

# An *Ab Initio* MO Study of the Pseudorotation in Cyclohexasulfur, S<sub>6</sub>, and Cycloheptasulfur, S<sub>7</sub>

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An *ab initio* MO study of different conformations of both cyclohexasulfur and cycloheptasulfur has been carried out using the 3-21G\* basis set for sulfur. After the full geometry optimization the electron correlation was taken into account using second-order Møller–Plesset perturbation theory. The chair conformations were, as expected, found to be the most stable of all conformations for both molecules, and the calculated molecular parameters are in good agreement with the experimental ones. In S<sub>6</sub> the inversion from the chair conformation to the boat conformation can be thought to proceed either by direct inversion or by pseudorotation about any of the six SS bonds. While the energy difference between the chair and boat conformations is only 63.3 kJ mol<sup>-1</sup>, the barrier to the inversion in both cases was found to be very high (132–137 kJ mol<sup>-1</sup>), thus explaining why the chair conformation of S<sub>6</sub> is very rigid. In contrast to this behaviour, S<sub>7</sub> is fluxional. The calculated barriers to pseudorotation (ca. 6 kJ mol<sup>-1</sup> between two chair conformations via an intermediate of symmetry C<sub>2</sub>, and ca. 18 kJ mol<sup>-1</sup> between the chair and boat conformations) agree well with the predicted barriers to pseudorotation of the molecule, and imply the coexistence of both the chair, twist and boat conformations in solution or in the liquid or gaseous state.

Sulfur and selenium exhibit extensive allotropy in the solid, molten and gaseous states comprising both homocyclic and open-chain molecules (for recent reviews see Refs. 1 and 2). The structural features of many of the allotropes have been established and indicate that the chalcogen–chalcogen bond is flexible, adapting to many different chemical surroundings. Indeed, the research emphasis has shifted from purely structural investigations towards a study of the properties of the different molecular species, with special interest in the interconversion reactions between the different molecules.

The six- and seven-membered ring molecules are particularly interesting, since they often coexist in significant amounts with eight-membered molecules in many molecular systems consisting of elemental sulfur or selenium. For example, at 115 °C the equilibrium melt of sulfur consists of ca. 95 % S<sub>8</sub>, with the remaining 5 % comprising mainly S<sub>6</sub> and S<sub>7</sub>.<sup>3,4</sup> It has also been suggested that both S<sub>6</sub> and S<sub>7</sub> play an important role in the polymerization of sulfur at ca. 160 °C.<sup>5,6</sup> Similarly, when Se<sub>8</sub> is dissolved in CS<sub>2</sub>, it decomposes instantly to form Se<sub>6</sub> and Se<sub>7</sub>.<sup>7</sup> An analogous reaction of S<sub>8</sub> is slow in CS<sub>2</sub> but instantaneous in acetonitrile.<sup>8,9</sup>

It is well established that the molecular structures of S<sub>8</sub> and Se<sub>8</sub> are similar.<sup>10–15</sup> It is therefore not surprising that in the solid state both S<sub>6</sub><sup>16</sup> and Se<sub>6</sub><sup>17</sup> are six-membered ring

molecules in the chair conformation with molecular symmetry D<sub>3d</sub> (Fig. 1). While the crystal structure of S<sub>7</sub> is known,<sup>18</sup> that of Se<sub>7</sub> is not. The Raman spectrum of Se<sub>7</sub>,<sup>19</sup> however, is consistent with the molecular structure similar to that of S<sub>7</sub>.<sup>20</sup> The X-ray crystallographic and vibrational spectroscopic studies of heterocyclic selenium sulfides further emphasize the similarity of the cyclic chalcogen molecules of the same ring size.<sup>19,21</sup> A theoretical rationalization for the structural similarities of small cyclic chalcogen molecules is provided by *ab initio* MO calculations which indicate that the valence electronic structures of the SeSe, SeS and SS bonds are indeed nearly identical.<sup>22,23</sup>

The seven-membered chalcogen rings contain a fragment of four approximately coplanar atoms resulting in a significant alternation in the bond lengths. This alternation has been explained in terms of the mutual p lone pair repulsion of the two central sulfur atoms in the planar four-atomic fragment and of the hyperconjugational interaction between these same lone pairs and the empty σ\* orbitals of the bonds connecting the fragment to the rest of the molecule.<sup>20</sup>

