While most elements form clusters which are difficult to characterize, the S_n structures have been determined by X-ray structural analyses for $n = 6-8, 10-13, 18, 20$.¹³ No simple structural model has yet been able to account for the characteristic variations of shape with the number of atoms. Semi-empirical MNDO and SINDO1 calculations have been performed for S_3 to S_8 ¹⁶ and S_2 , S_4 , S_6 and S_8 ,¹⁷ respectively. In the context of a molecular dynamics simulation for liquid sulphur, using parametrized pair and three-body forces, Stillinger *et al.*⁹ presented results for some small sulphur clusters. In this work (Chap. 3) the novel MD/DF method⁶ is applied to calculate the energy surfaces and electronic structures of sulphur clusters with up to 13 atoms. This represents the first parameter-free study of sulphur clusters of this size.

Although often discussed as an analog of sulphur, selenium shows qualitative differences in the vapour, liquid and solid phases. The main constituents of sulphur vapour up to ~ 800 K are S_6 , S_7 and S_8 ,¹³ with only minute amounts of smaller molecules. For *Se* in the same temperature range Se_5 , Se_6 and Se_7 predominate, with only traces of Se_8 .¹⁸ Crystalline S_8 melts at about 391 K to give a low viscosity liquid comprising S_8 molecules, and polymerizes into long chains above 435 K. Melting thermodynamically metastable crystalline Se_8 on the other hand proceeds via polymerization in the solid phase (between 418 K and 430 K) to a high viscosity liquid at about 490 K, the melting point of trigonal *Se*.¹⁸ Clusters of selenium occur in the vapour phase, in crystalline modifications (Se_{6-8}), and as major constituents of the liquids.^{18,15} Amorphous *Se* does not contain significant amounts of Se_n molecules, but small ring fragments appear to be incorporated into the infinite chains present.¹⁹ Reliable structural data for selenium clusters are limited to the crystalline phases of Se_6 ²⁰ and Se_8 ,²¹ although all Se_n ($n=2-9$) have been identified mass-spectrometrically.^{22,23} A study of the total energy surfaces of *Se* clusters should then predict the structures of Se_{3-5} , Se_7 , contribute to the understanding of Se_6 and Se_8 , and guide future investigations of the highly complex liquid and amorphous phases. No such study has been published yet. Chap. 4 therefore contains the first study of selenium clusters with a parameter-free method.

While the substitution of *Se* into *S*-rings leads to little change in ground state topologies (see Sect. 5.2), molecules containing oxygen are found to have the *O*-

atoms bonded to a closed S_n ring, i.e. $-S-O-S-$ bridge bonds are not favoured. To the best of our knowledge, compounds of the type $R-S-O-S-R'$ have only been postulated²⁴ as unstable reaction intermediates. This applies also to the aromatic sulfenic anhydrides $Ar-S-O-S-Ar$ reported repeatedly as stable products.²⁵ Rather, the corresponding hydrolysis of aromatic sulfenic chlorides $Ar-S-Cl$ was shown to lead to mixtures of thiolsulfonates $Ar-SO_2-S-Ar$ and disulfides $Ar-S-S-Ar$, presumably via the thiolsulfinate $Ar-SO-S-Ar$.²⁶ Sec. 5.1 presents the (successful) attempt to find the most stable isomer of a sulphur-oxygen compound (S_7O) starting from a topologically different initial geometry. Similar model calculations of chemical rearrangement reactions have previously been attempted only with empirical or semi-empirical quantum chemical methods. It also contains the geometries of several local minima in the energy surfaces of S_7O .

It is natural that mixtures of sulphur and selenium have also received much attention, not only in the vapour phase,^{27,28} but also as liquids or as solid solutions.^{29,30,31} Most samples prepared in the laboratory appear to comprise a range of molecules, and the characterization of the crystalline phases obtained from the melts has been difficult. The different Se_xS_y species crystallize together, so that the crystal structures reported are disordered with sulphur and selenium atoms distributed over the atomic sites.³² The possible complexity is evident from the example of eight-membered rings, where 30 different crown-shaped isomers can occur.

Sulphur and selenium have much in common and it is not surprising that mixed isomers have similar energies and can coexist. The identification and structure of the molecular units in heterocyclic $Se-S$ systems have been the subjects of continuing interest. Apart from the intrinsic interest in the molecules, an understanding of their structures should provide insight into the very complicated structures of related liquid and amorphous materials, including Se itself. Early kinetic work^{27,28} on the molecules was interpreted to exclude the possibility of $Se-Se$ bonds in S_nSe_{8-n} rings, and this was traced²⁷ to the fact that the $Se-Se$ bond is weaker than both $S-S$ and $Se-S$ bonds. Raman spectroscopy has shown, however, that $Se-Se$ stretching vibrations can readily be identified in such structures,³³ even for mixtures with very low Se concentrations. On the other hand, the $S-S$ stretching band was not seen if the nominal sulphur content dropped below that in Se_6S_2 , suggesting that the formation of $S-S$ homonuclear bonds is not favoured in mixed crystals with low sulphur content. The measurements indicate an apparent asymmetry between S -rich and Se -rich molecules, and this too was attributed to the relative weakness of $Se-Se$ bonds.³³ Sec. 5.2 presents ground state geometries and relative energies

of all isomers of the cyclic molecules Se_2S_6 , Se_6S_2 , Se_2S_5 and Se_5S_2 . We believe that this is the most extensive parameter-free study of mixed group VIA clusters to date.

The method used is described in Chap. 2, and concluding remarks and future prospects are found in Chap. 6.

2. METHOD OF CALCULATION

2.1. DENSITY FUNCTIONAL (DF) ASPECTS

The density functional formalism⁸ shows that a knowledge of the electron density, $n(\mathbf{r})$, is sufficient to determine the total energy and other ground state properties of a system of electrons in an external field, V_{ext} . The ground state energy, E_{gs} , can be found by minimizing the relationship between energy and density, $E[n]$, and this minimum is found for the ground state density, n_{gs} . It is convenient to write³⁴

$$E[n] = T_0[n] + \int d\mathbf{r} n(\mathbf{r}) \left(V_{ext}(\mathbf{r}) + \frac{1}{2} \Phi(\mathbf{r}) \right) + E_{xc}[n], \quad (2.1)$$

where T_0 is the kinetic energy which a system with density n would have in the absence of electron-electron interactions, $\Phi(\mathbf{r})$ is the classical Coulomb potential for electrons, and E_{xc} is the exchange-correlation energy. Since all terms in (1) except E_{xc} may be evaluated with arbitrary accuracy, approximations to the exchange-correlation energy play a central role in this theory. We adopt the widely used LSD approximation,

$$E_{xc}^{LSD} = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})], \quad (2.2)$$

where $\varepsilon_{xc}[n_{\uparrow}, n_{\downarrow}]$ is the exchange and correlation energy per particle of a homogeneous, spin-polarized electron gas with spin-up and spin-down densities $n_{\uparrow}$ and $n_{\downarrow}$, respectively. Thus one approximates the exchange-correlation energy of an inhomogeneous electron gas by the one of the homogeneous electron gas, corresponding to a locally slowly varying charge density $n(\mathbf{r})$. The LSD approximation yields reliable binding energy trends and equilibrium structures for a variety of molecules and solids.⁸ In the present calculations we use the electron gas parametrization of Vosko *et al.*³⁵

For a given set of atomic coordinates $\{\mathbf{R}_I\}$, the minimization of $E[n]$ in eq. (1) is usually performed by solving the Kohn-Sham equation

$$\left(-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + \Phi(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.3)$$

where $V_{xc} = \delta E_{xc} / \delta n(\mathbf{r})$. The density can be constructed from the eigenfunctions of this equation, $n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$, with i running over all occupied states. The procedure must be continued until self-consistency is reached.

We have chosen a pseudopotential representation of the electron-ion interaction,³⁶ V_{ext} ,

$$V_{ext}(\mathbf{r}) = \sum_I v_{ps}(\mathbf{r} - \mathbf{R}_I) \quad (2.4)$$

Local pseudopotentials avoid most of the complications associated with the use of the more generally applicable nonlocal potentials (see below for details). It is, however,

- sometimes impossible to derive local pseudopotentials leading to nodeless atomic valence pseudo-eigenfunctions that model the underlying full electron eigenfunctions equally well for all ℓ quantum numbers (first row elements) and
- in certain cases (e.g. sulphur) possible to derive an appropriate potential, but with highly localized features in $\mathbf{r}$ -space.³⁷ This leads to a very slow decay in $\mathbf{k}$ -space and is inconvenient or impossible to handle with the plane wave basis of the present work.

Selenium is not among these pathological cases and we have used a local pseudopotential of the form proposed by Starkloff and Joannopoulos,³⁸

$$\tilde{v}_{ps}(\mathbf{r}) = -\frac{Z}{r} \left(\frac{1 - e^{-\lambda r}}{1 + e^{-\lambda(r-r_c)}} \right) \quad (2.5)$$

It is convenient to subtract (and later add) the long-range Coulomb part. For consistency with the implementation of the nonlocal potential (see below) we subtract Gaussian-type core charges of radius R_c , so that in momentum space

$$v_{ps}(\mathbf{q}) = \frac{1}{\Omega} \int_{-\infty}^{+\infty} d^3\mathbf{r} \left[-\frac{Z}{r} \frac{1 - e^{-\lambda r}}{1 + e^{-\lambda(r-r_c)}} + \frac{Z}{r} \text{erf}\left(\frac{r}{R_c}\right) \right] e^{i\mathbf{q}\mathbf{r}} \quad (2.6)$$

or

$$v_{ps}(\mathbf{q}) = \frac{4\pi Z}{\Omega} \left[-\frac{1}{q^2} + \frac{e^{q^2 R_c^2/4}}{q^2} + \frac{1 + e^{\lambda r_c}}{q} \int_0^\infty \frac{\sin(qr)}{1 + e^{-\lambda(r-r_c)}} e^{\lambda r} dr \right] \quad (2.7)$$

The latter integral is evaluated numerically (piecewise 4-point Gaussian integration). For $\mathbf{q} \rightarrow 0$ a series expansion of all $\mathbf{q}$ -dependent terms in (7) to second order is sufficient. Ω is the volume of the periodically repeated unit cell, Z is the valence charge (6 throughout this work), the parameters for *Se* $r_c = 0.924$ a.u. and $\lambda = 10.4$ a.u.⁻¹ were optimized by fitting the tails of the valence electron orbitals to those of all-electron calculations and the choice of R_c is not critical.

For the nonlocal pseudopotential implementation for O, S, Se , we have adopted the formulation of Hamann *et al.*³⁹ and the parametrization of Bachelet *et al.*⁴⁰

$$v_{ps}(\mathbf{r}) = \sum_{l=0}^{\infty} v_l(\mathbf{r}) \hat{P}_l, \quad (2.8)$$

with

$$v_l(r) = -\frac{Z}{r} \left[\sum_{i=1}^2 c_i^{core} \text{erf}(\sqrt{\alpha_i^{core}} r) \right] + \sum_{i=1}^3 (A_i + r^2 A_{i+3}) e^{-\alpha_i r^2} \quad (2.9)$$

where $\hat{P}_l$ is the angular momentum projection operator and $c_i^{core}, \alpha_i^{core}, A_i$ and α_i are the pseudopotential parameters. If we assume that $v_l = v_{l_{max}}$ for $l \geq l_{max}$, the infinite sum in (4) can be written

$$v_{ps}(\mathbf{r}) = v_{l_{max}}(\mathbf{r}) + \sum_{l=0}^{l_{max}-1} \Delta v_l(\mathbf{r}) \hat{P}_l = v_{loc} + v_{non-loc} \quad (2.10)$$

with $\Delta v_l(\mathbf{r}) = v_l(\mathbf{r}) - v_{l_{max}}(\mathbf{r}) = \Delta v_l(r)$ or, in momentum space,

$$\Delta v_l(\mathbf{q}, \mathbf{q}') = \frac{4\pi}{\Omega} (2l+1) P_l(\cos \theta_{\mathbf{q}\mathbf{q}'}) \int_0^\infty dr r^2 \Delta v_l(r) j_l(qr) j_l(q'r). \quad (2.11)$$

P_l are Legendre polynomials, j_l are spherical Bessel functions, and $\theta_{\mathbf{q}\mathbf{q}'}$ is the angle between the momentum vectors $\mathbf{q}$ and $\mathbf{q}'$.

After eliminating rapidly varying atomic core states with pseudopotentials, the smooth (pseudo-)eigenfunctions of the Kohn-Sham equations (3) can conveniently be expanded in the plane wave basis

$$\psi_i(\mathbf{r}) = \psi_{j\mathbf{k}}(\mathbf{r}) = \sum_{n=1}^M c_{j\mathbf{G}_n}^{\mathbf{k}} \exp(i(\mathbf{k} + \mathbf{G}_n) \cdot \mathbf{r}) \quad (2.12)$$

Assuming locality of the pseudopotential (10), this leads to the self-consistent eigenvalue problem

$$\sum_n H_{mn} c_{j\mathbf{G}_n} = \epsilon_j c_{j\mathbf{G}_m},$$

$$H_{mn} = \delta_{mn} |\mathbf{G}_m|^2 + V_{ext}(\mathbf{G}_m - \mathbf{G}_n) + \Phi(\mathbf{G}_m - \mathbf{G}_n) + V_{xc}(\mathbf{G}_m - \mathbf{G}_n), \quad (2.13)$$

where the index $\mathbf{k}$ has been dropped (“one-k-point approximation”, see Sec. 2.3). The calculation of the total energy is based upon the momentum-space pseudopotential formalism by Ihm *et al.*⁴¹.

In the remainder of this section, we shall discuss some numerical aspects in solving the Schrödinger-like equations (3). Since the kinetic energy operator is diagonal in momentum space and the potential energy operating on a wave vector is

a convolution [see eq. (13)], the number of operations required to solve the eigenvalue problem eq. (13) can be reduced dramatically by using fast Fourier transform (FFT) and iterative diagonalization techniques. Performing the convolution in momentum space as a multiplication in direct space reduces the $O(M^2)$ operations necessary to compute $H \cdot \psi$ to $O(M \ln M)$. The calculation of a similar product of matrix and vector is a crucial step in most iterative diagonalization schemes.

In the present case, however, the action of a non-local correction potential, $v_{non-local}$ in eq. (10), is not a convolution and introduces $O(M^2)$ operations. This can be reduced to $O(M)$ operations if Δv_l is separable in momentum space,

$$\Delta v_l(\mathbf{q}, \mathbf{q}') = \sum_{s=1}^S W_s(\mathbf{q}) W_s(\mathbf{q}'), \quad S \ll M. \quad (2.14)$$

For $l_{max} = 1$, this can be achieved by approximating the radial integral in eq. (11) numerically⁴²

$$\int_0^\infty dr \, r^2 \Delta v_l(r) j_l(qr) j_l(q'r) \sim \sum_i w_i j_l(qr_i) j_l(q'r_i), \quad (2.15)$$

most conveniently with a 6-8 point Gauss-Hermite formula because of the Gaussian behaviour of $\Delta v_l(r)$ (see eq. (9)). For $l_{max} > 1$ we have used the separable non-local correction potential of the form suggested by Kleinman and Bylander,^{43,44}

$$\begin{aligned} \Delta v_l(\mathbf{q}, \mathbf{q}') &= \frac{4\pi}{\Omega} (2l+1) P_l(\cos \theta_{\mathbf{q}\mathbf{q}'}) \int_0^\infty dr \, r^2 \Delta v_l(r) j_l(qr) \phi_l(r) \times \\ &\times \int_0^\infty dr \, r^2 \Delta v_l(r) j_l(q'r) \phi_l(r) \left\{ \int_0^\infty dr \, r^2 \phi_l^2(r) \Delta v_l(r) \right\}^{-1}, \end{aligned} \quad (2.16)$$

where the $\phi_l(r)$ are atomic radial pseudo wave functions of the state used to generate the pseudopotential. The presence of the P_l in eq. (16) leads to $S = 1, 4, 11$ in (14) for $l = 1, 2, 3$, respectively. The use of eq. (16) with $l_{max} = 2$ is a convenient and stable method for sulphur, selenium and oxygen, provided that the numerical integrations are performed accurately. The geometries and binding energies changed by no more than 0.5% using radial functions, ϕ_l , calculated from, for example, the $S[s^2p^4]$, $S^+[s^2p^{2.5}d^{0.5}]$ and $S^{2+}[s^1p^{2.75}d^{0.25}]$ states. Spurious roots and other difficulties reported in the original work⁴³ were not encountered. However, we have found that potentials with a small non-local term can lead to numerical instabilities and slightly state-dependent results. An example is the pseudopotential of Se .⁴⁰

2.2. MOLECULAR DYNAMICS (MD) ASPECTS

The above arguments apply to any application of DF theory with a plane wave basis. It is possible, however, to view E as a function of two interdependent sets of degrees of freedom, the single particle eigenfunctions $\{\psi_i\}$ and the nuclear coordinates $\{\mathbf{R}_I\}$,

$$E[\{\psi_i\}, \{\mathbf{R}_I\}] = \sum_i \langle \psi_i(\mathbf{r}) | -\frac{\nabla^2}{2} | \psi_i(\mathbf{r}) \rangle + \int d\mathbf{r} n(\mathbf{r}) \left(V_{ext}(\mathbf{r}) + \frac{1}{2} \Phi(\mathbf{r}) \right) + \\ + E_{xc}[n(\mathbf{r})] + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} . \quad (2.17)$$

To minimize this function, we use a dynamical simulated annealing technique to follow the trajectories of $\{\psi_i\}$ and $\{\mathbf{R}_I\}$ given by the Lagrangian⁶

$$\mathcal{L} = \sum_i \mu_i \int_{\Omega} d\mathbf{r} |\dot{\psi}_i^* \dot{\psi}_i| + \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i\}, \{\mathbf{R}_I\}] + \sum_{ij} \Lambda_{ij} \left(\int_{\Omega} d\mathbf{r} \psi_i \psi_j^* - \delta_{ij} \right) \quad (2.18)$$

and the corresponding equations of motion

$$\mu \ddot{\psi}_i(\mathbf{r}, t) = F_i + F_{i,ortho} = -\frac{\delta E}{\delta \psi_i^*(\mathbf{r}, t)} + \sum_k \Lambda_{ik} \psi_k(\mathbf{r}, t) , \\ M_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E . \quad (2.19)$$

Here M_I and $\mathbf{R}_I$ denote the ionic masses and coordinates, μ_i are fictitious “masses” associated with the electronic degrees of freedom, dots denote time derivatives, and the Lagrangian multipliers Λ_{ij} are introduced to satisfy the orthonormality constraints on the $\psi_i(\mathbf{r}, t)$. It is very important to avoid any errors due to the implementation of these constraints because these errors accumulate. It can be shown that the *only* method to calculate the Lagrangian parameters Λ_{ij} fulfilling the holonomic constraints of orthonormality $\langle \psi_i | \psi_j \rangle - \delta_{ij} = 0$ *exactly* at each step of the integration is⁴⁵

$$\Lambda_{ij} = H_{ij} - \mu \int d\mathbf{r} \dot{\psi}_i^*(\mathbf{r}) \dot{\psi}_j(\mathbf{r}) \quad (2.20)$$

Other, more popular orthogonalization schemes like Gram-Schmidt, are not consistent with the Lagrangian (18) and lead to dissipation in the electronic subsystem. The method that is used to solve the equations of motion (19) is the well-known Verlet algorithm⁴⁶ shown here for the electronic part:

$$c_{i\mathbf{G}_n}(t + \Delta t) = 2c_{i\mathbf{G}_n}(t) - c_{i\mathbf{G}_n}(t - \Delta t) + (F_i(\mathbf{G}) + F_{i,ortho}(\mathbf{G})) \frac{\Delta t^2}{\mu} + O(\Delta t^4) \quad (2.21)$$

This leads to a non-linear system of equations for the Λ_{ik} in eq. (20) and we use the iterative scheme of Ryckaert *et al.* to solve it.⁴⁵ From the orbitals $\psi_i(\mathbf{r}, t)$ and the resultant density $n(\mathbf{r}, t) = \sum_i |\psi_i(\mathbf{r}, t)|^2$ we can use eq. (17) to evaluate the total energy E , which acts as the classical potential energy in the Lagrangian (18). The artificial second order Newton’s dynamics for the electronic degrees of freedom, together with the assumption $\mu_i \ll M_I$, effectively prevents an equilibration of the two subsystems and the transfer of energy from the classical to the quantum degrees of freedom over long periods of simulation.

This requires, however, that the electronic system be brought into the ground state at the beginning of every MD run. This can be accomplished via steepest descents (SD) or similar, more efficient⁴² techniques:

$$c_i \mathbf{G}_n(t + \Delta t) = c_i \mathbf{G}_n(t) + (F_i(\mathbf{G}) + F_{i,ortho}(\mathbf{G})) \frac{\Delta t^2}{\mu}, \quad (2.22)$$

In equilibrium $\{\ddot{\psi}_i\} = 0$, eq. (19) is identical to the Kohn-Sham equation (3) within a unitary transformation, and the eigenvalues of the matrix Λ are identical to the KS eigenvalues ϵ_i . For a small number of states, like in a small cluster, the KS eigenvalues can be computed routinely every couple of time steps. For a system with a large number of occupied states, the calculation of the eigenvalues becomes more cumbersome and should be done only every so often.

The SD procedure is an alternative way of solving the KS equations without treating them as a self-consistent eigenvalue problem. eq. (22) is formally equivalent to a time-dependent Schrödinger equation in imaginary time. The SD procedure effectively projects onto the ground state an initial trial state by propagating it in imaginary time. It should be noted that because of the invariance of physical properties under unitary transformations, the specific orthogonalization scheme chosen in this stage of the calculation is largely arbitrary (e.g. Gram-Schmidt).

The MD procedure is initiated by displacing the atoms randomly from an arbitrary geometry, with velocities $\dot{\psi}_i$ and $\dot{\mathbf{R}}$ set equal to zero. For this geometry we then determine those ψ_i that minimize E via the first order SD equations (22). With the electrons initially in their ground state, the dynamics (19) generate Born-Oppenheimer (BO) trajectories without the need for additional diagonalization/self-consistency cycles for the electrons over several thousand time steps. If we define a “temperature” T by the mean classical kinetic energy of the atoms, the atomic configurations observed during the annealing process then represent physical molecules at elevated temperatures. In the simulated annealing runs, the average instanta-

neous temperature $\langle T \rangle$ – the mean kinetic energy of the ions – is kept constant with $\sim 10\%$ tolerance by rescaling the ionic velocities uniformly with a factor $\sqrt{\langle T \rangle / T}$.