The ground-state chair conformation of the six-membered chalcogen ring molecules seems to be relatively rigid. In fact no boat conformation has been observed for the neutral species, although the cationic Te<sub>x</sub>Se<sub>6-x</sub><sup>2+</sup> is known to exist in the boat conformation.<sup>24</sup> In contrast to this behaviour, the seven-membered chalcogen homo- and het-

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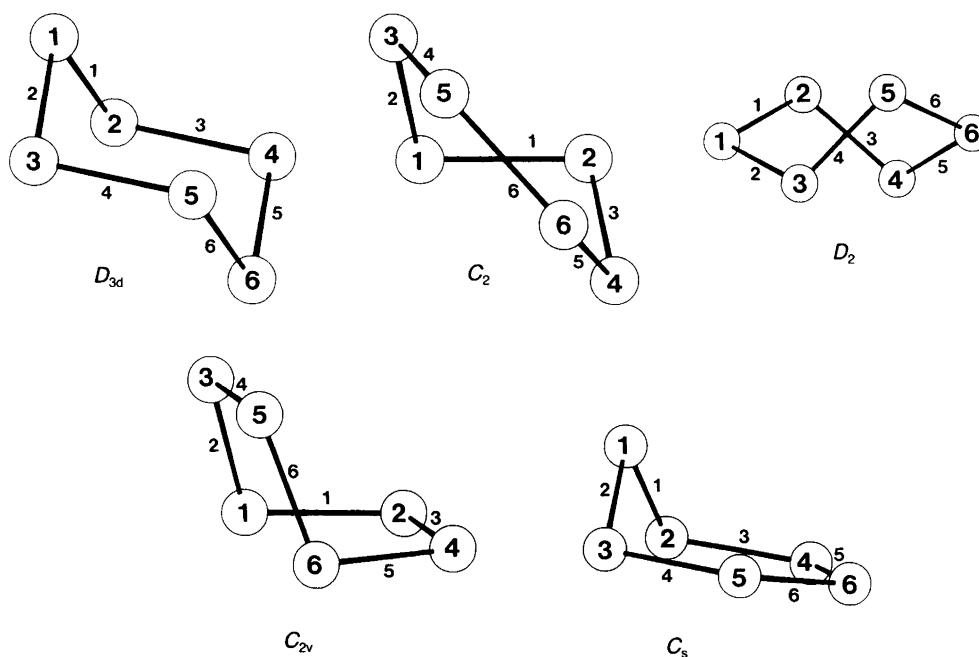


Fig. 1. Numbering of atoms and bonds in chair ( $D_{3d}$ ), twist ( $C_2$ ), twist ( $D_2$ ), boat ( $C_{2v}$ ) and semi-plane ( $C_s$ ) conformations of  $S_6$ .

erocycles are fluxional, undergoing facile pseudorotation both in solution and in the molten state, as predicted by theoretical considerations<sup>25</sup> and deduced from the Raman and natural-abundance  $^{77}\text{Se}$  NMR spectra of 1,2- $\text{Se}_2\text{S}_5$ ,<sup>26</sup> 1,2,3,4,5- $\text{Se}_5\text{S}_2$  and  $\text{Se}_7$ ,<sup>27</sup> as well as from the coupling pattern observed in the NMR spectrum of the  $^{77}\text{Se}$ -enriched 1,2,3,4,5- $\text{Se}_5\text{S}_2$  (enrichment 92 %).<sup>28</sup>

Theoretical studies on the chalcogen ring molecules are sparse. The molecular mechanics method has been applied to several homocyclic sulfur species  $S_n$  ( $n = 5-12, 14, 16, 18, 20$ ).<sup>29</sup> Small sulfur molecules have been studied by the Hückel method.<sup>30</sup> There are also some semiempirical calculations on  $S_6$  and  $S_8$  as well as on their selenium analogues,<sup>31-35</sup> with the main emphasis being on the interpretation of their photoelectron spectra. MNDO<sup>36,37</sup> has been used to study the geometries and energetics of small sulfur rings and chains, and SCF- $X\alpha$ -SW methods<sup>38,39</sup> have been applied to the investigation of the structural changes in  $S_n$  ( $n = 3, 4, 6, 8$ ) on oxidation and reduction as well as in the study of the electron deformation density distribution in  $S_8$ . With the development of computational techniques *ab initio* calculations at various levels of sophistication have been performed for small sulfur molecules.<sup>29, 40-47</sup> Recently the geometries of the prominent low-energy structures of the homocyclic sulfur<sup>48</sup> and selenium<sup>49</sup> molecules, as well as of the heterocyclic selenium sulfides,<sup>50</sup> have been studied using the density functional method combined with molecular dynamics and simulated annealing techniques. We present here an *ab initio* study of  $S_6$  and  $S_7$  to gain further information on the energetics occurring between the different conformations of the molecules. Because analogous sulfur and selenium rings are similar,  $S_6$  and  $S_7$  also serve as model compounds for the behaviour of  $\text{Se}_6$  and  $\text{Se}_7$ .