MD also provides a convenient method for determining the vibrational density of states $f(\omega)$ of the cluster in question via the Fourier transform of the velocity autocorrelation function $\varphi(t)$:⁴⁷

$$\varphi(t) = \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle}{\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle} \quad (2.23)$$

$$f(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \varphi(t) \cdot e^{i\omega t} dt. \quad (2.24)$$

This procedure has been used to calculate vibration frequencies of characteristic fundamental modes in S_2 and S_8 (see Sec. 3.1).

2.3. COMPUTATIONAL DETAILS

We have used a large fcc unit cell [lattice constant 15.9 Å] with constant volume [1000 Å³] and periodic boundary conditions in all calculations. This supercell geometry leads to a large separation between the individual clusters, and the accurate reproduction of the symmetries in the highly symmetric $(S, Se)_6$, $(S, Se)_8$ and S_{12} shows that the results are indeed insensitive to the choice of boundary conditions. All plane waves up to a certain cut-off energy were taken into account and typically only one k -point in the very small Brillouin zone of the superlattice is taken into account. The cut-off energies were

- 10.6 Ry for the S_n and $S_n Se_m$ calculations in Chapters 3 and 5, leading to ~ 4000 plane waves for each electronic state for a single point ($\mathbf{k} = 0$) in the Brillouin zone (BZ)
- 14.0 Ry for $\mathbf{k} = 0$ in the case of Se_n (Chap. 4), leading to ~ 6000 plane waves for the electronic states. The larger basis set had to be applied in order to achieve the same degree of convergence with the steeper local pseudopotential.
- 45 Ry in the case of S_7O (Sec. 5.1), corresponding to ~ 36000 plane waves for a single point ($\mathbf{k} = 0$) in the Brillouin zone.⁴⁸ The rapid spatial variation of the pseudopotential⁴⁰ for O meant that this expansion had to be very large.

The convergence properties of the equilibrium geometries and total energies with respect to basis set size and number of k -points have been checked thoroughly. In the case of S_{12} , increasing the cut-off energy to 31 Ry brought changes in bond lengths, bond angles and dihedral angles of not more than 0.8%. While the *relative* energies of different minima were remarkably insensitive to the above increase in basis set

size, the total valence electron energy changes by ~ 3 eV per atom when the cut-off is increased to 31 Ry, where we estimate the energy to be within 0.01 eV/atom of the convergence limit. The shape of the energy surfaces of S_n was found to converge much more rapidly than the absolute position on the energy scale. To check the restriction to the use of a single point in the BZ, we have performed calculations for S_{12} with two inequivalent points (Γ and L). The equilibrium geometries were unchanged and the change in the total valence electron energy (0.07 eV/atom) was negligible. The calculations for Se clusters reveal a comparable behaviour. A calculation for Se_8 using two points (Γ and L) gave a negligible correction to the total energy (0.015 eV per atom). A test calculation for S_7O employing a cutoff energy of 120 Ry (~ 150000 plane waves for each electronic state) has lead to negligible corrections of the ground state geometry and its relative energy to other minima.

In the simulated annealing calculations for S_n in Chap. 3, we use the nonlocal pseudopotential described in Sec. 2.1 with $l_{max} = 1$ in (12). Using $l_{max} = 2$ resulted in small contractions of the bonds, as we discuss further in Sec. 3.2. With appropriate values of the artificial mass for the electronic degrees of freedom μ (300 a.u.) and the integration time step (1.7×10^{-16} seconds), the equations of motion can be integrated accurately with the Verlet algorithm.⁴⁶ The energy surfaces are probed by varying the average kinetic energy of the nuclei ("temperature" T), and the optimum geometries found by slowly reducing $T \rightarrow 0$. With this parametrization, the electronic subsystem deviates from the ground state not more than 0.1 eV in several thousand time steps. Although not a necessary condition to find equilibrium structures this ensures that the molecular configurations observed during the annealing process represent physical molecules at elevated temperatures.

The procedure used in Chap. 4 to find the ground state geometries of Se_n clusters is essentially identical. Se was treated by both the local and non-local pseudopotentials described above. These potentials give very similar ground state geometries in Se_3 , Se_4 , and Se_5 , deviations being typically less than 1 % in bond lengths and angles. Using a value of $\mu=1800$ a.u. and an integration time step of 3.4×10^{-16} seconds, we find that the subsequent motion of the nuclei follows the BO surface very accurately.

In Sec. 5.1 (S_7O), we have treated the S and O atoms by non-local pseudopotentials with $l_{max} = 1$ in (12). The latter approximation leads to bond length overestimates of 1–2 %, comparable to what was observed in the case of S_n . With the appropriate values of μ (300 a.u.) and integration time step (7.3×10^{-17} sec-

onds), we find that the motion of the nuclei departs again little from the BO surface.

The calculations for S_nSe_m in Sec. 5.2 were checked very carefully for the basis set size, size of the unit cell and pseudopotential implementation because the energy differences between different minima turned out to be very small (of the order 10^{-2} eV). The results were insensitive to the unit cell size and the basis set previously employed for S_n sufficiently large to converge relative depths of different minima to the necessary degree. The application of nonlocal pseudopotentials with the usual approximation $l_{max} = 1$ was, however, inappropriate in this case and $l_{max} = 2$ had to be employed throughout these calculations. At that level of required accuracy, the uncertainty of relative energies due the choice $l_{max} = 1$ was intolerable.

After every 1000 – 5000 time steps we fix the ionic positions and bring the electrons back into their ground state. The energy change observed were usually small (no more than ~ 0.1 eV) in all cases and at all temperatures imposed.

In all the present work S_7O was computationally the most demanding object due to the necessary large basis set. Each time step required approximately 5 sec of CPU time on a Cray X-MP computer, while all the other systems under consideration demanded generally less than 1 sec per time step. Depending on the size of configuration space to be sampled, however, the total amount of CPU time required can become very large. Except for the smallest systems ($n = 2, 3$), the total number of time steps performed to find the most prominent low-lying minima was in the range 10000-100000, corresponding to a maximum of 30 CPU h on a Cray X-MP computer. This does not include the necessary consistency checks for cut-off energy, size of the unit cell and pseudopotential that can be very demanding calculations, too.

3. SULPHUR CLUSTERS S_2 – S_{13}

3.1. GROUND STATE STRUCTURES

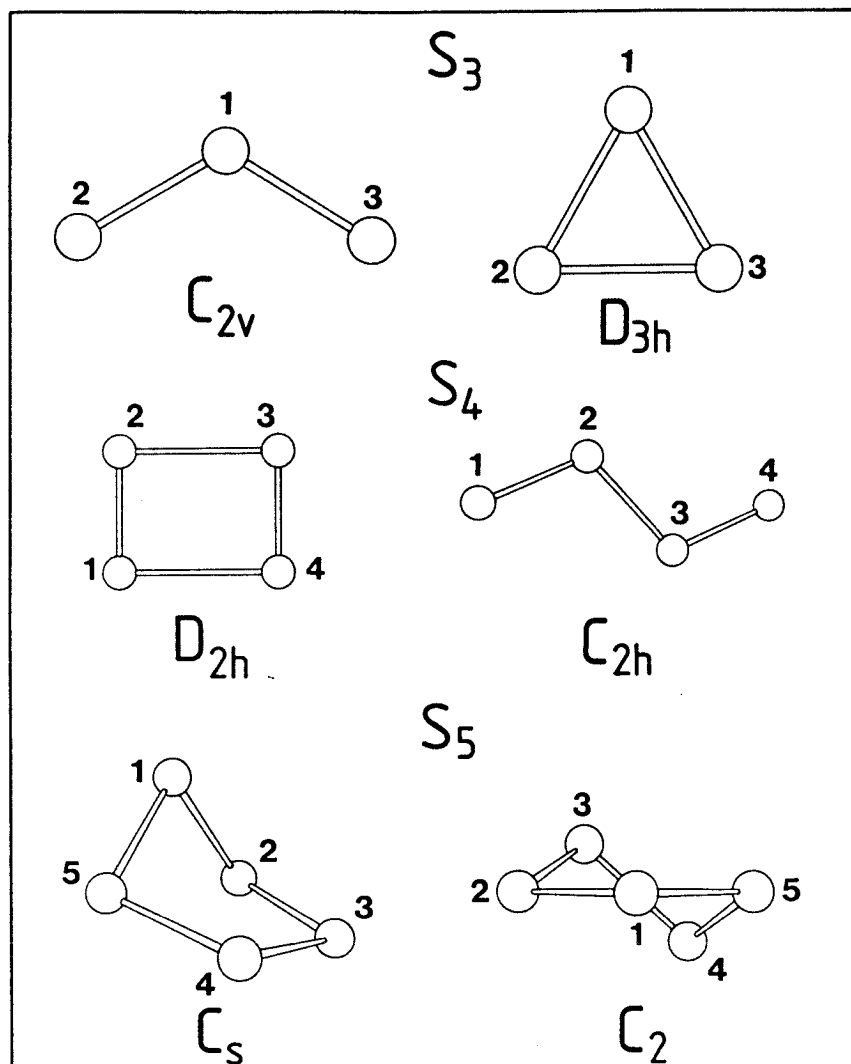


Fig. 1: The structures of S_3 , S_4 , and S_5 .

The spectroscopic parameters of the ground state of the S_2 molecule are given in Table 1 and the structural parameters for the lowest-lying singlet states of the larger clusters $S_3 - S_{13}$ are given in Tables 2-4. The results of X-ray structure analyses are given where available, and the structures are shown in Figures 1,2 and 5-7. Our calculations make no assumptions about the symmetry of the clusters, so that our results represent an appropriate average of the structural parameters. The same is true of the experimental parameters, as we discuss below. Our calculations show a remarkably uniform overestimate of bond lengths of approximately 2%. It may be assumed that this is also true in those cases where the structures are presently unknown.

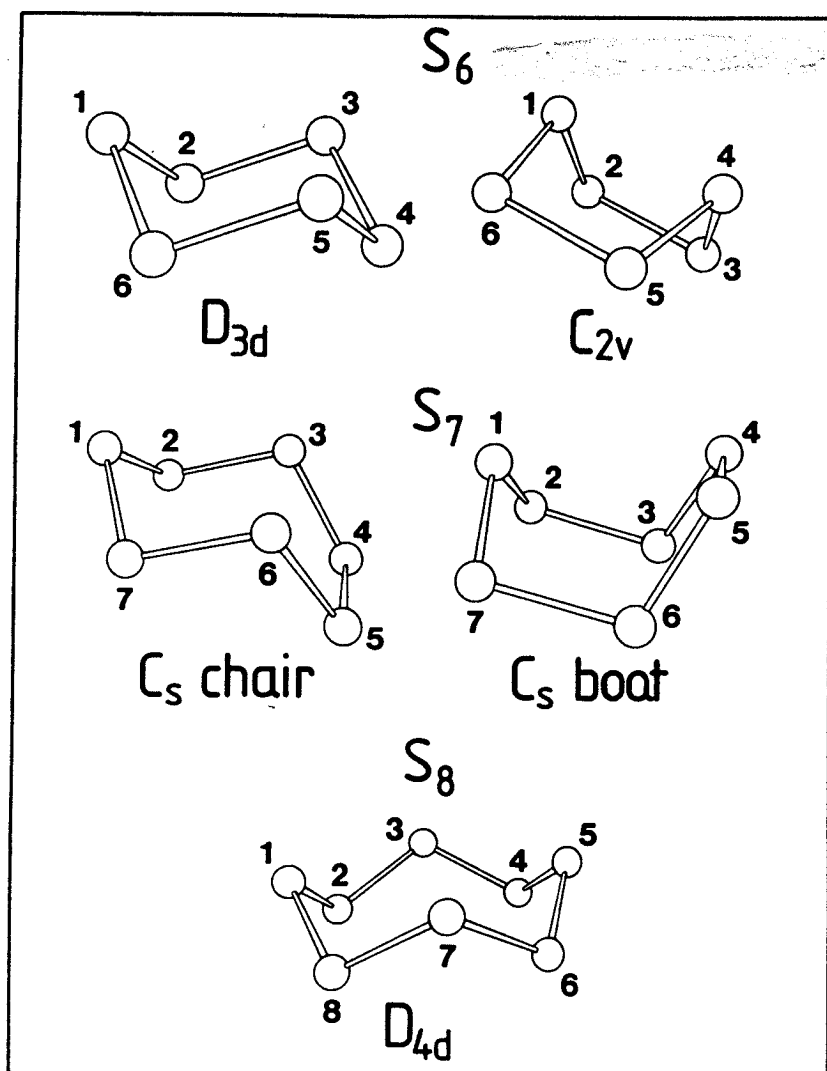


Fig. 2: The structures of S₆, S₇, and S₈.

S₂

The low-lying states of the sulphur dimer have been investigated extensively in the gas phase,⁴⁹ and the ground state has the same configuration ($^3\Sigma_g^-$) as the ground state of O₂. There have been several parameter-free calculations for this molecule, and the results are compared with the experimental spectroscopic parameters in Tab. 2. The deviations from experiment are consistent with past experience, with the Hartree-Fock calculations^{50,51} leading to underestimates of the bond length and overestimates of the vibration frequency. The CI calculations^{51,52} show deviations of opposite sign, with a steady improvement in all parameters as the basis set is improved and the number of configurations increased. The density functional calculations overestimate the bond length and underestimate the vibration frequency by modest amounts, and the agreement between the two sets of DF calculations is satisfactory. The overestimate in the well-depth by ~ 1.5 eV is consistent with

Tab. 2: Spectroscopic constants of S_2 ($^3\Sigma_g^-$). r_e denotes the equilibrium interatomic distance, ω_e the stretching vibration frequency; D_e and D_0^0 are the corresponding well depths, the latter taking into account the zero point vibration.

	$r_e(a.u.)$	$\omega_e(cm^{-1})$	$D_e(eV)$	$D_0^0(eV)$
Expt ^a	3.570	725.65	4.41	4.37
HF ^b	3.545	819	1.76	...
HF ^c	3.513	818	2.27	...
CI ^b	3.591	760	2.86	...
CI ^d	3.679	600	3.72	3.68
CI-SD ^c	3.551	767	3.16	...
CI-SDQ(D) ^c	3.574	736	3.70	...
CI-SDQ(S) ^c	3.581	728	3.82	...
DF-LMTO ^e	3.74	660	5.9	...
DF-MD ^f	3.67	680	5.5	...

(a) Huber and Herzberg.⁴⁹

(b) Swope *et al.*⁵⁰

(c) McLean *et al.*⁵¹

(d) Saxon and Liu.⁵²

(e) Jones.⁵³

(f) This work.

previous LSD calculations for molecules containing group VIA elements.^{10,53}

S_3

The sulphur trimer (thiozone) is the only other molecule in the present series which has been studied previously by parameter-free methods incorporating correlation effects. DF calculations using a localized linearized muffin-tin orbital (LMTO) basis⁵³ predicted a near degeneracy between the open (C_{2v} , $r = 3.78$ a.u., $\alpha = 114^\circ$) and ring (D_{3h} , $r = 4.09$ a.u.) structures, and this was also found in other parameter-free calculations. With an S (11s7p1d/6s4p1d) Gaussian basis, Rice *et al.*⁵⁴ found that CISD calculations favour the ring (D_{3h}) structure ($r = 3.97$ a.u.) by 0.10 eV over the C_{2v} ($r = 3.65$ a.u., $\alpha = 117.0^\circ$), while MR-CISD calculations favour the open structure ($r = 3.69$ a.u., $\alpha = 115.7^\circ$) over the cyclic ($r = 3.98$

a.u.) by 0.21 eV. Using a similar basis with an additional f -function, Ahlrichs⁵⁵ obtained comparable results. Coupled pair functional (CPF) calculations produce a C_{2v} ground state ($r = 3.66$ a.u., $\alpha = 116.9^\circ$) 0.19 eV below the D_{3h} ($r = 3.95$ a.u.), and CI calculations reverse the order of stability. Single-configuration HF calculations^{54,56,57} give a closed (D_{3h}) ground state between 0.40 eV and 1.12 eV below the open structure. The near-degeneracy found in LSD and correlated wave function calculations shows that correlation effects are much larger in the open structure, so that S_3 and the valence isoelectronic O_3 provide sensitive tests of methods of improving on HF calculations. In all these calculations^{53,54,55} the bond in the open state is notably shorter than the S - S bond in the sulphur chain, S_∞ [3.90 a.u.],¹² indicating a bond order between one and two. The bond lengths in the closed state are within the range typical for normal single bonds.

Although the existence of the S_3 molecule in the gas phase is well established, little is known experimentally about its electronic structure. Ionization efficiency curves for S_{2-8} have been measured by electron impact (EI) ionization⁶¹ and appearance potentials and average bond energies derived from these data. Low ion intensities for S_3^+ (and S_4^+) call for a cautious interpretation of these data. The maximum of the absorption in the visible region has been measured at $\lambda_{max} = 430$ nm (2.9 eV)⁶² and is most suitably interpreted as the spin- and symmetry-allowed single-electron transition $^1A_1 \rightarrow ^1B_2$ with 2.3 eV.⁵³ Matrix isolation studies suggest an open structure in the ground state, and the C_{2v} structure follows unambiguously from its vibration spectrum.⁶³ The MD-DF calculations lead to geometries for both states in good agreement with those of all-electron LMTO calculations.⁵³ However, although there is a near-degeneracy between these two states, the order is reversed, with the MD-DF calculations favouring the open structure by 0.16 eV, in agreement with experiment.⁶³ The present truncated plane wave basis LDF calculation and the all-electron calculations lead to very similar one-electron eigenvalue spectra. The ordering of the states is the same in both the C_{2v} ($1a_1 < 1b_2 < 2a_1 < 2b_2 < 1b_1, 3a_1 < 1a_2 < 3b_2, 4a_1$) and D_{3h} cases ($1a_1 < 1e' < 2a_1' < 1a_2'' < 2e' < 1e''$), with widths and spacings agreeing to within 0.1 eV in the p -bands and 0.5 eV in the s -bands. This is a further indication of the adequacy of the basis set. Both the MD-DF and all-electron calculations show the lowest triplet state 0.7 – 0.8 eV above the ground state (see Tab. 3).

Both the empirical MNDO¹⁶ and MD calculation⁹ are in marked disagreement with all the above CI and LDF calculations. MNDO favours the D_{3h} ring structure by 1.1 eV over the open structure (~ 0.3 eV when CI is included). The underlying

Tab. 3: Molecular parameters d , α and γ for low energy isomers of S_n , $n = 2 - 8$. Bond lengths d_{ij} (between atoms i and j) in a.u., bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees.

$S_2(^3D_{\infty h})$		$S_6(C_{2v})$			
d	3.67	$d_{12,16,34,45}$	3.92		
$S_3(C_{2v})$		$d_{23,56}$	4.20		
$d_{12,13}$	3.74	α_1, α_4	106°		
α_1	117°	$\alpha_2, \alpha_3, \alpha_5, \alpha_6$	101°		
$S_3(D_{3h})$		$\gamma_{12,61,34,45}$	75°		
d	4.00	$S_6(D_{3d})$		expt(a)	
α	60°	d	3.98	3.91	
$S_3(^3C_{2v})$		α	102°	102.6°	
$d_{12,13}$	3.86	γ	75°	73.8°	
α_1	92°	$S_7(C_s)$		expt(b)	
$S_4(C_{2h})$			boat	chair	
$d_{12,34}$	3.72	$d_{12,71}$	3.92	3.95	3.87
d_{23}	4.08	$d_{23,67}$	4.14	4.06	3.97
α_2, α_3	111°	$d_{34,56}$	3.79	3.84	3.78
$S_4(D_{2h})$		d_{45}	4.36	4.26	4.11
$d_{12,34}$	3.66	α_1	108°	107°	105.0°
$d_{23,41}$	4.84	α_2, α_7	101°	102°	102.1°
$S_5(C_s)$		α_3, α_6	108°	105°	105.3°
$d_{12,51}$	4.00	α_4, α_5	104°	108°	107.4°
$d_{23,45}$	3.91	$\gamma_{12,71}$	72°	76°	76.7°
d_{34}	4.14	$\gamma_{23,67}$	41°	106°	107.8°
α_1	90°	$\gamma_{34,56}$	86°	83°	83.7°
α_2, α_5	99°	$S_8(D_{4d})$		expt(c)	
α_3, α_4	101°	d	3.98	3.87	
$\gamma_{12,51}$	64°	α	108°	108.2°	
$\gamma_{23,45}$	40°	γ	99°	98.5°	
$S_5(C_2)$					
$d_{12,51}$	4.06				
$d_{23,45}$	3.91				
d_{34}	4.08				
α_1	100°				
α_2, α_5	103°				
α_3, α_4	94°				
$\gamma_{12,51}$	21°	(a)		Ref. ⁵⁸	
$\gamma_{23,45}$	54°	(b)		Ref. ⁵⁹	
γ_{34}	66°	(c)		Ref. ⁶⁰	

ing parametrization, however, considered only sulphur compounds and no molecules containing sulphur alone, and leads to considerable overestimates of ring strain energies and $S-S$ single bond strengths. Under these circumstances a near-degeneracy of the open and closed states of S_3 is unlikely. Stillinger *et al.*⁹ predict the opposite ordering in their parametrized MD based calculations, favouring the open form by 1.2 eV. As we discuss further in the case of S_5 , such calculations can lead to qualitatively incorrect geometries and energetic orderings, even though the interaction potential has been tuned to the structural chemistry of S_n molecules.

S₄

The lack of conclusive experimental information for S_4 is reminiscent of the situation in S_3 . An absorption at $\lambda_{max} = 530$ nm contributes to the color of liquid and gaseous sulphur and is the red chromophore in reddish ultramarine.^{62,64,65} A vibrational spectrum has been measured⁶⁶ and the EI study has been mentioned above.⁶¹ Apart from these measurements there are only thermodynamical data available for S_4 .⁶⁷ As in the case of S_3 , calculations have been performed for S_4 with a broad range of theoretical methods, including MD,⁹ extended Hückel (EH)^{61,62}, $X\alpha-SW$,⁶⁸ Hartree-Fock^{57,69}, MNDO^{16,70} and SINDO1.¹⁷ However, in contrast to the case of S_3 , where a consistent picture of the electronic and geometrical structures has resulted, the results for S_4 are inconclusive and confusing. To the best of our knowledge, reliable calculations incorporating correlation effects (either of CI or LDF type) have not been performed.

The MD calculations⁹ lead to a helical chain with C_2 symmetry as the ground state, with a local minimum with D_{4h} (square) symmetry well above it. The first HF calculations⁶⁹ also found a 3C_2 helical chain as lowest-lying state, configurations with ${}^3C_{2v}$ and ${}^3C_{2h}$ symmetry being the only ones with comparable energies. However, the ground state in more recent HF calculations⁵⁷ is a puckered ring with D_{2d} symmetry and a large torsion angle $\gamma = 86.22^\circ$, with the square as the next most stable. The least stable structures were a *cis*-chain (C_{2v}) and a branched SO_3 -like structure (D_{3h}). By contrast, the latter was found to be the most stable state of the EH calculations. The other semi-empirical MO calculations MNDO and SINDO1 predict nearly planar “roof” structures with D_{2d} symmetry as ground states. The corresponding geometries (MNDO: $d = 3.71$ a.u., $\gamma = 24.6^\circ$; SINDO1: $d = 3.89$ a.u., $\alpha = 84.9^\circ$, $\gamma = 47.7^\circ$) are reminiscent of the ground state of O_4 in the most recent CI calculations⁷¹ ($d = 2.71$ a.u., $\alpha = 87.2^\circ$, $\gamma = 24.8^\circ$ for the highest level of CI used).

These highly contradictory predictions show the need for a more sophisticated method that can nevertheless sample large regions of configuration space. We have therefore performed simulated annealing calculations beginning with slightly perturbed linear chains. The predicted ground state at $T \rightarrow 0$ comprises two weakly bound S_2 units in a rectangular entity with ${}^1D_{2h}$ symmetry (see Fig. 1 and Tab. 3). The shorter $S - S$ distances are practically identical to monomeric S_2 and those between the dimers are the longest encountered in the present calculations (see also the discussion in Sec. 3.2). This has been attributed to the fact that “the highest occupied molecular orbitals are always antibonding π -orbitals”.¹⁸ Our calculations show that this is not true in S_4 (and Se_4), where only three out of the four possible combinations of out-of-plane p_x atomic orbitals on every atom are occupied, the uppermost π -antibonding being the LUMO (a_2 , molecule in yz -plane). S_4 should therefore be compared not with the C_2 symmetric (“gauche”) H_2S_2 or H_2O_2 , but with $O-S-S-O$, which is indeed planar.⁷² On the other hand, occupation of the uppermost antibonding π -orbital in S_4^{2-} or $Cl-S-S-Cl$ is energetically so unfavourable that these species distort to the “gauche” conformations.^{72,73} We find that two of the p_x combinations (HOMO and HOMO–5, both b_1) and three of the $p_{y,z}$ combinations (HOMO–1, HOMO–6 and HOMO–7, all a_1) are weakly bonding between atoms 1 and 4. This favours the *cis*- over the *trans*-isomer and leads to smaller bond angles in the former. The energy surface in the vicinity of the minimum is extremely flat, especially for a simultaneous lengthening of bond 1–4 and a shortening of bond 2–3. Deforming the rectangle continuously to C_{2v} symmetry with $d_{12,34} = 3.72$ a.u., $d_{23} = 4.08$ a.u., and $\alpha_{2,3} = 111^\circ$, the total energy increases monotonically by only 0.1 eV. The LSD approximation is known to overbind loosely coupled “van-der-Waals” like aggregates like these,⁷⁴ so that it is not inconceivable that the energy difference to other minima is less than the 0.4 eV computed here. The rectangular structure remains a plausible candidate for the lowest-lying structure of S_4 in spite of this tendency.

Other structures were encountered during the course of the annealing procedure, and the relative stabilities of several have been studied using steepest descent quenches. We have also considered structures proposed by other authors as low-lying states. A planar *trans*-isomer with C_{2h} symmetry (see Fig. 1) lies ~ 0.4 eV above the ground state, separated from a hypothetical *cis*-isomer with the same bond lengths and angles by a rotational barrier of ~ 1 eV. Neither the intermediate C_2 structures nor any tetrahedron structure were found to be stable local minima. The local minimum closest to the tetrahedron is a roof-like D_{2d} structure 0.76 eV

above the ground state ($d = 4.04$ a.u., $\alpha = 85^\circ$, $\gamma = 33^\circ$). A structure resembling SO_3 with D_{3h} symmetry is also a local minimum, more than 1 eV above the ground state. As in S_3 , Se_3 and Se_4 , all triplet states of S_4 lie well above the $^1D_{2h}$ ground state, and diradical chains can be ruled out as possible ground states.

S_5

No definite structural information is available for S_5 . It occurs in sulphur vapour⁶⁷ and is a possible component of liquid sulphur even at moderate temperatures.¹⁵ Recently, S_5 has been identified and analyzed quantitatively with a chromatographic method in solutions of sulphur subjected to photolysis.⁷⁵ The appearance potentials of S_5 from EI experiments⁶¹ are consistent with previous photoionization measurements,⁶⁷ in that S_5 shows the lowest ionization potential of all sulphur clusters measured. This and the thermodynamical data^{61,67} have been interpreted as evidence for a ring structure, and this hypothesis is supported strongly by the existence of *cyclo* - $S_5 = O$.⁷⁶

Initiating the simulated annealing process with a slightly displaced linear chain, heating to a maximum average “temperature” of 1000 K and then letting $T \rightarrow 0$, we find an envelope-shaped ground state of C_s symmetry (see Fig. 1 and Tab. 3). This process is visualized for the analogous Se_5 in Chap. 4. Chain structures and planar ring structures can therefore be excluded as the state of lowest energy. Several subsequent heating and cooling cycles always led to the same stable C_s ground state. Coupling the cluster to a heat bath of $T = 600K$ for 3000 time steps and following the simulation graphically, we observed two visits to another pronounced minimum with comparable energy but different structure. Both visits lasted only about $170 \Delta t$ and the total energies observed were still somewhat above the C_s ground state (≥ 0.1 eV). A subsequent steepest descent quench led to a *degenerate* state with C_2 symmetry (see Fig. 1). The catchment region in configuration space is apparently much smaller for the second minimum.

The present results for S_5 indicate that S_5 molecules with envelope (majority) and “half chair” (minority) geometries might coexist at $T \gg 0$. It is possible that two distinct forms could occur at $T \rightarrow 0$. Large relative temperature fluctuations due to the small number of particles in our simulations and limited simulation times make it currently impossible to give quantitative C_s/C_2 ratios as a function of temperature.

HF⁷⁷ and MNDO¹⁶ calculations lead to results that are qualitatively similar to ours. Both methods find a pair of almost degenerate C_s envelope and C_2 “half chair”

structures as possible ground states. The variation of bond distances, however, is much smaller than in the present work and the structures found by both methods do not conform to the empirical rule that long bonds in homocyclic sulphur molecules are adjacent to short ones (see Sec. 3.2). Both of the studies rule out a planar D_{5h} ring, but the HF calculation lists a triplet chain as the lowest-lying state. The MD empirical potential calculations⁹ lead to a planar D_{5h} ground state, in contrast to all the other results and the experimental evidence.⁷⁶

S_6

Crystalline rhombohedral S_6 contains molecular units which are six-membered rings with D_{3d} symmetry.⁵⁸ The minimum ratio of intra- to intermolecular distances in the crystal is rather large (1.66) and the low standard deviation of the available crystal data indicates very small intermolecular interactions. All the available calculations lead to results in very good agreement with experiment (e.g. MNDO,^{16,70} CNDO,⁷⁸ SINDO1,¹⁷ empirical MD,⁹ EH⁶²). Most of the theoretical studies find a boat isomer with C_{2v} symmetry between 0.08 eV⁹ and 1 eV⁷⁸ above the chair-shaped ground state. Such a structure has not yet been identified in an allotrope of a group VIA element, but the mixed ions $Te_xSe_{6-x}^{2+}$ or $Se_4Te_2^{2+}$ with similar shapes are well characterized.^{79,80}

We have initiated the annealing process from slightly displaced planar hexagons and linear chains. Our $T \rightarrow 0$ ground state geometry matches the experimental configuration very closely (see Fig. 2 and Tab. 3). We emphasize that, in contrast to previous theoretical work, our choice of initial conditions did *not* exploit available experimental information for S_6 . A “boat” isomer was not observed during the annealing process but explicitly checked via steepest descent quenches and low temperature annealing. The corresponding minimum was found to be ~ 0.5 eV above the ground state.

S_7

Homocyclic S_7 is a well-known constituent of sulphur vapour, liquid sulphur and quenched liquid sulphur, of irradiated sulphur solutions and of some chemically synthesized sulphur modifications.⁵⁹ There are four crystalline allotropes of S_7 ,⁵⁹ of which two have been characterized structurally. The molecular units found in δ - S_7 and γ - S_7 have almost identical geometries with approximately C_s symmetry. The shortest intermolecular distances are 6.43 a.u., slightly less than in S_6 . The molecular units are distorted from perfect C_s symmetry by crystal packing effects, the “equivalent” torsion angles differing by up to $\sim 2^\circ$. The experimental geometry

given in Tab. 3 has been averaged for the γ -form. The MNDO calculation of Baird is in qualitative agreement with experiment,¹⁶ reproducing in part the pattern of widely varying bond distances.

As in the case of S_6 , we have not used the experimental structure as input to our annealing procedure, but have started from a perturbed planar heptagon. After “melting” the cluster at $T \leq 2000$ K the subsequent cooling process converged surprisingly rapidly in ~ 1000 time steps to the chair structure with C_s symmetry shown in Fig. 2. The agreement with experiment is very good, and other pronounced minima were not observed. Distorting the molecule by increasing the torsion angle at bond 4-5 with simultaneous relaxation of the other bond parameters was found to cost almost no energy. A torsion angle of zero will therefore not be observable at finite temperatures, in agreement with the distortions found in crystalline S_7 ⁵⁹ and Se_5S_2 .⁸¹

Another candidate for the ground state is the boat isomer shown in Fig. 2. This structure has been explicitly checked by steepest descent quenches and low temperature annealing and was found to be the lowest excited state, only 0.1 eV above the ground state. The boat form of S_7 may therefore be observable experimentally.

We have coupled the cluster in its ground state geometry to a heat bath at $T = 1500$ K and observed a simultaneous motion about several of the ring bonds, corresponding to a migration of the bond with torsion angle $\gamma = 0$ around the molecule. The time required for a single migration to the neighbouring site is about 4000 time steps, and the overall shape of the molecule remains the same. Steudel *et al.*⁸² have inferred such a “pseudorotation” in S_7 and Se_2S_5 at room temperature from Raman and ^{77}Se NMR spectra (see Sec. 5.2). We have used a substantially higher temperature to overcome the short time scale in our simulations [the simulations proceed roughly a factor of 10^{15} slower than the corresponding real process, a well-known problem in all MD calculations].

S_8

Cyclooctasulphur S_8 is the most common and best characterized allotrope of elemental sulphur and a large amount of experimental data is available.¹³ There are three crystalline forms of S_8 (α -, β -, γ -)^{12,13} consisting of crown-shaped (D_{4d}) ring molecules. The crystal structure data given in Tab. 3 are for the thermodynamically stable orthorhombic (α -) S_8 at 100 K.⁶⁰ The minimum ratio of intra- to intermolecular distances in the crystal is 1.64 and the small crystal forces distort the ring marginally from perfect D_{4d} symmetry. Previous theoretical studies^{9,16,17,68,70,83}

have given good agreement with experiment.

As in the case of S_6 and S_7 we have initiated the annealing process from a planar octagon with small random perturbations. The $T \rightarrow 0$ ground state (see Fig. 2 and Tab. 3) is the familiar crown structure. The agreement with experimental data is very satisfactory, except for the small overestimate of the bond lengths (see Sec. 3.2).

The converged ground state geometry was then randomly displaced with sufficient amplitude to excite all vibrational modes, and the subsequent constant energy MD evolution followed for 35000 time steps. The peak positions in the vibrational DOS calculated from eq. (2.23, 2.24) agree well with the experimental Raman and IR spectra of S_8 .^{84,85,86} The highest frequency bands in the DOS are $\nu_{ss} = 443 \text{ cm}^{-1}$ [experiment: 472.5 cm^{-1} (Raman), 471 cm^{-1} (IR)], $\nu_{ss} = 426 \text{ cm}^{-1}$ [439 cm^{-1} (Raman)], $\nu_{ss} = 345 \text{ cm}^{-1}$ [418 cm^{-1} (Raman⁸⁷)] and $\delta_{ss} = 262 \text{ cm}^{-1}$ (triplet) [249 cm^{-1} , 245.5 cm^{-1} (Raman), 243 cm^{-1} (IR)].

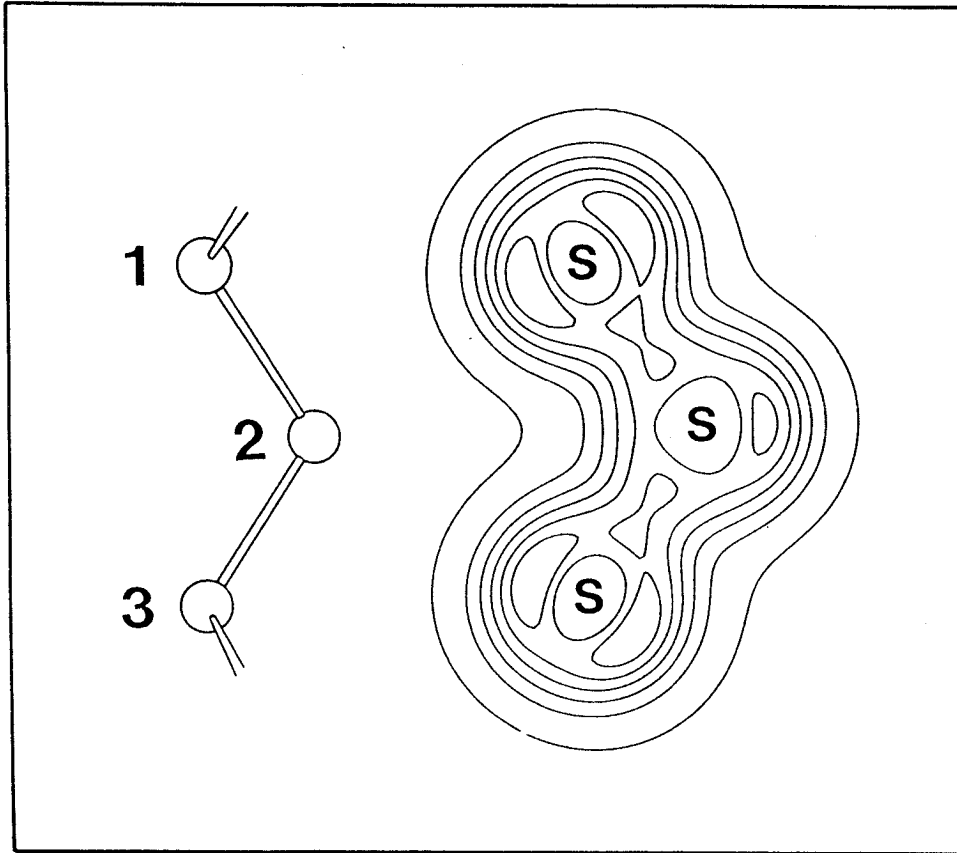


Fig. 4: Contour plot of the (pseudo-)density in S_8 in a plane containing three adjacent sulphur atoms. The contour separation is $0.1 \text{ electrons per } \text{\AA}^3$. Contours in the core region ($\leq 0.8 \text{ a.u.}$ from the nuclei) are not shown.

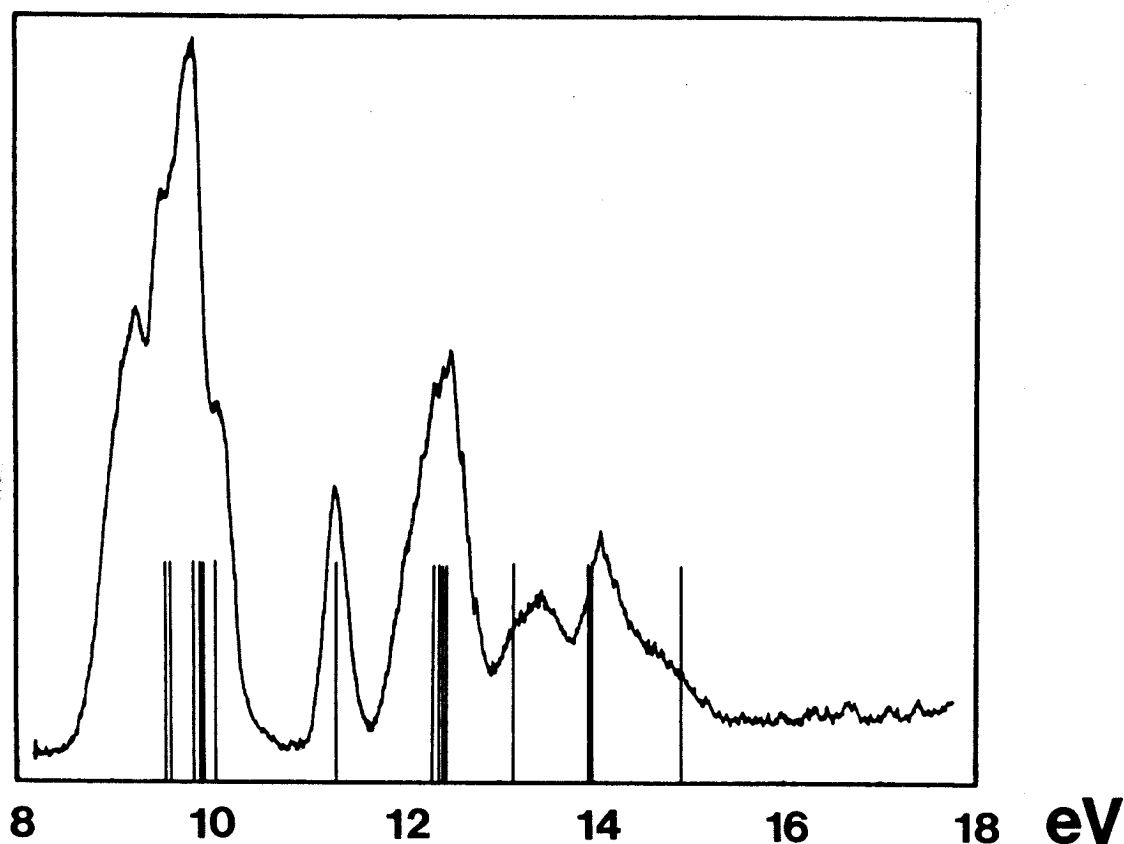


Fig. 3: Comparison of the calculated ground state eigenvalue spectrum of S_8 with the photoelectron spectrum. Vertical lines indicate the energetic position (in eV) of the molecular orbitals in the p band. The calculated spectrum has been shifted uniformly so that the calculated and measured peaks near 11.3 eV coincide.

In Fig. 3 we compare the calculated ground state eigenvalue spectrum of S_8 with the He(I) photoelectron spectrum of sulphur vapour at 413 K.⁸⁸ The width and spacing of the energy levels in the p -band agree satisfactorily. Small deviations from perfect D_{4d} symmetry split degenerate levels up to 0.05 eV.

The calculated charge densities for the equilibrium structure of S_8 are shown in Fig. 4. The qualitative shape of the electron density compares very well with $X - N$ and $X - X$ deformation densities measured by Coppens *et al.*⁶⁰ The lone pair lobes are clearly evident and the peculiar double maximum distribution along the $S - S$ lines⁶⁰ is reproduced (in contrast, S_3 shows a marked accumulation of electron density near the center of the bond). Contours closer to the nuclei than ~ 0.8 a.u. have been discarded because we use nodeless pseudo-wavefunctions, and

Tab. 4: Molecular parameters d , α and γ for low energy isomers of S_9 . Bond lengths d_{ij} (between atoms i and j) in a.u., bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees.

$S_9(C_2)$		$S_9(C_s, \text{"boat"})$	
$d_{12,91}$	3.98	$d_{12,91}$	3.99
$d_{23,89}$	3.95	$d_{23,89}$	3.87
$d_{34,78}$	3.99	$d_{34,78}$	4.27
$d_{45,67}$	3.97	$d_{45,67}$	3.74
d_{56}	3.98	d_{56}	4.55
α_1	103°	α_1	110°
α_2, α_9	108°	α_2, α_9	106°
α_3, α_8	108°	α_3, α_8	104°
α_4, α_7	107°	α_4, α_7	107°
α_5, α_6	107°	α_5, α_6	101°
$\gamma_{12,91}$	74°	$\gamma_{12,91}$	86°
$\gamma_{23,89}$	75°	$\gamma_{23,89}$	109°
$\gamma_{34,78}$	66°	$\gamma_{34,78}$	7°
$\gamma_{45,67}$	114°	$\gamma_{45,67}$	100°
γ_{56}	81°		
$S_9(C_s, \text{"chair"})$		$S_9(C_s, \text{"cage"})$	
$d_{12,91}$	3.97	$d_{12,91}$	4.00
$d_{23,89}$	3.94	$d_{23,89}$	3.91
$d_{34,78}$	4.06	$d_{34,78}$	4.14
$d_{45,67}$	3.84	$d_{45,67}$	3.81
d_{56}	4.22	d_{56}	4.34
α_1	105°	α_1	112°
α_2, α_9	109°	α_2, α_9	105°
α_3, α_8	110°	α_3, α_8	113°
α_4, α_7	103°	α_4, α_7	113°
α_5, α_6	109°	α_5, α_6	110°
$\gamma_{12,91}$	105°	$\gamma_{12,91}$	62°
$\gamma_{23,89}$	96°	$\gamma_{23,89}$	66°
$\gamma_{34,78}$	127°	$\gamma_{34,78}$	27°
$\gamma_{45,67}$	107°	$\gamma_{45,67}$	76°

calculated and experimental results are unreliable in that region.