## Calculations

The calculations were carried out with the Gaussian 88 and Gaussian 90 series of programs.<sup>51,52</sup> A full geometry optimization for all relevant conformations of both molecules was carried out numerically involving a series of single-point

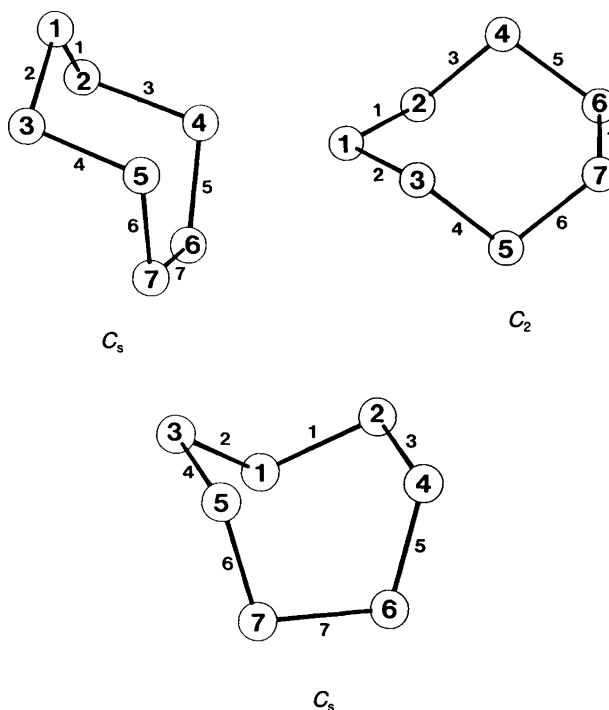


Fig. 2. Numbering of atoms and bonds in chair ( $C_s$ ), twist ( $C_2$ ) and boat ( $C_s$ ) conformations of  $S_7$ .

Table 1. The optimized HF/3-21G\* geometries of the various conformations of S<sub>6</sub>.<sup>a</sup>

Conformation	Bond length	Calc. /pm	Exptl. /pm	Bond angle	Calc. /°	Exptl. /°	Torsion <sup>b</sup> angle	Calc. /°	Exptl. /°
Chair ( <i>D</i> <sub>3d</sub> )	<i>r</i> <sub>1-6</sub>	207.3	206.8 <sup>c</sup>	$\alpha_{1-6}$	102.4	102.6 <sup>c</sup>	$\tau_{1-6}$	74.1	73.8 <sup>c</sup>
Twist ( <i>C</i> <sub>2</sub> )	<i>r</i> <sub>1</sub>	206.5		$\alpha_{1,2}$	98.7		$\tau_1$	95.8	
	<i>r</i> <sub>2,3</sub>	202.6		$\alpha_{3,4}$	108.5		$\tau_{2,3}$	68.8	
	<i>r</i> <sub>4,5</sub>	212.1		$\alpha_{5,6}$	115.7		$\tau_{4,5}$	23.5	
	<i>r</i> <sub>6</sub>	215.8					$\tau_6$	0.0	
Twist ( <i>D</i> <sub>2</sub> )	<i>r</i> <sub>1,2,5,6</sub>	209.0		$\alpha_{1,6}$	103.1		$\tau_{1,2,5,6}$	39.6	
	<i>r</i> <sub>3,4</sub>	203.5		$\alpha_{2-5}$	102.8		$\tau_{3,4}$	86.8	
Boat ( <i>C</i> <sub>2v</sub> )	<i>r</i> <sub>1,2,5,6</sub>	204.4		$\alpha_{1,6}$	103.3		$\tau_{1,2,5,6}$	70.6	
	<i>r</i> <sub>3,4</sub>	221.2		$\alpha_{2-5}$	104.7		$\tau_{3,4}$	0.0	
Semi-plane ( <i>C</i> <sub>s</sub> )	<i>r</i> <sub>1,2</sub>	204.8		$\alpha_1$	98.6		$\tau_{1,2}$	83.2	
	<i>r</i> <sub>3,4</sub>	205.9		$\alpha_{2,3}$	105.7		$\tau_{3,4}$	40.8	
	<i>r</i> <sub>5,6</sub>	212.7		$\alpha_{4,5}$	113.5		$\tau_{5,6}$	0.0	
				$\alpha_6$	117.9				