S_9

The S_9 molecule is particularly interesting. While it can be prepared in mi-

crocrystalline form,^{13,89} and even occurs in biological systems,⁹⁰ the absence of single crystals has ruled out an X-ray structure determination. However, information about the α - and β -modifications can be obtained from the Raman spectra, since these spectra are very different from those of all other S molecules studied to date.⁸⁹ By analogy to the spectra of S molecules with known structures, Steudel *et al.* concluded that the constituent molecules have nearly identical structures with $S-S$ bonds which are neither unusually long or short, and they predicted values between 3.84 a.u. and 3.95 a.u. The relationship between d_{SS} and the corresponding torsion angle (see Sec. 3.2) indicates that $70^\circ \leq \gamma \leq 130^\circ$, i.e. geometries with four consecutive atoms nearly in a plane can be excluded. This rules out the possibility of C_s symmetry, and allows only C_1 and C_2 . Three-fold axes can be excluded.

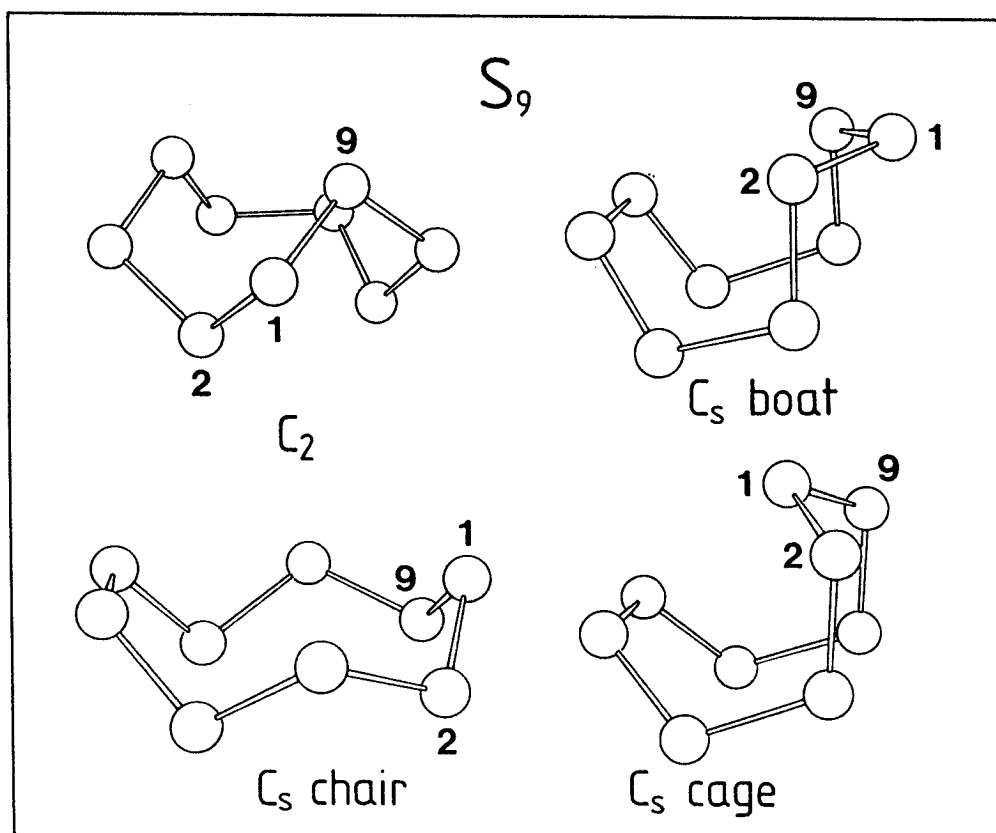


Fig. 5: Four low-lying structures of S_9 .

A theoretical study of S_9 has not been reported previously. The calculations presented here were again started from a randomly displaced planar ring. The process of "heating" and "cooling" leads to a ground state structure (Fig. 5 and Tab. 4) that fulfills all of the above criteria. It has C_2 symmetry, approximately equal bond lengths, and torsion angles between 66° and 114° . The structure cannot be rationalized on the basis of the previous results and most closely resembles S_{10}

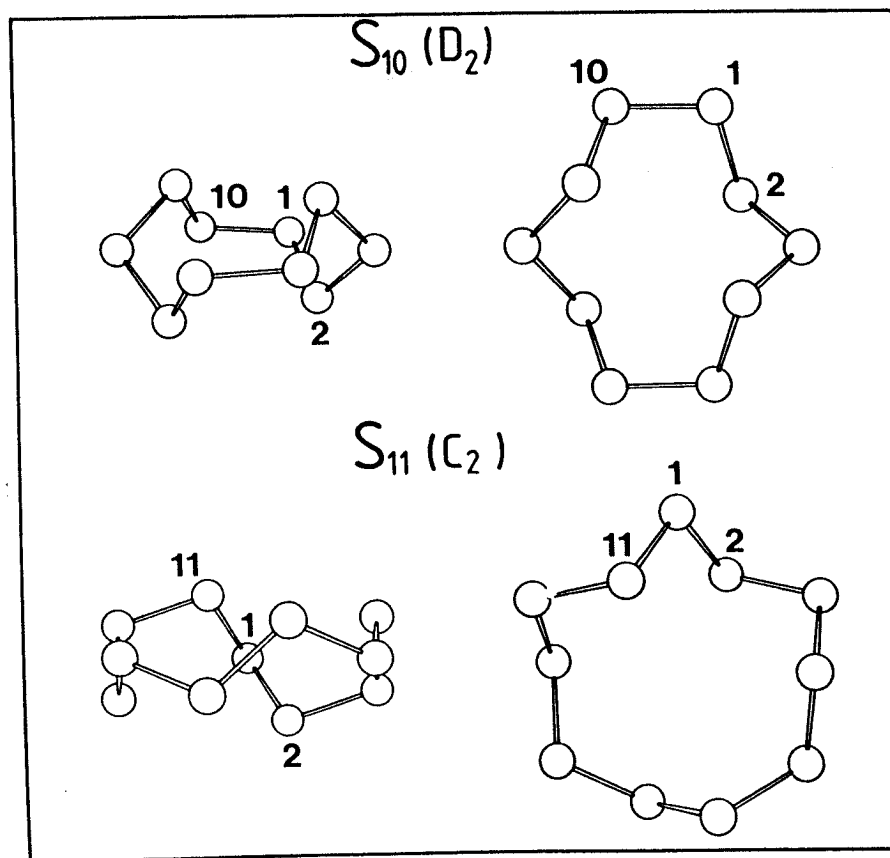


Fig. 6: The structures of S_{10} and S_{11} .

with one S_2 unit replaced by a single atom (see Fig. 6 and the discussion of S_{10} below). Three low-lying structures result by adding S_2 units to S_7 (C_s “boat”, C_s “cage”) and replacing a single atom in S_8 (C_s “chair”) by a dimer. The fully relaxed structures are also shown in Fig. 5. None of these structures conforms to the above spectroscopic findings, and they lie ≥ 0.2 eV above the ground states according to our calculations.

S_{10-13}

The less common allotropes S_{10-13} occur only as minor components of liquid sulphur⁹¹ and irradiated sulphur solutions.⁷⁵ The ability to prepare pure S_{10} , S_{11} , S_{12} and S_{13} via chemical reactions and/or isolation procedures provided the basis for a thorough characterization. Apart from a variety of spectroscopic, chemical and thermodynamical data,¹³ the crystal structures of all four species have been determined via X-ray analyses.^{92,93,94} The structures are increasingly complicated homocycles with symmetries ranging from C_2 (S_{11} , S_{13}) to D_{3d} (S_{12}). Theoretical investigations have not been performed on any of them.

We have carried out MD-DF simulated annealing calculations for S_{10-13} in a

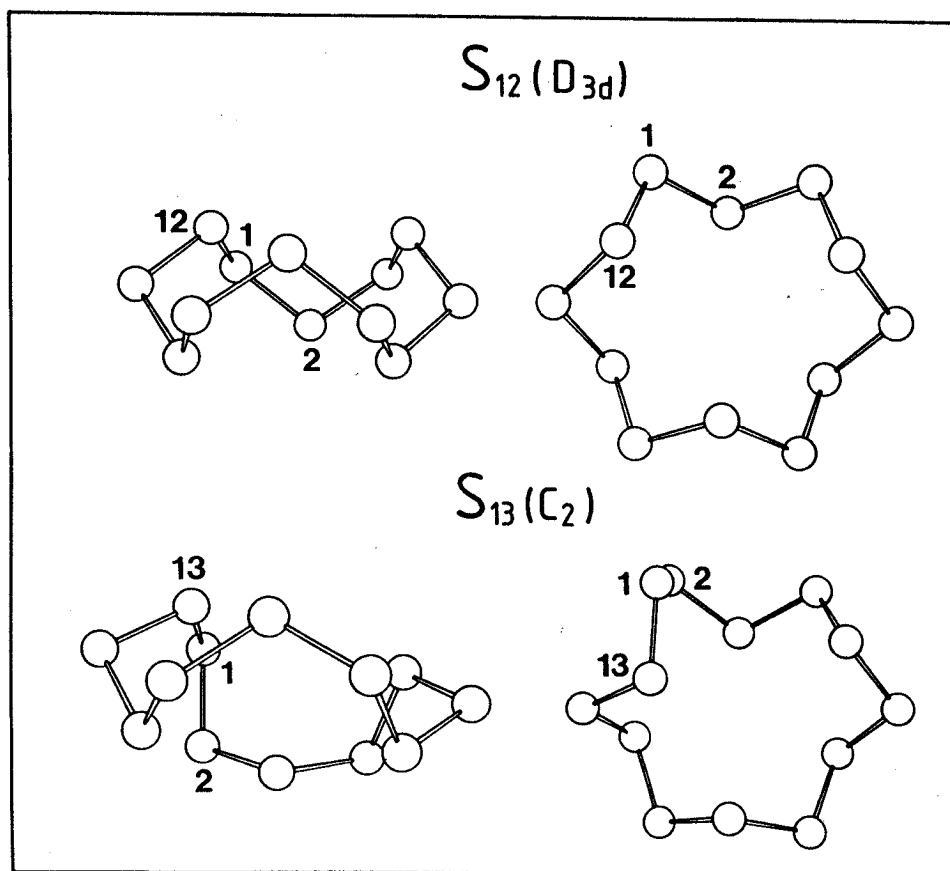


Fig. 7: The structures of S_{12} and S_{13} .

fashion similar to S_{3-8} . To accelerate the convergence to the $T \rightarrow 0$ ground states, we displaced the atoms slightly from the initial planar rings according to the experimental pattern rather than randomly. The calculated ground state geometries are shown in Fig. 6, 7 and in Tab. 5. The computations show that the molecules become more flexible with increasing ring size, with the following two consequences:

(a) The agreement between calculated and experimental dihedral angles and associated bond distances (see Fig. 8) worsens with increasing ring size, due to the very shallow energy surfaces in the vicinity of the minimum. In particular, changing dihedral angles away from their optimal values and relaxing all other parameters simultaneously costs very little energy (especially for γ outside the range $75-110^\circ$). Any method that relies on force evaluations would have comparable difficulties for these extraordinarily flexible species.

(b) For the same reason, deviations from perfect symmetry are greater as the ring size increases. The data in Tab. 3-5 are the appropriate averages, but the departures from symmetry are included in Fig. 1-6. Increasing structural flexibility is also evident in the crystal structures and is not an artefact of our calculations.

The cyclic S_{10} molecule exhibits the same D_2 conformation in both crystalline

Tab. 5: Molecular parameters d , α and γ for low energy isomers of S_n , $n = 10 - 13$. Bond lengths d_{ij} (between atoms i and j) in a.u., bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees.

$S_{10}(D_2)$			expt(a)	$S_{12}(D_{3d})$			expt(c)
$d_{12,45,67,9-10}$	4.00		3.92	d	3.97		3.88
$d_{23,34,78,89}$	3.96		3.87	α	106°		106.2°
$d_{56,10-1}$	3.94		3.85	γ	88°		87.2°
$\alpha_1, \alpha_5, \alpha_6, \alpha_{10}$	107°		107.6°	$S_{13}(C_2)$			expt(b)
$\alpha_2, \alpha_4, \alpha_7, \alpha_9$	103°		103.4°	d_{12}	3.97		3.96
α_3, α_8	110°		110.2°	$d_{23,13-1}$	3.98		3.77
$\gamma_{12,45,67,9-10}$	120°		122.6°	$d_{34,12-13}$	3.97		3.92
$\gamma_{23,34,78,89}$	80°		78.5°	$d_{45,11-12}$	3.96		3.86
$\gamma_{56,10-1}$	72°		76.1°	$d_{56,10-11}$	3.98		3.89
$S_{11}(C_2)$			expt(b)	$d_{67,9-10}$	3.98		3.88
$d_{12,11-1}$	3.96		3.88	$d_{78,89}$	3.99		3.88
$d_{23,10-11}$	3.97		3.90	α_1, α_2	106°		109°
$d_{34,9-10}$	3.96		3.86	α_3, α_{13}	107°		108°
$d_{45,89}$	4.00		3.91	α_4, α_{12}	101°		103°
$d_{56,78}$	3.96		3.85	α_5, α_{11}	104°		105°
d_{67}	4.03		3.96	α_6, α_{10}	106°		106°
α_1	103°		104°	α_7, α_9	110°		106°
α_2, α_{11}	105°		105°	α_8	111°		107°
α_3, α_{10}	108°		105°	γ_{12}	54°		30°
α_4, α_9	107°		107°	$\gamma_{23,13-1}$	63°		74°
α_5, α_8	110°		108°	$\gamma_{34,12-13}$	101°		114°
α_6, α_7	111°		107°	$\gamma_{45,11-12}$	86°		90°
$\gamma_{12,11-1}$	90°		91°	$\gamma_{56,10-11}$	70°		82°
$\gamma_{23,10-11}$	75°		71°	$\gamma_{67,9-10}$	99°		94°
$\gamma_{34,9-10}$	81°		83°	$\gamma_{78,89}$	88°		87°
$\gamma_{45,89}$	120°		116°	(a)		Ref. ⁸⁹	
$\gamma_{56,78}$	104°		103°	(b)		Ref. ⁹²	
γ_{67}	127°		139°	(c)		Ref. ⁹³	

S_{10} and crystals of the complex $S_{10} \cdot S_6$.⁹² The intermolecular distances become as small as 1.55 times the longest intramolecular $S - S$ -bond and the standard deviations of the X-ray data are slightly larger than in S_6 and S_8 . The individual molecules have D_2 symmetry to a very good approximation and occupy sites of C_2 symmetry. The values for S_{10} are compared with the calculated geometry in Tab. 5.

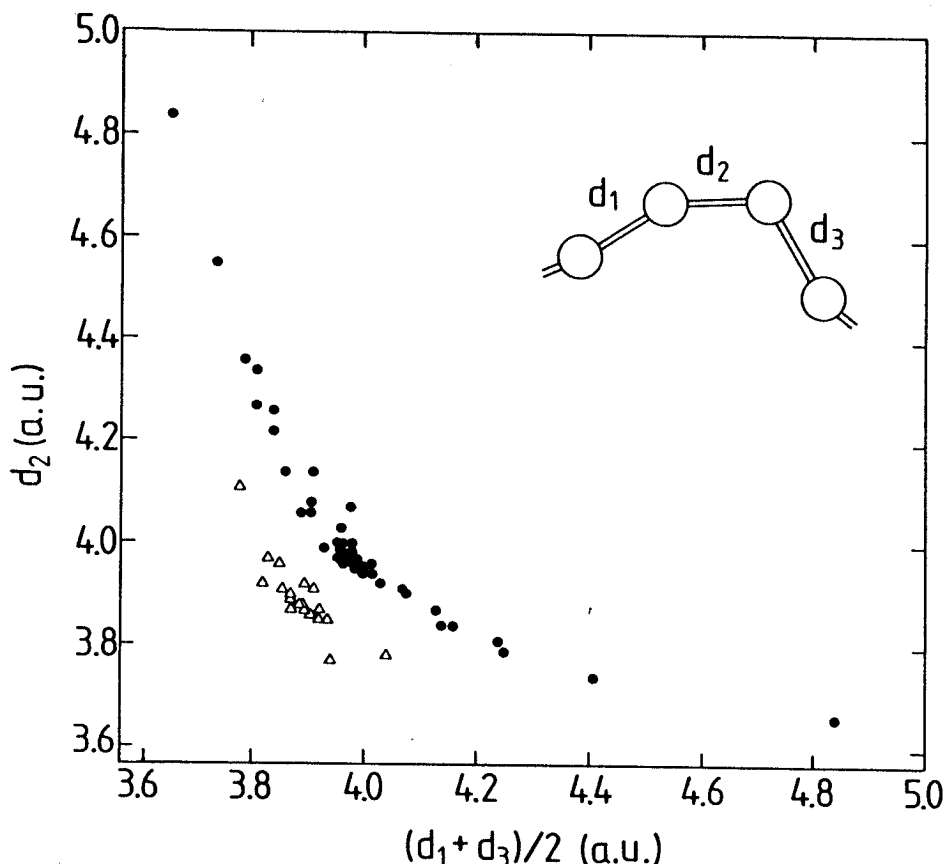


Fig. 8: Plot of bond length, d_2 , against the mean length of the two neighbouring bonds $((d_1 + d_3)/2)$ in S_5 to S_{13} . Experimental values are shown by triangles and calculated values by full circles.

The agreement is very good, although increasing inaccuracies in the dihedral angles are apparent.

S_{11} and S_{13} are very similar, and single crystals of both allotropes contain two non-equivalent molecules with approximately C_2 symmetry occupying sites of C_1 symmetry.⁹³ The experimental values shown in Tab. 5 are the averages of the four appropriate values, and they are in good agreement with our calculations in the case of S_{11} . For S_{13} we find the least satisfactory agreement in the present series of calculations, with the differences being largest for the dihedral angles and their associated bond lengths. The relative locations of atoms 6 and 7 are not reproduced accurately, leading to unusually large errors in the related parameters. The structure of the molecule away from the immediate neighbourhood of this bond is given satisfactorily. It should be noted again that the departures from C_2 symmetry found in the measurements⁹³ are not negligible. The values of γ_{56} and γ_{78} in S_{11} , for example, range from 98.7° to 109.0° ; in S_{13} , d_{12} varies from 3.92 a.u. to 3.99

a.u., and $\alpha_{1,2}$ from 106.6° to 111.1°

After S_8 , cyclododecasulphur S_{12} is the second most common modification of sulphur. The photochemical, thermal and thermodynamical stabilities of S_{12} are almost as high as for S_8 , with average bond energies⁹¹ nearly the same. X-ray structural analyses have been performed for S_{12} and the solvent adduct $CS_2 \cdot S_{12}$.⁹⁴ The S_{12} units have D_{3d} symmetry and occupy sites of C_{2h} symmetry in solid S_{12} . The calculated and experimental geometries agree very well when appropriate averages are taken. In the crystal data and the calculations, respectively, bond lengths vary by 0.02 a.u. [0.007], bond angles by 1.2° [1.6°] and dihedral angles by 3.4° [12.3°]. The shapes of both S_{11} and S_{13} can be derived from S_{12} by inserting an S_2 dimer in place of an S_3 unit or a single atom, respectively.

3.2. BINDING ENERGY AND STRUCTURAL TRENDS

Calculated atomization energies are compared with available thermodynamic data^{91,95} in Tab. 6. It should be noted that the experimental data have been analyzed assuming that only ring structures are present, whereas we have seen that S_3 probably exists as an open structure. In spite of a tendency to overestimate bond strengths in *sp*-bonded materials,⁷⁴ DF calculations with the LSD approximation for exchange and correlation have provided a consistently reliable picture of bonding trends. Both features are apparent in Tab. 6. The atomization energies are overestimated in all cases, but S_5 , S_6 , S_8 and S_{12} are shown to be relatively more stable than the remainder by our calculations and the experimental data.

In the case of S_3 there is a density functional calculation available using an LMTO basis.⁵³ The atomization energies are smaller in the MD-DF calculations by ~ 0.4 eV per atom. This difference reflects the pseudopotential approximation used in the present work and the different convergence of the basis set expansions in the two methods.

Some interesting structural trends in sulphur ring molecules have been pointed out by Steudel and co-workers.^{13,96,97} The first is that the longest bonds in these molecules are always adjacent to short bonds. In fact, the bond length d is inversely related to the mean of the two neighbouring bonds. In Fig. 8 we plot these two quantities for all the bonds in *all* the structures given in Tab. 3–5 for S_5 to S_{13} . While the data base from the calculations is substantially greater, the inverse behaviour is very pronounced in both calculated and measured structures. The origin of the plot corresponds to the experimental bond length of S_2 , which would be the asymptotic value for both axes. The comparison between the experimental and calculated dis-

Tab. 6: Calculated atomization energies^{a)} for $S_n, n = 2 - 13$. Comparison with thermodynamically^{b)} derived values for gas phase S_n (energies in eV).

n	E_{at}^{calc}	$\frac{E_{at}^{calc}}{n}$	$\frac{E_{at}^{therm}}{n}$	ΔE_{at}^{calc}	ΔE_{at}^{therm}
2 ($D_{\infty h}$)	5.48	2.74	2.19	...	...
3 (${}^3C_{2v}$)	8.16	2.72	2.36	...	...
3 (D_{3h})	8.65	2.89	2.36	...	...
3 (C_{2v})	8.81	2.94	2.36	3.33	2.71
4 (C_{2h})	12.18	3.04	2.37	...	...
4 (D_{2h})	12.61	3.15	2.37	3.80	2.42
5 (C_2)	16.59	3.32	2.63	3.98	3.64
5 (C_s)	16.59	3.32	2.63	3.98	3.64
6 (C_{2v})	19.92	3.32	2.68	...	...
6 (D_{3d})	20.44	3.41	2.68	3.85	2.97
7 (C_s , "boat")	23.88	3.41	2.70	...	...
7 (C_s , "chair")	23.98	3.43	2.70	3.54	2.81
8 (D_{4d})	27.69	3.46	2.73	3.71	2.96
9 (C_s , "cage")	30.27	3.36	2.74	...	...
9 (C_s , "boat")	30.65	3.41	2.74	...	...
9 (C_s , "chair")	30.70	3.41	2.74	...	...
9 (C_2)	30.96	3.44	2.74	3.28	2.48
10 (D_2)	34.40	3.44	2.74	3.44	2.75
11 (C_2)	37.84	3.44	2.74	3.44	2.74
12 (D_{3d})	41.52	3.46	2.76	3.68	2.98
13 (C_2)	44.98	3.46	2.74	3.46	2.57

^{a)} $\Delta E_{at} \equiv E_{at}(n) - E_{at}(n - 1)$

^{b)} S_{2-8} : Ref.⁹⁵, S_{9-13} : Ref.⁹¹.

tributions is further evidence for a small and uniform overestimate of bond lengths in the latter. Calculations on S_3 , S_6 , S_7 and S_{11} with $l_{max} = 2$ in eq. (2.12) show that the restriction to $l_{max} = 1$ is responsible for about half of this discrepancy.

The second relationship evident from the measured structures is between the bond length, d , and the torsion angle, γ , whereby d is shortest for torsion angles

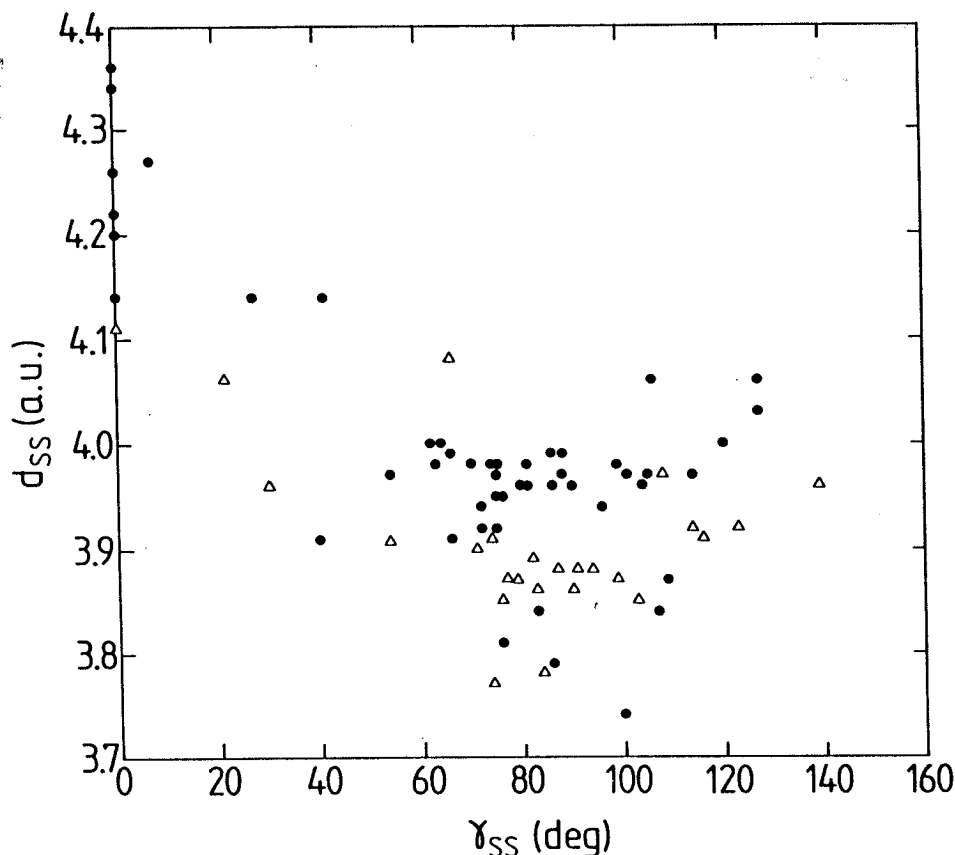


Fig. 9: Plot of bond length, d , against corresponding torsion or dihedral angle, γ . Experimental values are shown by triangles, calculated values by full circles.

near 90° . The results are shown for the experimental and calculated structures in Fig. 9. The statistics are less convincing in this case, but the scatter in the bond lengths in any small range of γ (~ 0.2 a.u.) is much less than the total range of bond lengths observed (~ 0.6 a.u.). The preference for torsion angles around 100° had been noted earlier by Pauling,⁹⁸ who referred to this as the “normal” value for γ in $S-S$ bonds. The torsion angle is defined, of course, by the coordinates of four successive atoms in a chain. The substantial variation of bond length with torsion angle is then an indication that four-body forces may be important. In the case of silicon, Mistriotis *et al.*⁹⁹ have found that four-body interactions are essential to give good agreement with the melting point of the crystal, as well as the geometries and relative energies of low-lying states of small clusters.

Perhaps the most interesting feature of the *structural* trends in this family of molecules is, however, the difficulty of interpolating between or extrapolating from known structures. The most striking example is S_9 , where the structures of *three* members of the family on either side are known. Nevertheless, neither the structure

nor even the pattern of torsion angles or “motif”,^{13,100} of the ground state of this molecule can be predicted. We have found that isomers with quite different structures can have very similar energies. The assignment of the ground state depends then on subtle effects which require quantitative measurements or calculations rather than qualitative arguments.

4. SELENIUM CLUSTERS $Se_3 - Se_8$

Tab. 7: Molecular parameters d , α and γ for low energy isomers of Se_n , $n = 3 - 8$. Bond lengths d_{ij} (between atoms i and j) in a.u., bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees.

$Se_3(C_{2v})$		$Se_6(C_{2v})$	
$d_{12,13}$	4.16	$d_{12,16,34,45}$	4.35
α_1	118°	$d_{23,56}$	4.74
$Se_3(D_{3h})$		α_1, α_4	107°
d	4.46	$\alpha_2, \alpha_3, \alpha_5, \alpha_6$	98°
α	60°	$\gamma_{12,61,34,45}$	79°
$Se_4(C_{2h})$		$Se_6(D_{3d})$	
$d_{12,34}$	4.14	d	4.42
d_{23}	4.52	α	101°
α_2, α_3	110°	γ	76°
$Se_4(D_{2h})$		$Se_7(C_s)$	
$d_{12,34}$	4.07		chair boat
$d_{23,41}$	5.15	$d_{12,17}$	4.40 4.36
$\alpha_1, \alpha_2, \alpha_3, \alpha_4$	90°	$d_{23,67}$	4.55 4.63
$Se_5(C_s)$		$d_{34,56}$	4.26 4.20
$d_{12,15}$	4.48	d_{45}	4.70 4.80
$d_{23,45}$	4.32	α_1	106° 108°
d_{34}	4.65	α_2, α_7	101° 100°
α_1	87°	α_3, α_6	106° 108°
α_2, α_5	100°	α_4, α_5	105° 103°
α_3, α_4	100°	$\gamma_{12,71}$	75° 71°
$\gamma_{12,51}$	66°	$\gamma_{23,67}$	110° 44°
$\gamma_{23,45}$	42°	$\gamma_{34,56}$	86° 89°
		$Se_8(D_{4d})$	
		d	4.42
		α	109°
		γ	98°

This chapter presents ground state structures for selenium clusters obtained with the same procedure described in detail in the previous sections. Not unexpectedly, the results are qualitatively identical to those for the sulphur system. Although interesting differences in the chemistry of S and Se exist (see Chap. 1 and Sec. 5.2), the shapes of the energy surfaces and the relative depths of local minima for the

allotropes behave very similarly. The reader is therefore referred to Fig. 1–2 for the structures of the lowest-lying singlet states calculated for Se_{3-5} and Se_{6-8} . The geometrical parameters in Tab. 7 are different mainly because of the larger atomic radius for Se .

Se₃

The trimer has nearly degenerate ring (D_{3h}) and open (C_{2v}) structures. The bond in the open state is notably shorter than a normal $Se-Se$ single bond (4.42 a.u.¹⁸), indicating a bond order between one and two. We have compared these results with those of all-electron calculations with the method used previously for S_3 ,⁵³ where open and closed structures with very similar energies are also the lowest singlet states. The equilibrium geometries are essentially identical in the two calculations. Bond lengths agree within 0.1 a.u. and bond angles within 1°. The all-electron calculations indicate a slightly lower energy (~ 0.3 eV) for the open isomer, in agreement with matrix isolation studies¹⁰¹ The atomization energies are larger in the MD-DF calculations by ~ 0.5 eV per atom. This difference is due to the pseudopotential approximation and to the different convergence of the basis set expansions in the two methods. Both the MD-DF and all-electron calculations show the lowest triplet state ~ 1 eV above the singlet ground state, as in S_3 .⁵³

Se₄

Only thermodynamic data^{22,23} are available for Se_4 , and our calculations predict a rectangular singlet ground state of D_{2h} symmetry. A planar *trans*-isomer (C_{2h}) with similar bond lengths and angles is a low-lying excited state separated by a rotational barrier of ~ 1 eV. Insight can be gained by comparison with S_4 (see Sec. 3.1) and its derivatives. The most striking features of the two lowest Se_4 structures are again their planarity and the pattern of bond lengths. As in S_4 , the terminal bonds are shorter than normal $Se-Se$ bonds and the central bonds significantly longer, conforming to the observation that the long $S-S$ bonds in sulphur compounds are generally adjacent to shorter ones (see Sec. 3.2). Similarly, four consecutive planar Se (like S) atoms are usually energetically unfavourable, with long, weak bonds. As in S_4 , the lowest-lying triplet state lies above the singlet ground state (by 0.3 eV), contradicting the common assumption that group VIA chain fragments must be diradicals.¹⁰² We have also studied the energy surface in the vicinity of the ground state configurations of refs.^{102,69}. The SO_3 analog (D_{3h}) is in our calculations a stable local minimum 1.4 eV above the ground state. A helical triplet

state with C_2 symmetry, the ground state in the HF calculations,⁶⁹ is not a stable local minimum but relaxes to a rectangle (D_{2h} , with bond lengths 4.30 a.u. and 4.80 a.u.) 0.3 eV above our singlet D_{2h} ground state.

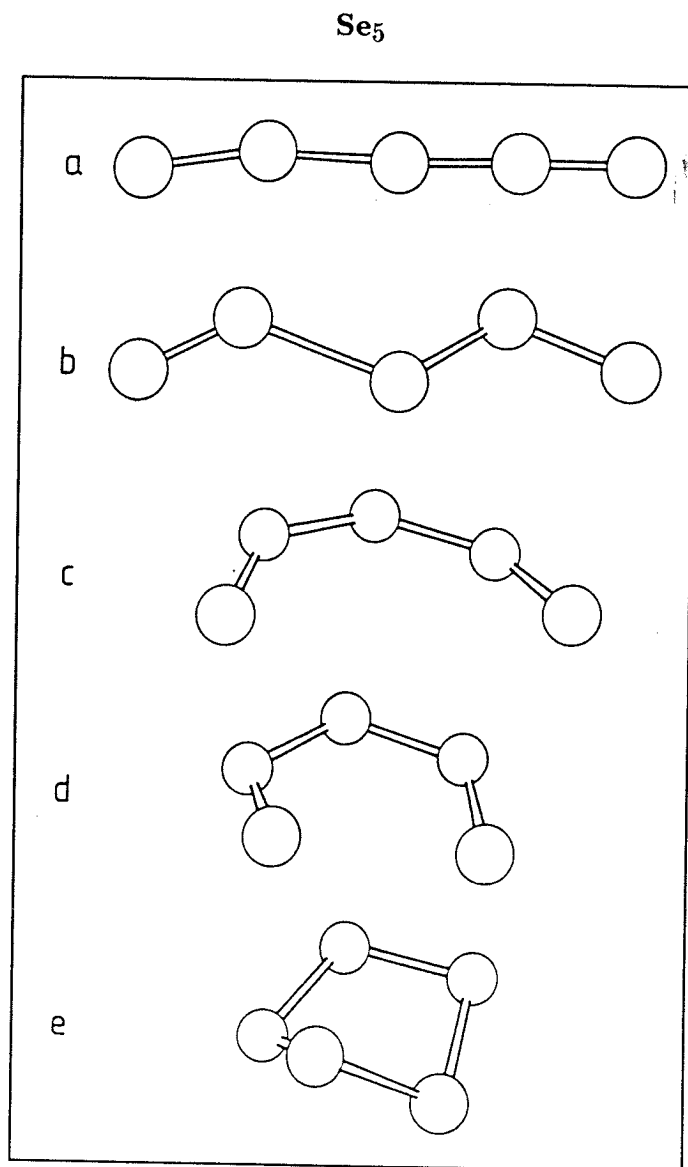


Fig. 10: Temporal evolution of Se₅ from a chain to a ring structure in the simulated annealing procedure.

As in S_5 , no definite structural information is available for Se_5 . Thermodynamical data^{13,18} and the structure of S_5O (Sec. 3.1) suggest a ring structure. An analogous procedure as described for S_5 in Sec. 3.1 leads to a cyclic ground state with C_s symmetry (see Fig. 10), with several slightly disordered structures nearby. These are stable local minima with almost degenerate energies, some within 0.02 eV of the ground state. It is remarkable how efficiently we reach the ground state

(ring) starting from a very different initial state (linear chain) in a few thousand time steps. Because of its small extent in configuration space, we did not encounter the C_2 “half chair” state reported above for S_5 . The structure has not been checked explicitly by SD methods, either.

Se₆

Crystalline Se_6 contains molecular units which are six-membered rings with D_{3d} symmetry.²⁰ The bond lengths (4.452 ± 0.017 a.u.), bond angles ($101.3 \pm 0.3^\circ$) and torsion angles ($76.2 \pm 0.4^\circ$) agree very well with our values for the ground state configuration of Se_6 . The “boat” isomer (C_{2v}) (see Sec. 3.1) is a low-lying excited state. As expected from the zero torsion angles at the central bonds (2-3,5-6), these are far weaker and longer than normal single bonds.

Se₇

No structural data are available for microcrystalline Se_7 . However, the crystal structures of S_7 ⁵⁹ and Se_5S_2 ⁸¹ (see Sec. 3.1 and 5.2) suggest that Se_7 will have a chair-like structure with C_s symmetry, and the ground state we find has this geometry. Moreover, bond and torsion angles agree well with the experimental data for S_7 ,⁵⁹ and scaling the lengths⁵⁹ with the single bond distances found in Se_8 and S_8 reproduces the values in Tab. 7 (chair) remarkably well. The boat isomer is found to be the lowest excited singlet state, but the excitation energy is very small (0.07 eV) and this conformation may be accessible experimentally. In both chair and boat forms of Se_7 , increasing the torsion angle at bond 4-5 costs almost no energy. This compares well with the same findings in S_7 and torsion angle of zero in Se_7 will therefore not be observable at finite temperatures.^{59,81} The widely varying bond lengths and an abnormally long bond (4-5) associated with zero torsion angle are reminiscent of Se_4 , Se_5 and Se_6 (C_{2v}). Qualitatively, Se_5 can be derived from Se_4 by adding one atom, Se_6 (D_{3d}) by adding another, and Se_7 (chair) by adding two atoms at the edge 3-4 of Se_5 , identical to the structures in the series Se_4 – Se_7 .

Se₈

The three crystalline forms of Se_8 (α -, β -, γ -^{12,18,21}) consist of crown-shaped (D_{4d}) ring molecules. The structural parameters for our ground state geometry compare very well with the experimental data ($d = 4.414 \pm 0.011$ a.u., $\alpha = 105.7 \pm 1.6^\circ$, $\langle \gamma \rangle = 101.3^\circ$ for the α -form²¹).

Binding energy trends comparable to S_n are apparent in Tab. 8, where we com-

Tab. 8: Calculated atomization energies¹⁾ for $Se_n, n = 3 - 8$. Comparison with thermodynamically²⁾ derived values for gas phase Se_n . (All energies in eV)

n	E_{at}^{calc}	$\frac{E_{at}^{calc}}{n}$	$\frac{E_{at}^{therm}}{n}$	ΔE_{at}^{calc}	ΔE_{at}^{therm}
3 (D_{3h})	8.31	2.77	1.82	...	...
3 (C_{2v})	8.32	2.77	1.82	...	...
4 (C_{2h})	11.51	2.88	1.95	...	2.36
4 (D_{2h})	12.02	3.01	1.95	3.70	2.36
5 (C_s)	15.85	3.17	2.14	4.34	2.87
6 (C_{2v})	18.98	3.16	2.19	...	2.47
6 (D_{3d})	19.34	3.22	2.19	3.49	2.47
7 (C_s , "boat")	22.66	3.24	2.21	...	2.33
7 (C_s , "chair")	22.73	3.25	2.21	3.39	2.33
8 (D_{4d})	26.22	3.28	2.24	3.49	2.45

1) $\Delta E_{at} \equiv E_{at}(n) - E_{at}(n - 1)$

2) Ref.⁹⁵

pare calculated atomization energies for Se_3 to Se_8 with measured values.⁹⁵ Se_5 is stable relative to its neighbours, and both Se_6 and Se_8 are relatively more stable than Se_7 . It would be very interesting to have experimental data of higher resolution and a structure determination for Se_7 .

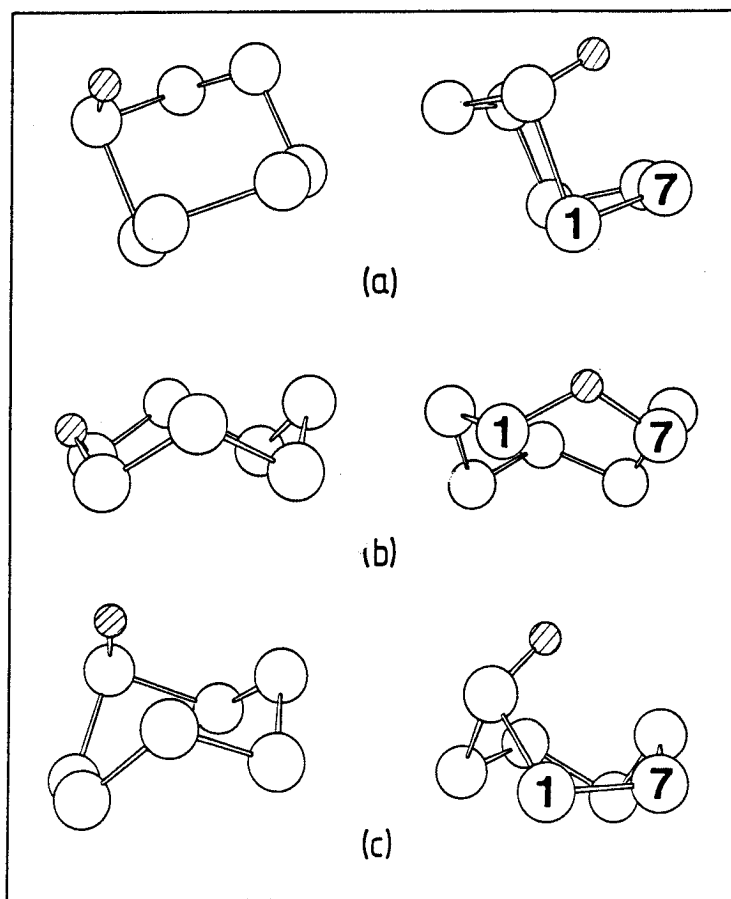


Fig. 11: The structures of the (a) ground state, (b) “ring”, and (c) “intermediate” forms of S_7O . The sulphur atoms are numbered cyclically, the oxygen atom is shaded.

5. HETEROCYCLIC CLUSTERS: S_7O , S_nSe_{7-n} and S_nSe_{8-n}

5.1. CYCLOHEXASULPHUR MONOXIDE (S_7O)

An important advantage of the techniques presented here is their ability to locate energy minima corresponding to geometries far removed from the starting structure. In this section, our goal was to further test the ability of MD/DF to find low energy structures far removed from the initial geometries. We have started with the calculated geometry for the ground state of S_8 (D_{4d}), perturbed each of the coordinates by a random amount (between -0.1 a.u. and 0.1 a.u.) and located the nearest minimum. In practice, this procedure can be accelerated by increasing electron mass and time step to $\mu = 50000$ a.u. and $\Delta t = 8.5 \times 10^{-16}$ sec and following a steepest descent path to the local minimum $\{R_I, \psi_i\}^{min} E[\{R_I\}, \{\psi_i\}]$ at $T = 0$.

The resulting ring structure (C_s) is shown in Fig. 11(b) and corresponds to a

Tab. 9: Molecular parameters d , α and γ for the fully relaxed C_s (“ring”) isomer of S_7O [see Fig. 10(b)]. Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees. Sulphur atoms are numbered 1-7, the oxygen atom is denoted by O .

$d_{O1,O7}$	1.78
$d_{12,67}$	2.06
$d_{23,56}$	2.15
$d_{34,45}$	2.11
α_O	119
α_1, α_7	110
α_2, α_6	109
α_3, α_5	106
α_4	108
$\gamma_{O1,O7}$	102
$\gamma_{12,67}$	94
$\gamma_{23,56}$	95
$\gamma_{34,45}$	98

stable local minimum. The structural parameters are given in Tab. 9. From this structure we allowed the system to evolve at 2000 K (mean kinetic energy of the ions, second term in eq. (2.18)) for 1000 time steps. In spite of the large ionic motion, this produced no significant changes in either the total energy or the basic structural “motif”,¹⁰⁰ i.e. the pattern of torsion angles. A further 1200 time steps, however, brought the dramatic structural changes shown in Fig. 12(a-i) at intervals of 150 time steps. The S_1-O and S_7-O bonds become longer, the S_1-O-S_7 angle is reduced sharply, and the O atom is pushed out of the ring, forming a bond with the sulphur atom (number 2) which was originally its next nearest neighbour. The structure at this point [Fig. 12(i)] is an oxygen atom outside the familiar S_7 ring structure. However, the topology is different from the measured ground state, where the oxygen is attached to an S_3 group, with long bonds to an S_4 group which is approximately planar. If the system is now cooled, the structural motif remains the same and the lowest energy of this conformation is 0.47 eV above that of the ring structure.

The fully relaxed structure is shown in Fig. 11(c) and the parameters are given in Tab. 10. We have also continued the high-temperature simulation from the geometry shown in Fig. 12(i), reducing the temperature in stages to a low value ($< 100K$) and finally reaching the bottom of the minimum via steepest descents techniques. We have found that the structure changes continuously into the ground state form shown in Fig. 11(a) and Fig. 12(j). The total number of time steps used in this stage

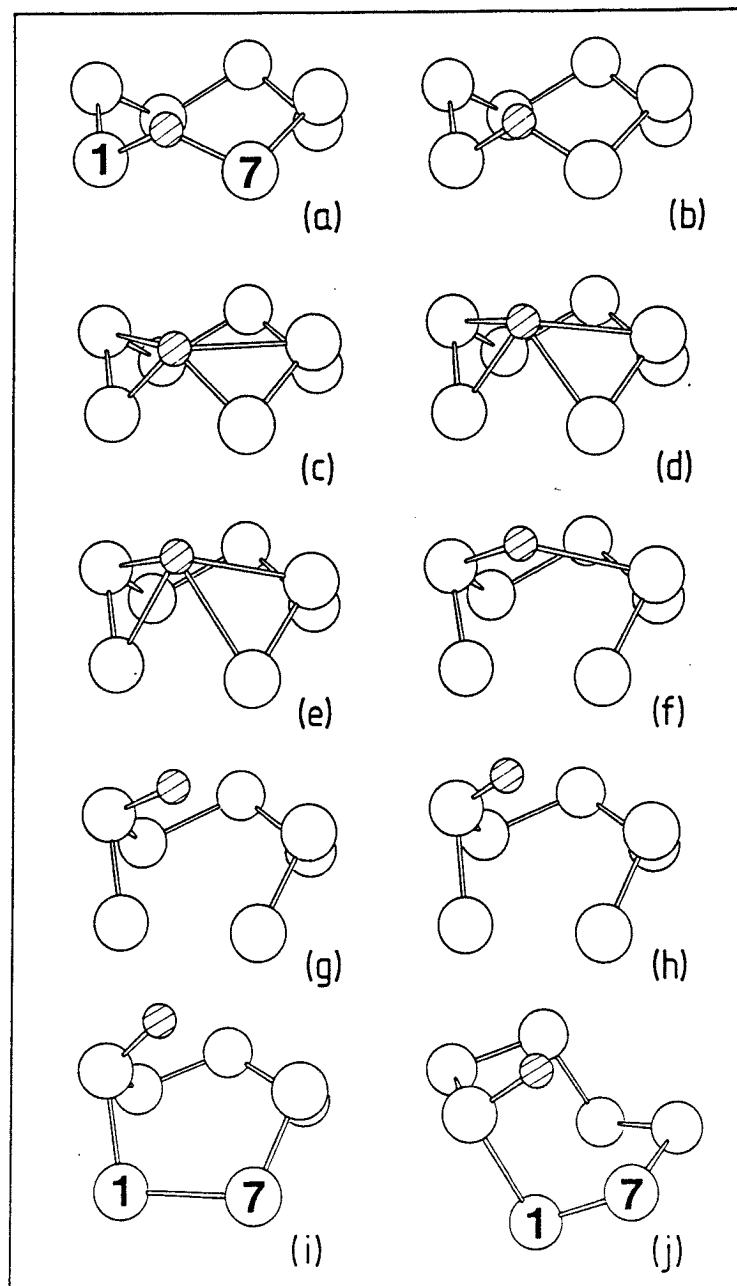


Fig. 12: (a)-(i) Evolution of the “ring” structure into the “intermediate” structure. The interval between each frame is 150 time steps. (j) The ground state structure from the same perspective. It is apparent that the change from (i) to (j) proceeds via a conformational change in the molecule, not by a migration of the O atom.

of the calculation, including the cooling procedure, was approximately 6000. The lowest energy we find is a stable minimum 0.13 eV below that of the ring structure [Fig. 11(b)]. The calculated geometry is compared with that determined from X-ray

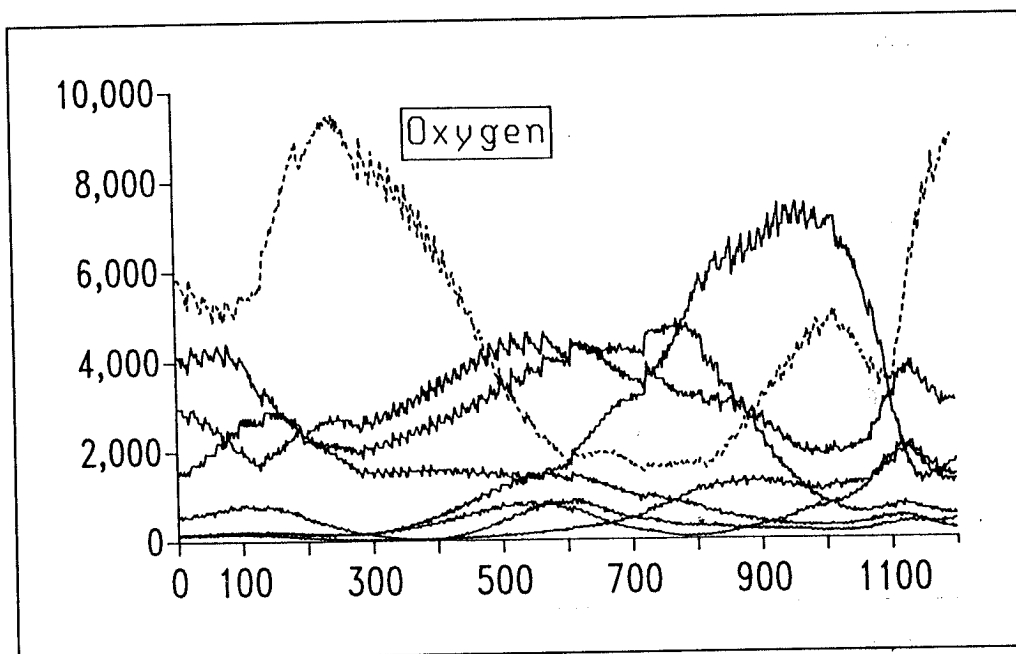


Fig. 13: Variation of the instantaneous kinetic energy (in units of T [°K]) of the eight particles with time (in units of Δt) during the rearrangement phase Fig. 12(a)-(i). The dashed line represents the oxygen atom, the other lines correspond to sulphur atoms.

diffraction³⁰ in Tab. 10. The overall agreement is very good. Experimental bond and torsion angles are generally reproduced to within 2–3°, lengths of shorter bonds are overestimated by 1–4 %, while the particularly long bonds d_{12} and d_{23} are overestimated by slightly more. The calculated distance between the oxygen atom and the remote neighbour S_7 (2.88 Å) is shorter than the measured value (2.96 Å). The d_{7O} separation is associated with a small torsion angle and is correspondingly long.³⁰ The discrepancies in the bond lengths are due to the pseudopotential description we have adopted and to the extreme flatness of the energy surface near the minimum. While the agreement between theory and experiment is very good, it is perhaps even more remarkable that this structure has been found in only 8000 time steps ($\sim 10^{-12}$ seconds) from a starting configuration with a very different topology.

Although the ground state structure of S_7O is well established,³⁰ the unusual behaviour of oxygen in only forming rings *outside* homocyclic sulphur rings is not well understood.¹⁰³ In fact, it has not been clear whether the ring structure corresponds to a stable local minimum in the energy surface or deforms spontaneously into another structure with lower energy.¹⁰³ The existence of the molecule $Cl-O-Cl$ with an “open” ground state structure¹⁰⁴ suggests that there is no fundamental

Tab. 10: Molecular parameters d , α and γ for C_1 conformations of S_7O . Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees.

	C_1^{int} (a)	$C_1^{int,T \rightarrow 0}$ (b)	$C_1^{g.s.}$ (c)	expt.
d_{12}	2.20	2.25	2.46	2.28
d_{23}	2.60	2.39	2.28	2.16
d_{34}	1.95	2.04	2.04	2.01
d_{45}	2.05	2.15	2.21	2.12
d_{56}	2.32	2.12	2.02	1.99
d_{67}	2.02	2.10	2.29	2.20
d_{71}	2.45	2.12	1.99	1.96
d_{7O}			2.88	2.96
d_{O2}	1.69	1.54	1.56	1.47
α_1	100	105	95	99.9
α_2	84	91	95	97.0
α_3	112	104	100	100.4
α_4	118	106	106	102.9
α_5	112	98	102	105.7
α_6	94	112	103	105.7
α_7	112	112	106	106.5
α_{32O}	113	109	108	107.0
α_{O21}	117	111	98	101.5
γ_{12}	113	111	113	111.9
γ_{23}	104	105	75	78.4
γ_{34}	63	84	92	81.0
γ_{45}	65	79	114	112.3
γ_{56}	98	103	82	80.5
γ_{67}	78	67	7	6.3
γ_{71}	13	29	94	89.5
γ_{712O}	17	17	4	2.9
γ_{O234}	13	7	26	25.9

(a) intermediate C_1 structure, see Fig. 12(i).

(b) quenched intermediate C_1 structure, see Fig. 11(c).

(c) ground state C_1 structure, see Fig. 11(a) and Fig. 12(j).

reason why $S-O-S$ bond angles near 90° should not occur. As noted above, Se substitution into a S_n ring proceeds with comparatively small structural changes – modest increases in bond lengths and no change in the structural motif and the topology.

Our calculations shed some light on these issues. We find that the C_s ring

structure is a stable local minimum lying approximately 0.13 eV above the lowest energy for the $C_1^{g.s.}$ structure. The energy barrier for the change from “ring” to ground state is substantial, and the structural change involved is very interesting. As the simulation proceeds, the $S-O-S$ bond angle becomes substantially less and, together with the lengthening of the S_7-O and S_1-O bonds, results in the O atom being pushed out of the ring. In the structure in Fig. 12(e), for example, $\alpha_{S_1OS_7} = 65^\circ$, $r_{S_1O} = 2.41 \text{ \AA}$, and $r_{S_7O} = 2.51 \text{ \AA}$. The energy of this structure is close to the top of the barrier between the “ring” [Fig. 12(a)] and “intermediate” [Fig. 12(i)] structures. The height of the barrier is $\sim 5 \text{ eV}$, which is substantially larger than the thermal energy available initially. The energy fed into the system to maintain the average kinetic energy of the nuclei means that the system is far from equilibrium during most of the simulation. This is exemplified in Fig. 13 where the variation of the kinetic energies of the eight atoms during the critical rearrangement phase of the simulation is shown (Fig. 12 (a)-(i)). The oxygen atom acquires up to five times the average kinetic “temperature” and helps the system to climb an energy barrier of 5.7 eV at time step no. 600. This opens a downhill way in the energy surface for sulphur atom no. 6, that by itself then gets essentially all the available kinetic energy at time step no. 900 (see Fig. 13). The non-equilibrium partitioning of the kinetic energy in the system seems to be an important factor in overcoming energy barriers with the MD procedure.

The tendency of α_{SOS} to be of smaller values than α_{SSS} is apparent in calculations for triatomic molecules.^{10,53} Calculations for O_3 , SO_2 , SOS and S_3 all lead to two low-lying singlet states (1A_1) with minima for bond angles near 60° (“closed”) and 115° (“open”). The relative stabilities of these states, however, shows a pronounced variation from molecule to molecule. In SOS , for example, the ground state is a “closed” structure with $\alpha \sim 75^\circ$, whereas the corresponding minimum in SO_2 is over 4 eV above the “open” ground state. This remarkable difference can be traced directly to the fact that the valence p -eigenvalue lies much higher in S than in O ,⁵³ which is consistent with the small core in O and the more compact p -orbitals in first-row atoms. By contrast, the valence eigenvalues and the extent of the valence eigenfunctions in Se are very similar to those in S , consistent with the minor structural changes observed in Se substitution.¹⁰⁵

The trends in bond lengths known to exist in sulphur rings^{13,96,97} (see Sec. 3.2) can be applied to $S-O$ bonds in an analogous fashion. In Tab. 11 we compare experimental bond lengths for diatomic⁴⁹ and triatomic¹⁰⁴ molecules with the results of density functional calculations.^{53,106} Also shown are the corresponding results for

Tab. 11: Calculated and measured $S-O$ and $S-S$ bond lengths ($\text{\AA}$). For both the ground state (g.s.) and ring structures of S_7O the $S-S$ lengths refer to the bonds closest to the O atom.

	$S-O$ (expt)	$S-O$ (calc)	$S-S$ (expt)	$S-S$ (calc)
SO	1.481 ^a	1.54 ^b		
OSO	1.432 ^c	1.46 ^b		
SSO	1.465 ^c		1.884 ^c	
S_7O (g.s.)	1.474 ^d	1.56 ^e	2.163, 2.283 ^d	2.28, 2.46 ^e
SOS (open)		1.70 ^f		
SOS (ring)		1.76 ^f		
S_7O (ring)		1.78 ^e		2.06, 2.15 ^e
S_2			1.889 ^a	1.98 ^f
S_3				2.00 ^f
S_8			2.05 ^g	2.11 ^g

(a) Ref.⁴⁹

(b) Ref.¹⁰⁶

(c) Ref.¹⁰⁴

(d) Ref.³⁰

(e) This work.

(f) Ref.⁵³

(g) This work (Chap. 3).

S_8 and S_7O . The $S-O$ bond lengths are remarkably similar if the oxygen atom is at the extremity of a small molecule or outside a ring, as in the ground state of S_7O (i.e. double bonds). In SOS and in the ring conformation of S_7O (i.e. single bonds), however, d_{SO} is substantially greater, with the bond in the latter being 5% longer than in SOS . A similar effect can be seen in S_3 and in S_8 , where the bond in the ring structure is also 5% longer. As we may expect from the alternation in bond strengths in sulphur ring molecules noted above, the extremely long $S-O$ bond in cyclic S_7O is associated with neighbouring $S-S$ bonds which are respectively 2% shorter and 2% longer than in S_8 .

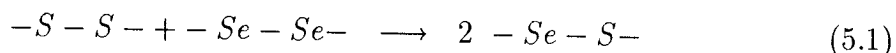
The results we have obtained show that trends in the di- and triatomic molecules are indeed apparent in larger systems. DF calculations indicate that the “closed”

conformation of SOS is more stable than the “open” structure, and make plausible the tendency of the $-S-O-S-$ bridge structure to break up on increasing the kinetic energy. However, the energy difference between the ring and ground state structures is so small (~ 0.1 eV) that qualitative arguments cannot be expected to predict the ground state. The situation is similar to that in S_7 or S_9 , where several structures have similar total energies and detailed calculations are essential to determine the most stable conformation.

5.2. MIXED SULPHUR-SELENIUM CLUSTERS Se_xS_y

The last decade has seen considerable use of Raman spectroscopy to study mixed sulphur-selenium systems, with impressive results. The structures of the eight-membered systems $1,2,3-Se_3S_5$ ¹⁰⁷ and $1,2,5,6-Se_4S_4$ ¹⁰⁸ have been determined qualitatively, and the first rings with less than eight atoms $[(1,2)-Se_2S_5]$ and SeS_5 prepared and characterized.¹⁰⁹ Ring molecules with a majority of Se atoms (Se_5S , Se_5S_2 , Se_6S_2)⁸¹ have also been studied. A comparison with Urey-Bradley force field calculations of fundamental vibration frequencies of six- and seven-membered $Se-S$ heterocycles¹¹⁰ showed that the ground state of the last of these contained adjacent Se atoms. ^{77}Se NMR spectroscopy has been used recently¹¹¹ to identify isomers of Se_nS_{8-n} obtained from molten mixtures of the elements. The main components were found to be SeS_7 and $(1,2)-Se_2S_6$, with smaller amounts of twelve others. For a given chemical composition, isomers with all Se atoms adjacent to each other were the most abundant. In the case of Se_2S_5 , the ^{77}Se NMR signal in CS_2 solution has a single peak at room temperature, so that the Se atoms are magnetically equivalent on the NMR time scale.¹¹² This was viewed as evidence for “pseudorotation”, by which all ring atoms become equivalent within a certain time interval due to the simultaneous rotation about several of the ring bonds.

Predictions of the relative stability of different isomers have been difficult to make. The interconversion of various Se_xS_y molecules and complicated ring-chain equilibration processes involve the rupture and formation of $S-S$, $Se-Se$ and $Se-S$ bonds, and a theoretical study of reactions involving the groups



has been performed recently using Hartree-Fock techniques with a minimal Gaussian basis.¹¹³ Even with a single configuration and a restricted basis, the computing effort required for parameter-free calculations of eight-membered rings was considered impracticable, and these authors restricted their attention to a number of hydrides

containing these bonds. It was found that the energy changes of various rearrangement reactions related to (1) were very small (between 0 and -2 kJ mol^{-1}). Not even the calculated exothermicity of the reaction is consistent with calorimetric measurements in the liquid [for an equimolar solution, the reaction enthalpy for (1) was concluded to be close to the enthalpy of mixing $\Delta H_m = +1.3 \text{ kJ mol}^{-1}$].¹¹⁴ For diatomic molecules in the gas phase,¹¹⁵ the enthalpy change is $+7.9 \pm 6.7 \text{ kJ mol}^{-1}$ and the sum of the dissociation energies on the left side of (1) is greater than the sum on the right.

The stated uncertainties ($10\text{-}20 \text{ kJmol}^{-1}$) of energy differences in these calculations are, however, substantially greater than the energy differences themselves. Moreover, previous experience with other molecules containing group VIA elements has shown that the inclusion of correlation effects (i.e. those beyond the Hartree-Fock approximation) is essential.¹⁰ Predictions of the small energy differences in Se_xS_y molecules require a method that is free of adjustable parameters, includes correlation effects, and permits both full geometry optimization and a thorough study of the convergence of the numerical technique, particularly the basis set. These are severe demands on *any* method.

Se_2S_6 , Se_6S_2 .

The cyclic structures possible in Se_2S_6 and Se_6S_2 are shown in Fig. 14 . The numeration of the atoms begins in each case on one of the minority atoms. The relative energies of the low-lying molecular states are shown in Fig. 15 , and the geometries corresponding to each structure are given in Tab. 12, 13. The calculations make no assumptions about the symmetry of the molecules, and it can be seen that the departures from the symmetries given in the table are very small.

The structures show a number of remarkable features. In all eight structures, the three bond lengths ($S-S$, $S-Se$, $Se-Se$) are not only the same within $0.01 \text{ \AA}$ ($2.08 \text{ \AA}$, $2.23 \text{ \AA}$, $2.35 \text{ \AA}$), but the $S-S$ and $Se-Se$ bonds are the same as found in our previous calculations for the ring structures of S_8 and Se_8 . All three are merely the sums of the corresponding atomic radii. The idea of transferability between different structures is enhanced by the observation that the *average* of the structural parameters is the same for each of the four structures [$\langle d_{ij} \rangle = 2.15 \text{ \AA}$, $\langle \alpha_i \rangle = 108.0^\circ$, $\langle \gamma \rangle = 98.7^\circ$ in Se_2S_6 ; $\langle d_{ij} \rangle = 2.29 \text{ \AA}$, $\langle \alpha_i \rangle = 107.4^\circ$, $\langle \gamma \rangle = 99.5^\circ$ in Se_6S_2]. If we take these parameters and extrapolate to Se_0S_8 and Se_8S_0 , we obtain structures close to the known structures of S_8 and Se_8 .

The deviations found from the average values of the structural parameters are

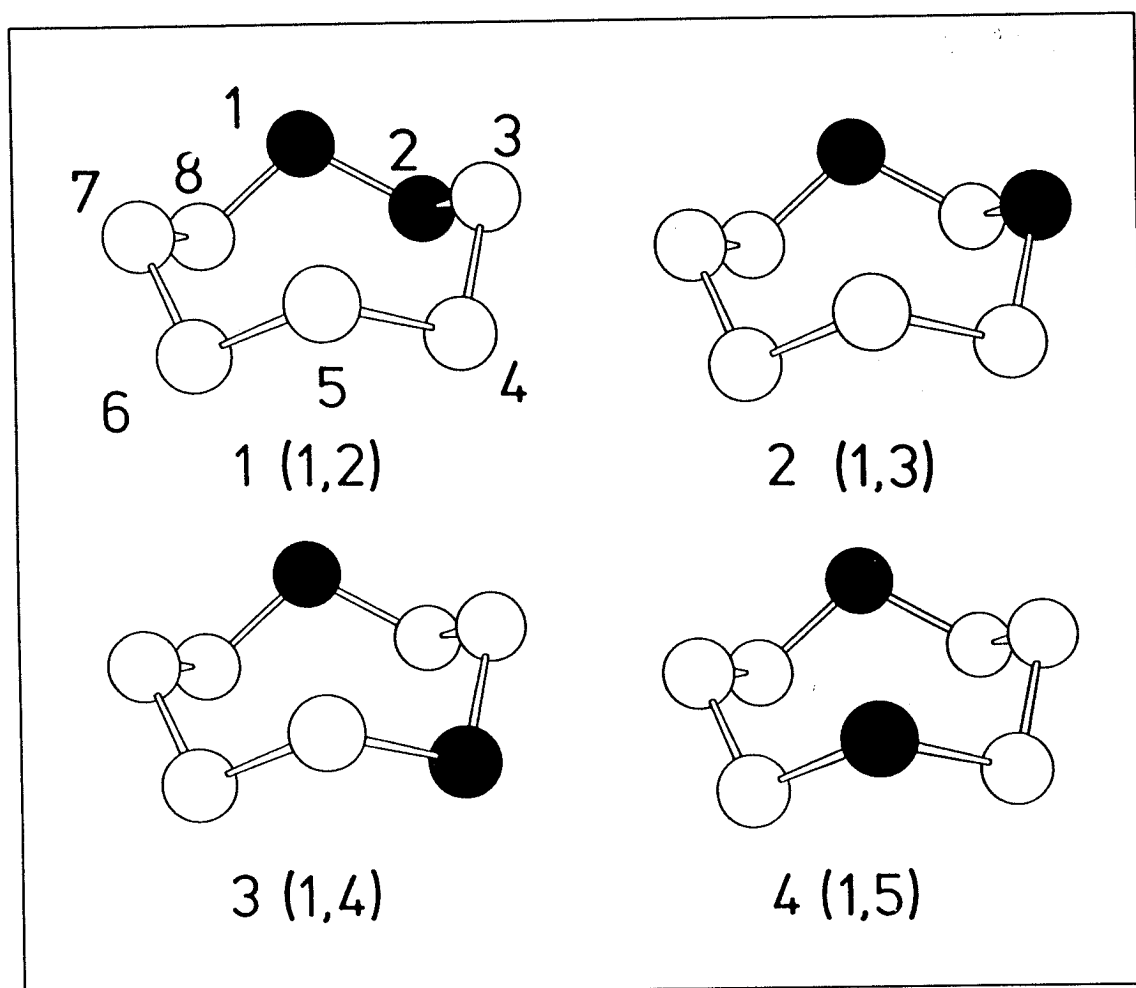


Fig. 14: Structures of Se_2S_6 (and Se_6S_2).

also quite regular. Replacing S by Se leads to the increased bond length expected from the atomic radii and locally to a reduction in both bond and dihedral angles. While the angle changes that result from changing a single atom type are not as localized as changes in the bond length, the perturbations are only of the order of 2° , so that the basic structures are very similar.

The relative energies shown in Tab. 12 show that the (1,2) structures are the ground states in both Se_2S_6 and Se_6S_2 . The energies of the other structures are degenerate to within 3 meV and lie 0.08 eV above the ground state in each case. We note here that the (1,2)-isomer is the most prominent detected in the NMR spectra of Se_2S_6 – there are smaller amounts of the other three – and the only one found in NMR spectra of Se_6S_2 .¹¹¹

Se_2S_5 , Se_5S_2 .

The twelve different cyclic *trans*-structures of Se_2S_5 and Se_5S_2 are shown in Fig. 16. The structures 4, 8, and 11 have a single mirror plane (C_s symmetry), while

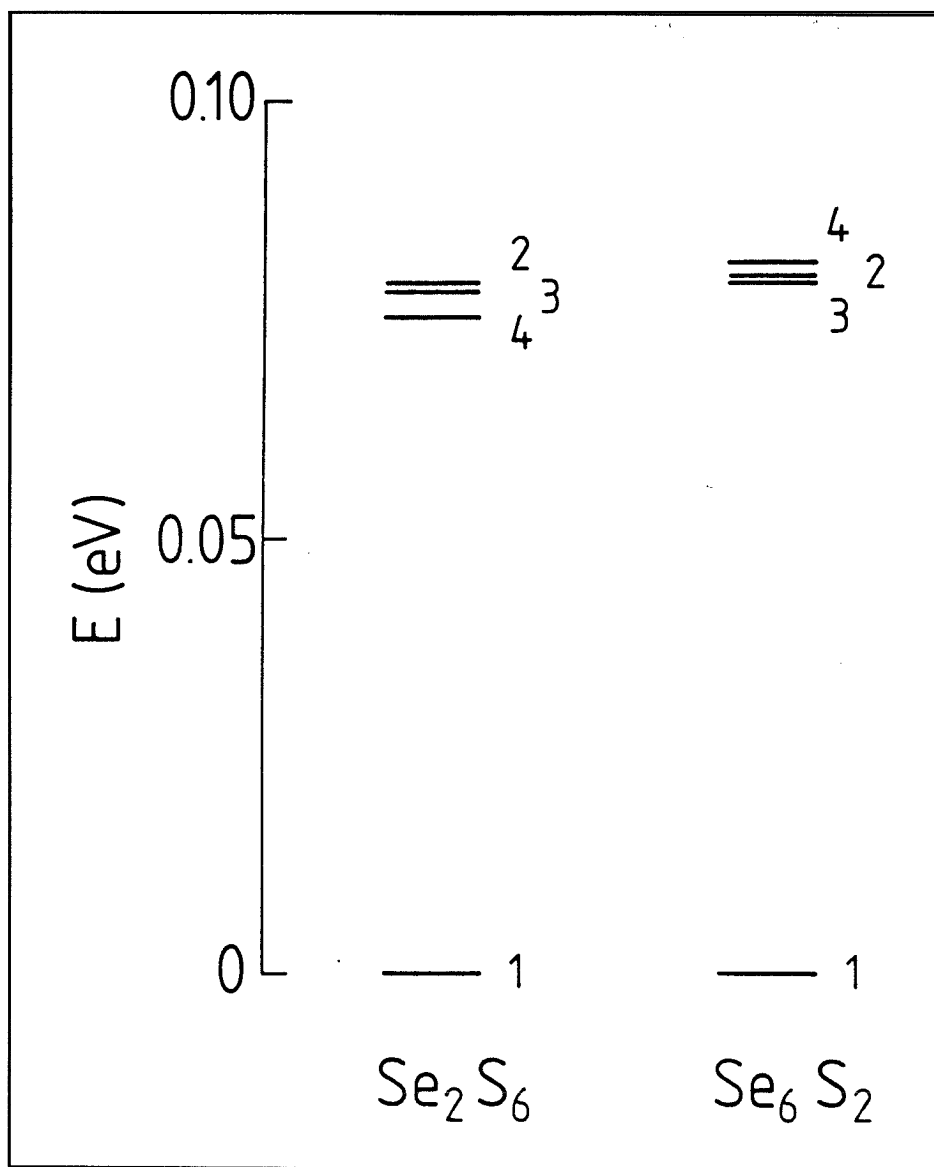


Fig. 15: Relative energies of different structures in Se_2S_6 and Se_6S_2 .

there are no symmetry elements (other than the identity) in the other structures. The lower symmetries reflect the fact that the the C_s chair structure of S_7 has lower symmetry than the crownlike D_{4d} structure of Se_8 and S_8 , the basis for the structures in the preceding section.

The structural parameters are given in Tab. 14, 15. They reflect well-established trends in cyclic group VIA molecules,^{13,116} including the relationship between the bond length and dihedral angle, γ , (the shortest bonds have γ -values near 90° due to minimal lone-pair repulsion between neighboring atoms, see Sec. 3.2) and the fact that long bonds are adjacent to short bonds. The bonds 1-2, 2-3, 3-4, 4-5 are not related by symmetry in any of these clusters, and the ranges of bond lengths (1.99 Å

Tab. 12: Molecular parameters d , α and γ for all isomers of Se_2S_6 . Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees.

	(1,2) [C_2]	(1,3) [C_s]	(1,4) [C_2]	(1,5) [C_{2v}]
d_{12}	2.34	2.22	2.22	2.23
d_{23}	2.23	2.22	2.07	2.08
d_{34}	2.07	2.22	2.23	2.08
d_{45}	2.08	2.08	2.23	2.23
d_{56}	2.09	2.08	2.08	2.23
d_{67}	2.08	2.08	2.07	2.07
d_{78}	2.07	2.08	2.08	2.08
d_{81}	2.23	2.22	2.23	2.23
α_1	105.9	106.1	106.7	106.7
α_2	105.8	108.1	108.2	108.9
α_3	108.1	106.2	108.2	108.6
α_4	108.8	108.4	106.7	108.4
α_5	109.1	108.7	108.5	106.5
α_6	109.2	109.2	108.7	109.2
α_7	108.8	108.7	108.8	108.7
α_8	108.2	108.5	108.6	108.5
γ_{12}	96.8	98.0	98.3	99.1
γ_{23}	97.2	96.6	97.8	96.6
γ_{34}	97.6	96.1	96.3	98.2
γ_{45}	100.6	100.4	99.1	100.5
γ_{56}	102.9	102.1	101.1	99.0
γ_{67}	100.5	100.4	98.9	96.5
γ_{78}	97.5	99.0	99.1	97.7
γ_{81}	97.3	97.6	99.1	100.4

to 2.50 Å) and dihedral angles are much greater than in the eight-membered rings. Within each bond type, however, we find the same transferability as noted above. The average 1–2 and 7–1 bond lengths, for example, are 2.06 Å, 2.21 Å, and 2.33 Å for $S - S$, $S - Se$, and $Se - Se$, respectively. As in the eight-membered rings, the replacement of S by Se leads to longer bonds and smaller bond angles.

The relative energies of the different structures are shown in Fig. 17. The results are similar to those in Se_2S_6 and Se_6S_2 in that the structures with lowest energies have adjacent minority atoms. However, there is no evidence of systematic degeneracies, and the energy spread is larger in Se_5S_2 than in Se_2S_5 . Our calculations have been restricted to the vicinity of the cyclic *trans*- (or “chair”) structures derived from the ground state structure of S_7 or Se_7 . The previous calculations (Chapters 3 and 4) indicate, however, that the *cis*- or “boat” structure lies only

Tab. 13: Molecular parameters d , α and γ for all isomers of Se_6S_2 . Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees.

	(1,2) [C_2]	(1,3) [C_s]	(1,4) [C_2]	(1,5) [C_{2v}]
d_{12}	2.07	2.22	2.23	2.23
d_{23}	2.23	2.22	2.34	2.35
d_{34}	2.35	2.23	2.23	2.35
d_{45}	2.35	2.34	2.22	2.22
d_{56}	2.35	2.35	2.35	2.23
d_{67}	2.35	2.35	2.35	2.35
d_{78}	2.35	2.35	2.35	2.35
d_{81}	2.23	2.23	2.22	2.22
α_1	109.3	109.2	108.9	109.1
α_2	109.3	107.4	107.2	107.2
α_3	107.0	109.1	107.0	106.6
α_4	106.9	107.1	109.0	107.0
α_5	106.3	106.6	106.9	109.1
α_6	106.4	106.4	106.8	107.3
α_7	106.8	106.5	106.5	106.6
α_8	107.1	106.8	106.8	106.9
γ_{12}	101.9	100.9	100.6	97.8
γ_{23}	100.9	100.8	100.4	100.2
γ_{34}	99.8	100.4	100.9	101.1
γ_{45}	98.2	98.0	98.6	98.4
γ_{56}	96.3	98.5	98.1	97.6
γ_{67}	98.2	98.6	100.2	100.1
γ_{78}	99.8	98.2	98.4	101.1
γ_{81}	100.9	100.4	98.6	98.5

~ 0.1 eV higher. We therefore expect that heterocyclic structures possibly derived from the latter will also lead to a band of total energies similar to those for the *trans*-form, so that the final spectrum for each molecule will be very complicated. While structures with neighbouring minority atoms are the best candidates for the states with lowest energy, the precise ordering of the remainder within the bands is difficult to predict. This ordering may also be irrelevant, as many structures are likely to coexist in any given system.

Dynamics in Se_2S_5 .

Chemists prefer to view mixtures of different molecules in solution and in the liquid phase (whether isomers and conformers) as static for the individual molecules: The single molecule is not seen as dynamically changing entity, apart from vibrations

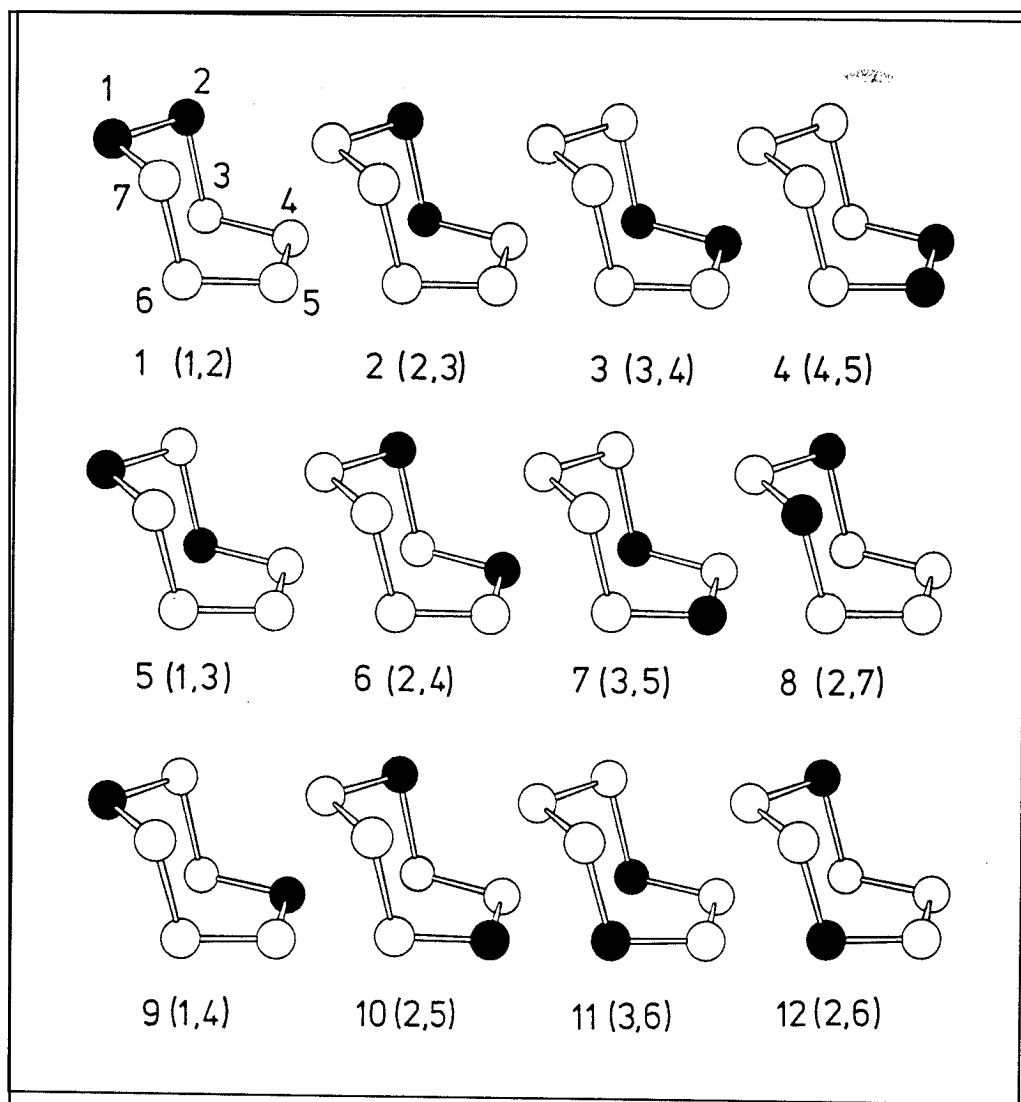


Fig. 16: Structures of Se_2S_5 (and Se_5S_2).

around the equilibrium geometry. This view is fostered by numerous theoretical calculations aimed at finding highly symmetric minimum total energy structures at $T=0$ and characteristic vibrational modes. However, solutions and liquids are usually kept at temperatures $T \geq 0$ K and dynamical phenomena other than small amplitude vibrations can be expected to influence the structural behaviour of every single constituent molecule. At least for the species under consideration here, the picture emerging from our MD/DF calculations is a quite different one. We have coupled a single example molecule (Se_2S_5) to a heat bath of $T=300$ K, simulating the interaction with the environment by a rescaling of the atomic velocities.¹¹⁷

As we have noted above, there is spectroscopic evidence in Se_2S_5 at room temperature¹¹² for “pseudorotation” between different (1,2)-conformers [labelled 1 to 4 in Fig. 16]. This is consistent with the torsional barrier of $S-S$ bonds in sulphur

Tab. 14: Molecular parameters d , α and γ for all isomers of Se_2S_5 . Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees. Structures 4, 8 and 11 have a single mirror plane [C_s symmetry], the remainder have C_1 symmetry.

	1	2	3	4	5	6	7	8	9	10	11	12
	(1,2)	(2,3)	(3,4)	(4,5)	(1,3)	(2,4)	(3,5)	(2,7)	(1,4)	(2,5)	(3,6)	(2,6)
d_{12}	2.33	2.23	2.07	2.07	2.21	2.22	2.07	2.21	2.21	2.22	2.06	2.21
d_{23}	2.30	2.39	2.29	2.13	2.28	2.28	2.28	2.30	2.13	2.29	2.29	2.30
d_{34}	1.99	2.15	2.26	2.15	2.14	2.15	2.14	1.99	2.15	1.99	2.14	1.99
d_{45}	2.24	2.22	2.38	2.50	2.23	2.38	2.37	2.24	2.38	2.38	2.22	2.23
d_{56}	1.99	1.99	1.99	2.15	1.99	1.99	2.15	1.99	1.99	2.15	2.14	2.14
d_{67}	2.14	2.16	2.16	2.13	2.15	2.15	2.14	2.30	2.14	2.14	2.29	2.29
d_{71}	2.21	2.05	2.06	2.07	2.20	2.06	2.06	2.21	2.21	2.06	2.06	2.06
α_1	98.7	98.9	102.0	102.5	102.5	99.0	102.5	99.5	101.6	99.3	102.6	99.4
α_2	107.3	103.1	104.7	106.6	104.0	107.3	104.0	107.5	106.9	107.2	104.0	107.6
α_3	106.3	107.0	102.8	103.1	106.9	102.4	106.8	106.4	102.8	106.1	107.9	107.3
α_4	106.5	108.0	106.6	103.1	107.5	106.5	103.6	106.4	106.4	103.0	107.9	107.0
α_5	107.3	107.3	107.1	106.6	107.1	107.0	107.1	107.5	106.9	107.0	104.0	104.2
α_6	101.8	103.3	102.5	102.5	101.9	102.8	102.4	99.6	101.8	102.6	102.6	102.9
α_7	102.9	106.8	107.2	107.2	103.0	106.6	107.2	106.7	102.8	106.7	107.5	107.0
γ_{12}	71.4	74.5	75.5	75.9	73.7	73.0	76.3	73.0	74.1	73.2	77.0	73.6
γ_{23}	108.2	103.3	105.1	110.9	105.3	106.8	107.0	108.4	110.4	109.1	106.1	108.1
γ_{34}	86.6	83.8	82.8	84.0	84.9	84.8	82.8	87.1	85.9	85.0	82.5	84.4
γ_{45}	0.3	2.4	2.5	0.0	4.0	0.3	2.9	0.1	0.1	0.1	0.1	3.4
γ_{56}	88.1	85.5	84.5	84.0	85.2	86.5	83.8	87.2	85.9	86.2	82.6	85.2
γ_{67}	112.2	110.8	113.8	110.9	112.6	113.5	110.7	108.3	113.1	110.9	106.0	106.2
γ_{71}	74.4	76.4	77.0	75.9	74.6	76.3	76.7	73.0	74.4	76.0	76.9	76.1

Tab. 15: Molecular parameters d , α and γ for all isomers of Se_5S_2 . Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees. Structures 4, 8 and 11 have a single mirror plane [C_s symmetry], the remainder have C_1 symmetry.

	1 (1,2)	2 (2,3)	3 (3,4)	4 (4,5)	5 (1,3)	6 (2,4)	7 (3,5)	8 (2,7)	9 (1,4)	10 (2,5)	11 (3,6)	12 (2,6)
d_{12}	2.05	2.21	2.33	2.33	2.21	2.21	2.33	2.21	2.22	2.21	2.33	2.22
d_{23}	2.29	2.13	2.29	2.40	2.28	2.28	2.29	2.29	2.40	2.28	2.28	2.27
d_{34}	2.27	2.15	1.99	2.14	2.15	2.14	2.14	2.27	2.16	2.26	2.15	2.27
d_{45}	2.50	2.49	2.38	2.22	2.49	2.37	2.38	2.52	2.36	2.37	2.50	2.51
d_{56}	2.28	2.28	2.27	2.14	2.28	2.26	2.14	2.27	2.28	2.14	2.15	2.15
d_{67}	2.40	2.40	2.40	2.40	2.39	2.40	2.40	2.29	2.40	2.39	2.28	2.28
d_{71}	2.23	2.34	2.34	2.33	2.22	2.33	2.34	2.21	2.22	2.33	2.33	2.33
α_1	103.3	103.1	100.6	99.5	100.9	103.3	100.1	102.4	101.5	101.3	99.7	102.1
α_2	104.9	107.5	107.4	104.3	107.2	105.0	107.2	105.0	105.7	105.0	107.2	105.3
α_3	104.6	104.9	107.6	108.4	104.2	108.2	103.9	103.6	108.8	104.8	103.9	104.7
α_4	103.7	103.9	104.0	108.4	103.9	104.4	108.0	103.7	105.8	107.1	103.9	103.2
α_5	104.2	103.1	104.1	104.2	104.0	104.0	105.5	104.9	106.8	103.5	107.2	105.5
α_6	100.2	99.8	99.1	99.5	100.0	99.9	99.7	102.4	100.0	99.9	99.7	100.6
α_7	107.9	104.3	104.1	103.3	107.7	104.2	103.9	103.8	108.3	103.9	103.9	105.4
γ_{12}	77.4	75.6	74.3	76.1	75.1	76.3	74.0	76.0	76.1	77.0	74.2	74.1
γ_{23}	111.1	114.3	113.2	108.4	112.0	111.4	111.7	112.3	105.9	110.8	112.4	109.4
γ_{34}	84.9	87.4	87.6	86.3	86.5	85.7	89.8	84.8	86.6	85.7	87.6	85.9
γ_{45}	0.2	2.7	1.9	0.1	2.1	0.3	0.8	0.0	4.5	1.5	0.1	0.4
γ_{56}	83.8	84.6	86.8	86.3	85.6	85.0	84.0	84.9	80.8	85.7	87.6	87.2
γ_{67}	108.6	108.5	107.6	108.3	108.4	107.7	108.8	112.3	106.5	109.8	112.5	113.0
γ_{71}	75.8	74.3	74.6	76.1	75.5	74.3	74.9	76.0	77.1	75.8	74.2	73.7

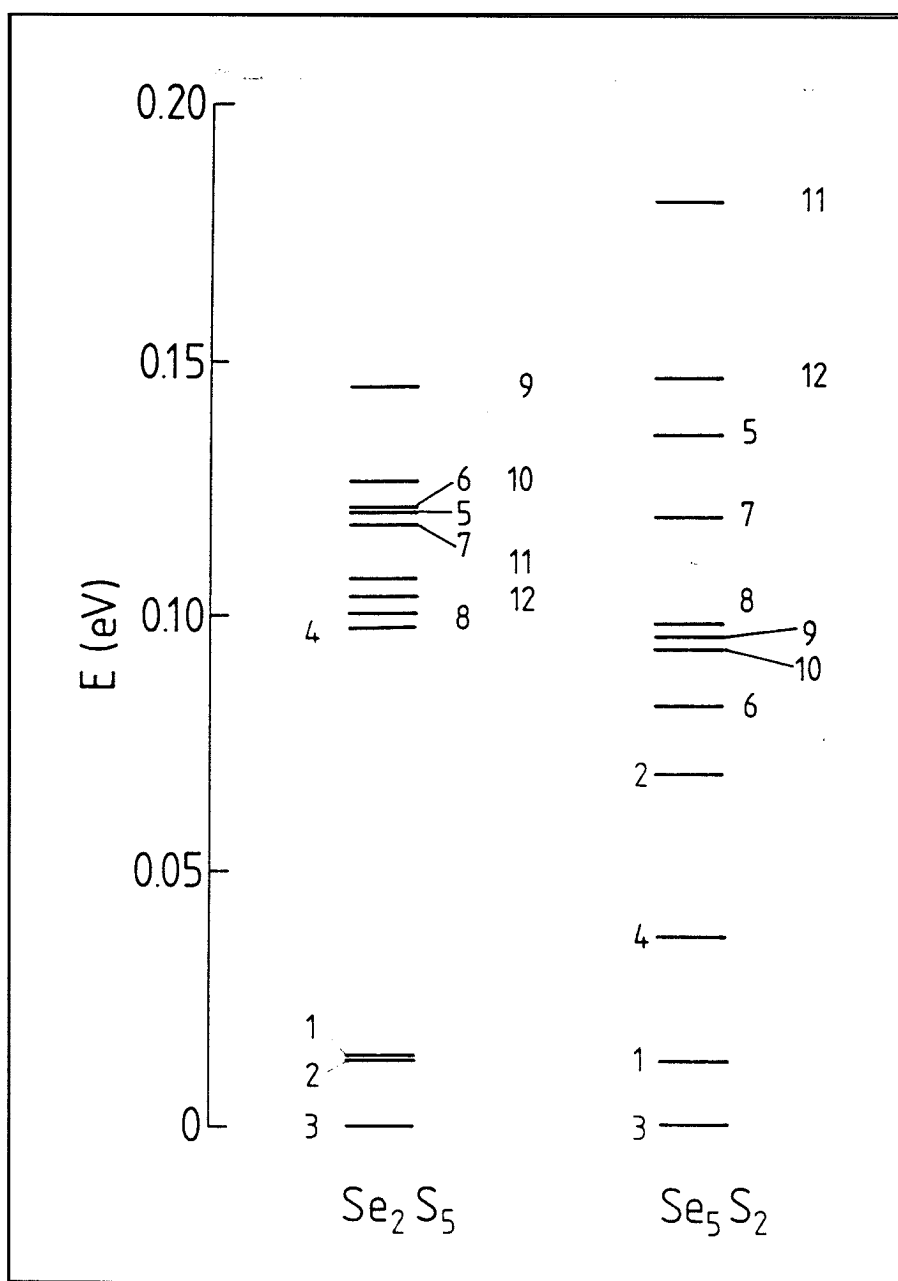


Fig. 17: Relative energies of different structures in Se_2S_5 and Se_5S_2 .

rings, which has been estimated from the heat of formation of S_7 to be ≤ 24 kJ mol⁻¹.¹¹⁶ The (4,5)-structure [4 in Fig. 16] has the highest energy of the structures with neighbouring $Se - Se$ atoms.

After finding the C_s structure with energy shown in Fig. 17, we continued the molecular dynamics at a temperature of 300 K, and show the geometry changes occurring in the first 3.5×10^{-13} s (3500 time steps, $\Delta t = 8.5 \times 10^{-17}$ sec.) in Fig. 18. The energy rises initially and passes through two pairs of local maxima

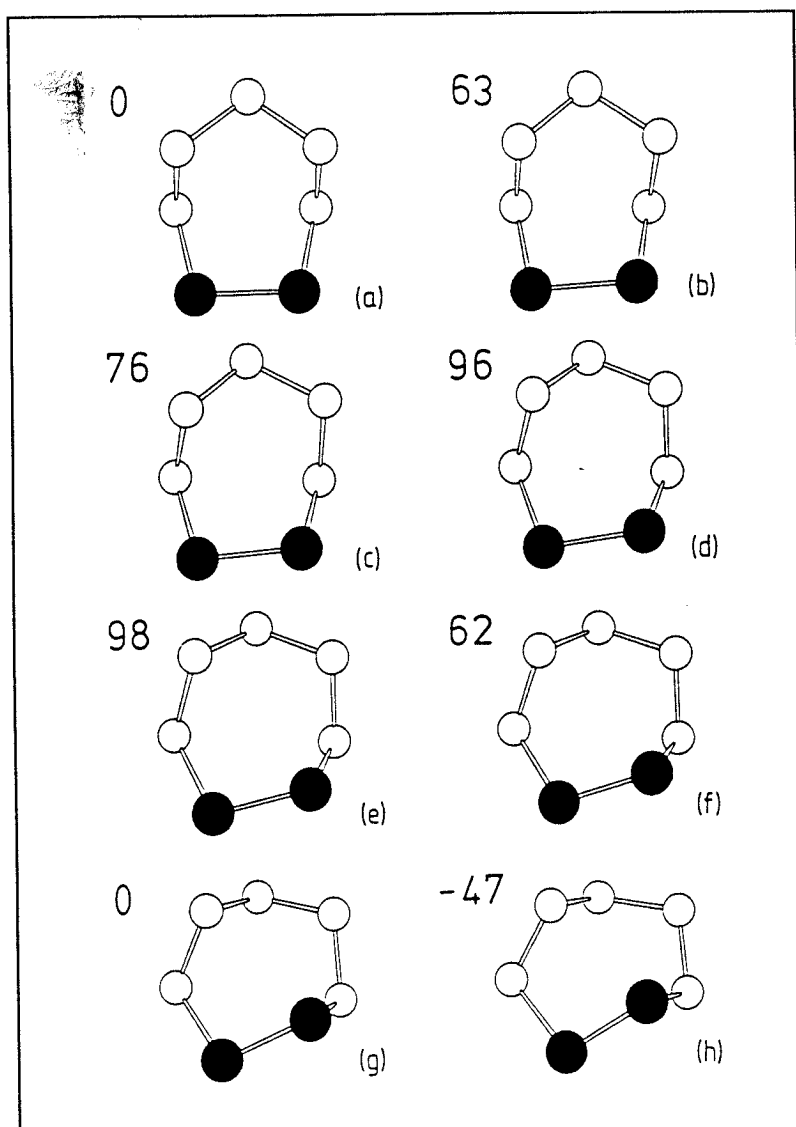


Fig. 18: Molecular dynamics of Se_2S_5 at $T = 300$ K, showing the change from the (4,5)-structure (a) to the (3,4)-ground state structure (h). The interval between each plot is $500\Delta t$, with $\Delta t = 8.5 \times 10^{-17}$ sec.

and minima to a saddle point in the energy surface 0.12 eV above the starting energy. The corresponding geometry is very close to the one shown in Fig. 18 (e). After crossing this barrier, the molecule has a structure with the same pattern of torsion angles (“motif”)¹⁰⁰ as the ground state, and the energy falls rapidly to a local minimum corresponding to Fig. 18 (h). If we now use the above procedure to locate the bottom of the energy minimum and the corresponding $T = 0$ energy, we find precisely the ground state energy and structure given in Tab. 14. The energy is 0.22 eV [20 kJ mol^{-1}] below the saddle point, similar to the value of the torsion barrier quoted above for S_7 .

A comparison of the (4,5)- and (3,4)-structures [Tab. 14] shows that the geometry changes are substantial. The $Se - Se$ bond length changes from 2.50 Å to 2.26 Å, and the dihedral angle from zero to 82.8°. In fact, the bond length *increases* to 2.52 Å before decreasing to its final value. The bond angle changes are much smaller. Fig. 18 shows that the change in structure involves a concerted change of the positions of all atoms, with the largest motion apparent in the Se atom 4. During this simulation, the maximum instantaneous temperature fluctuations $\langle T - \langle T \rangle \rangle$ were found to be as high as 750°, i.e. the kinetic energy is again (Sec. 5.1) distributed over the atoms in a far from uniform fashion.

In order to study the dynamics further, we have carried out an extended simulation of 60000 time steps from the ground state structure in Fig. 16(3). The system went through a large number (~ 200) of extrema in the energy surface, with a maximum energy ~ 0.12 eV above the ground state energy. This was obviously insufficient for the system to cross a barrier to one of the neighbouring stable local minima depicted in Fig. 16. The system remained in the basin of attraction of the ground state structure throughout.

This suggests that in solutions or in the liquid phase statistical averages over structurally different molecules dominate the properties in question. The individual constituents can constantly change their shapes as dictated by the temperature of the bath and the shape of the energy surface. In the 7-membered rings basins of attraction (local minima) of different extent are separated by barriers that can be overcome at $T = 300$ K. The temporal order of magnitude for a conversion $4 \rightarrow 3$ in Se_2S_5 is $t = 4 \times 10^{-13}$ s, far beyond the NMR time scale. Our maximum simulation period (5 ps) was not long enough to observe another structural change out of that dominant minimum. The basin of attraction for the ground state Fig. 16 (3) is not only deeper by ≥ 0.05 eV, but apparently more extended.

6. CONCLUDING REMARKS

The combination of molecular dynamics and density functional methods has given excellent results for small sulphur and selenium clusters, and useful results in S_7O , where the geometry changes and the energy barrier between the ring and ground state structures are both very large. In the heterocyclic ring molecules Se_xS_y we have studied the opposite extreme – structures with very small energy differences and energy barriers that are small on a thermal scale. The results are very encouraging. While no method can guarantee finding the absolute energy minima in low-symmetry clusters of this size, we believe that the methods and strategies presented in this thesis are presently the most promising approach to locating the most relevant minima.

Four different factors are important in enabling the MD simulated annealing procedure to locate the optimal energy minima, in spite of the complexity of the energy surfaces and large energy barriers. (1) The continuous supply of kinetic energy via the external heat bath is essential to overcome potential energy barriers that are large on a thermal scale (> 5 eV at $\langle T \rangle = 2000$ K in the case of S_7O). This process is effective unless the energy surface is so steep that the kinetic energy loss cannot be compensated at the imposed $\langle T \rangle$. (2) The kinetic energy can be partitioned among the individual atoms of the molecule in a very non-uniform way, allowing one atom in a small cluster to acquire essentially all available kinetic energy. (3) The trajectories generated by the MD equations of motion appear to be very successful in locating reaction pathways to low-lying minima. (4) Our experience with group VIA clusters has shown that the lowest-lying minima are significantly more extended than higher ones. However, it is conceivable that the reverse could be true in other systems, and an extension to group VA elements is currently in progress.

The techniques require no assumptions about the equilibrium structure, although the procedure can be accelerated by starting the calculation with initial geometries based on some knowledge of the structures. Entropy arguments suggest, for example, that it would be more difficult to locate a highly symmetric minimum if we start in a conformation with low symmetry. The agreement with available experimental data is very encouraging, and the predictions in the other cases should be reliable. It is not universally appreciated how complex the energy surfaces are in such molecules. There are generally very many local minima, and it is not realistic to expect that conventional methods, either using correlated wave function or den-

sity functional techniques, will be able to find a path in configuration space between low-lying minima. This situation will be true even if gradient techniques are used, as the analytical properties of the energy as a function of the coordinates are by no means simple. In principle, the same method could be applied to Hartree-Fock or configuration interaction techniques, but the CPU time required with current implementations of these methods would be much greater than the 5 seconds a combined diagonalization/self-consistency/MD step requires with the present approach for the most difficult case of S_7O . The introduction of a kinetic energy (“temperature”) term in eq. (2.18) enables the system to locate the most favourable geometry in a large region of configuration space. It is, of course, possible that there are regions which are not probed by this method, and there is no guarantee that we have found the absolute minimum of the energy E in all cases. The calculations performed here have been very extensive, however, and most candidates for the ground state structures have been tested.

We are confident that the approach in its current implementation will be of value in numerous other systems where the pseudopotential/plane wave approximation is appropriate, and that the MD-DF method should be a valuable complement to traditional quantum chemical techniques in studying energy surfaces in general. Apart from the search for ground state geometries, the method could be of value to study dynamical phenomena in small molecules like chemical reactions. Most of the calculations here mimic the isokinetic ensemble and it is unclear exactly how this affects the dynamics we observe. In the thermodynamic limit, the average static properties should be identical to those obtained in the microcanonical ensemble appropriate for an isolated cluster in the gas phase. The fluctuations, however, will be different and this affects the dynamics without any doubt.

The combined MD/DF method is currently *the* most reliable method to perform molecular dynamics simulations of disordered bulk systems aiming at properties and processes that occur on time scales of a few picoseconds and length scales of a few (≤ 10) atomic distances. Although a more efficient implementation is conceivable, these limitations impose very serious constraints for studying a number of interesting questions. The ultimate limit one encounters is the cubic scaling of the orthonormalization constraints, and that regime is reached with ~ 250 atoms.

One natural extension of the method is towards an ability to deal with more localized orbitals, essential for treating late transition metals or f-elements. This could be accomplished in either of two ways. Several attempts have been made to incor-

porate localized basis functions like, for example, linear combinations of muffin-tin orbitals, Gaussians or finite elements. The success is very limited and no implementation working nearly as efficiently as the current one has been reported to date. Another possibility is the development of optimally smooth pseudopotentials¹¹⁸ for first row elements, transition metals and f-elements and an increase in efficiency of dealing with a very large plane wave basis.

Ultimately, fundamentally different methods of dealing with the Coulomb interaction in many-electron systems in conjunction with ever faster supercomputers will be necessary. Quantum Monte Carlo methods¹¹⁹ offer some interesting prospects, but, in their attempt to find the *exact* wavefunction, are currently several orders of magnitude *less* efficient than density functional approaches like the one described here. Analytical and synthetic chemists are, however, less interested in an isolated few of extremely accurate numbers than in chemical trends across the periodic system of elements. MD/DF calculations as presented in this thesis can answer many of the questions *now* that “exact” methods will perhaps not be able to answer over the next decades.

Appendix A. FAST FOURIER TRANSFORM (FFT)

It has been pointed out in Sec. 2.1, eq. (2.13), that the computational cost of the product $H\psi$ necessary for the evaluation of the unconstrained forces on the electronic degrees of freedom (2.19)

$$\frac{\delta E}{\delta \psi_i^*(\mathbf{r}, t)} = H\psi_i(\mathbf{r}, t) \quad (A.1)$$

can be reduced significantly using FFT techniques. Straightforward matrix multiplication in eq. (2.19) results in a dot operation count of $O[NM^2]$ (the $O[MN^2]$ operations due to the orthonormalization will be left aside here). N is again the number of electronic states and M the number of plane wave coefficients per state. The kinetic energy part of the Hamiltonian (2.13) acting on the wavefunctions in reciprocal space requires only $O[MN]$ operations, but the action of the potential energy operator is a convolution that can conveniently be calculated as multiplication in real space. As will be shown further below, transforming V and ψ to real space and $V\psi$ back to reciprocal space requires only $O[N\tilde{M}\log_2\tilde{M}]$ operations when FFT techniques are employed. $\tilde{M}$ is the total number of points used in the 3-D Fourier transform grid and its lowest possible value is subject to a consistency criterion that contains the absolute value G_{max} of the wave vector of the most rapidly varying plane wave components used to represent the potential V and – equivalently – the density ρ . Let us start with the density in reciprocal space

$$\rho(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} \quad (A.2)$$

or, using a DFT grid,

$$\rho(\mathbf{G}) = \frac{1}{\Omega} \sum_{\mathbf{r}} \rho(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} \frac{\Omega}{\tilde{M}} \quad (A.3)$$

Replacing $\rho(\mathbf{r})$ with the Fourier transform of $\rho(\mathbf{G})$ yields

$$\rho(\mathbf{G}) = \frac{1}{\tilde{M}} \sum_{\tilde{\mathbf{G}}} \rho(\tilde{\mathbf{G}}) \sum_{\mathbf{r}} e^{-i(\tilde{\mathbf{G}}-\mathbf{G})\mathbf{r}} \quad (A.4)$$

which gives us the criterion

$$\frac{1}{\tilde{M}} \sum_{\mathbf{r}} e^{-i(\tilde{\mathbf{G}}-\mathbf{G})\mathbf{r}} = \delta(\tilde{\mathbf{G}} - \mathbf{G}, 0) \quad (A.5)$$

This is, however, different with a finite mesh size

$$\frac{1}{\tilde{M}} \sum_{\mathbf{r}} e^{-i(\tilde{\mathbf{G}}-\mathbf{G})\mathbf{r}} = \delta(\tilde{\mathbf{G}} - \mathbf{G}, 0 + \mathbf{g}) \quad (A.6)$$

where $\mathbf{g}$ is the reciprocal lattice vector of the $\mathbf{r}$ lattice, in a simple cubic lattice

$$\mathbf{g} = \frac{2\pi}{a}(\tilde{M})^{\frac{1}{3}} \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} \quad (\text{A.7})$$

n_1, n_2, n_3 are the corresponding integer indices and a is the lattice constant. Eq. (6) is fulfilled when $\mathbf{g}\mathbf{r} = 2\pi N$ for all integer N . In the *sc* lattice the smallest possible absolute value of $\mathbf{g}$ is

$$g_{min} = \frac{2\pi}{a}(\tilde{M})^{\frac{1}{3}} \quad (\text{A.8})$$

which in order to be consistent with eq. (4) must fulfill the condition

$$g_{min} > 2G_{max} \quad (\text{A.9})$$

and so

$$(\tilde{M})^{\frac{1}{3}} > \frac{4\pi}{a}G_{max} \quad (\text{A.10})$$

which serves to fix $\tilde{M}$ once an appropriate cutoff G_{max} has been determined from the accuracy required in the calculation. Analogous criteria can be derived for lattices of different symmetries.

In general, the cutoff G_{max} for the expansion of potential and density must be $2G_{max}(\psi)$, twice the value for the electronic eigenstates, but we found that this criterion can be relaxed to $G_{max} \sim 1.5G_{max}(\psi)$ with substantial savings in computational effort due to eq. (10). A unique cutoff for all expansions in plane waves as proposed by Martins *et al.*¹²⁰ based on physically intuitive arguments was, however, inadequate and leads to substantial inaccuracies and convergence problems when based solely on $G_{max}(\psi)$.

Let us now turn to the question of how multi-dimensional DFTs like in eq. (3) are performed efficiently on a digital (vector) computer.^{121,122} For the sake of simplicity we start from a 1-D transform $g := \hat{F}_n f$ of a sequence f with period n in generalized notation ($\hat{F}_n$ is the corresponding discrete Fourier operator)

$$\begin{aligned} g_\mu &= \frac{1}{n} \sum_{\nu=0}^{n-1} f_\nu e^{-i\mu\nu/n} \\ &= \frac{1}{n} \sum_{\nu=0}^{n-1} f_\nu W_n^{-\mu\nu} \end{aligned} \quad (\text{A.11})$$

As noted above, this resembles a matrix multiplication and appears to be an $O[n^2]$ process. The **F**ast **F**ourier **T**ransform algorithm, well-known already in the 19th

century but rediscovered in 1965 by Cooley and Tukey, permits a reduction to $O[n \log_2 n]$ operations. To apply the FFT n must be factorisable as a product of at least two integers $n = pq$ so that the indexing of the data f can be done *mod* p

$$\begin{aligned} f_j &= f_{\nu+\mu p}, j = 0, 1, \dots, n-1, \\ \nu &= 0, \dots, p-1, \\ \mu &= 0, \dots, q-1, \end{aligned} \quad (A.12)$$

We obtain then

$$(\hat{F}_n f)_\lambda = \frac{1}{p} \sum_{\nu=0}^{p-1} \left\{ \frac{1}{q} \sum_{\mu=0}^{q-1} f_{\nu+\mu p} W_q^{-\mu\lambda} \right\} W_n^{-\nu\lambda} \quad (A.13)$$

where $\lambda = 0, 1, \dots, n-1$, the inner sum being a DFT of length q so that we can write

$$(\hat{F}_n f)_\lambda = \frac{1}{p} \sum_{\nu=0}^{p-1} \left\{ \hat{F}_q f^{(\nu)} \right\}_\lambda W_n^{-\nu\lambda} \quad (A.14)$$

Eq. (14) performs $\hat{F}_n f$ with $n(p-1)$ multiplications and p DFTs $\hat{F}_q f^{(\nu)}$. The root of the FFT is now the recursive application of eq. (14) until only trivial DFTs of size 1 are left. The number of multiplications A_n necessary to compute a DFT where n factorises as

$$n = p_1 p_2 \dots p_{k+1}, p_{k+1} = 1 \quad (A.15)$$

is then only

$$A_n = n \sum_{\nu=1}^k (p_\nu - 1) \quad (A.16)$$

In the case of $p_1 = p_2 = \dots = p_k = 2$ this becomes

$$A_n = \frac{n}{2} \log_2 n \quad (A.17)$$

It is obvious that the same procedure can be applied to reduce the operation count in a d -dimensional DFT

$$g_{\mu_1 \mu_2 \dots \mu_d} = \frac{1}{n^d} \sum_{\nu_1=0}^{n-1} \dots \sum_{\nu_d=0}^{n-1} W_n^{-\nu_1 \mu_1 - \dots - \nu_d \mu_d} f_{\nu_1 \nu_2 \dots \nu_d} \quad (A.18)$$

which can be separated into d 1-D DFTs with n^{d-1} index combinations each:

$$g_{\mu_1 \mu_2 \dots \mu_d} = \frac{1}{n} \sum_{\nu_1=0}^{n-1} W_n^{-\nu_1 \mu_1} \dots \frac{1}{n} \sum_{\nu_d=0}^{n-1} W_n^{-\nu_d \mu_d} f_{\nu_1 \nu_2 \dots \nu_d} \quad (A.19)$$

The number of multiplications is then always less than $dn^{d-1} A_n$.

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 $\alpha_1^{core} = 4.07$ $\alpha_2^{core} = 1.61$ $c_1^{core} = 1.1360$ $c_2^{core} = -0.1360$;
 $\alpha_1 = 4.99$ $\alpha_2 = 6.15$ $\alpha_3 = 7.21$ $C_1 = -1.1374$ $C_2 = 0.2008$
 $C_3 = 0.0584$ $C_4 = 0.1253$ $C_5 = 0.0699$ $C_6 = 0.0153$ ($\ell=0$);
 $\alpha_1 = 1.05$ $\alpha_2 = 3.19$ $\alpha_3 = 4.22$ $C_1 = 0.5255$ $C_2 = -0.2293$
 $C_3 = 0.0149$ $C_4 = 0.0897$ $C_5 = 0.1298$ $C_6 = 0.3884$ ($\ell=1$)
yields geometries and energy differences for the minima of *S₇O* in Fig. 10 that are virtually identical to those obtained with the sharper potential in the original work. The *S-O* distances agree within ~ 0.01 Å and the energy differences within ~ 0.001 eV. Thus, the plane wave basis set with a cut-off energy of 45 Ry is sufficient to represent the rapidly varying pseudopotential for *O* in *S₇O* but the softer potential of Gillert and Scheffler and a reduced basis set could be applied where appropriate.
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