<sup>a</sup>For numbering of atoms and bonds, see Fig. 1. <sup>b</sup>The signs of the torsion angles proceeding clockwise around the ring and starting from atom 1 are as follows [(+) clockwise, (-) anticlockwise]: (a) chair (*D*<sub>3d</sub>) -+-+--+, (b) twist (*C*<sub>2</sub>) +-+0+-, (c) twist (*D*<sub>2</sub>) -+-+--+, (d) boat (*C*<sub>2v</sub>) +0-+0-, (e) semi-plane (*C*<sub>s</sub>) -0000+. <sup>c</sup>Ref. 16.

energy calculations in each case. Since it is well established that the correct geometry prediction of the molecules containing SS bonds requires the addition of the 3d-polarization functions to the basis set of sulfur,<sup>53</sup> we utilized the polarized 3-21G\* basis set<sup>54</sup> in the geometry optimization of all conformations. A second-order Møller–Plesset correction for the electron correlation<sup>55–57</sup> was performed using the optimized geometries. To test the method used, the geometry optimization of the chair conformation of S<sub>6</sub> was also carried out at the MP2/3-21G\* level of theory. The optimized geometry was virtually identical with that obtained at the HF/3-21G\* level of theory. In order to establish the nature of the stationary points, the fundamental

vibrations of the different conformations were calculated at the HF/3-21G\* level.

The internal coordinates of all conformations of S<sub>6</sub> and S<sub>7</sub> are defined in Figs. 1 and 2.

## Results and discussion

The optimized geometries of the different conformations of S<sub>6</sub> are shown in Table 1 and those of S<sub>7</sub> in Table 2. The calculated bond parameters of the chair conformations of both molecules can be compared to those extracted from crystal structure determinations:<sup>16,18</sup> the calculated and ex-

Table 2. The HF/3-21G\* optimized geometries of the various conformations of S<sub>7</sub>.<sup>a</sup>

Conformation	Bond length	Calc. /pm	Exptl. /pm	Bond angle	Calc. /°	Exptl. /°	Torsion <sup>b</sup> angle	Calc. /°	Exptl. /°
Chair ( <i>C</i> <sub>s</sub> )	<i>r</i> <sub>1,2</sub>	205.6	204.6–205.6 <sup>c</sup>	$\alpha_1$	105.9	105.0–106.3 <sup>c</sup>	$\tau_{1,2}$	77.7	74.4–77.7 <sup>c</sup>
	<i>r</i> <sub>3,4</sub>	208.3	209.7–210.6	$\alpha_{2,3}$	102.8	101.5–102.8	$\tau_{3,4}$	105.7	106.8–108.8
	<i>r</i> <sub>5,6</sub>	201.5	199.5–199.8	$\alpha_{4,5}$	105.6	104.6–106.1	$\tau_{5,6}$	81.3	82.5–84.3
	<i>r</i> <sub>7</sub>	220.0	217.5–218.2	$\alpha_{6,7}$	108.8	106.5–107.5	$\tau_7$	0.0	0.3–2.4
Twist ( <i>C</i> <sub>2</sub> )	<i>r</i> <sub>1,2</sub>	209.9		$\alpha_1$	108.5		$\tau_{1,2}$	105.9	
	<i>r</i> <sub>3,4</sub>	206.2		$\alpha_{2,3}$	107.2		$\tau_{3,4}$	86.7	
	<i>r</i> <sub>5,6</sub>	204.5		$\alpha_{4,5}$	101.6		$\tau_{5,6}$	67.5	
	<i>r</i> <sub>7</sub>	208.3		$\alpha_{6,7}$	107.4		$\tau_7$	45.4	
Boat ( <i>C</i> <sub>s</sub> )	<i>r</i> <sub>1,2</sub>	204.9		$\alpha_1$	108.6		$\tau_{1,2}$	70.3	
	<i>r</i> <sub>3,4</sub>	214.1		$\alpha_{2,3}$	103.9		$\tau_{3,4}$	39.0	
	<i>r</i> <sub>5,6</sub>	199.6		$\alpha_{4,5}$	107.3		$\tau_{5,6}$	84.3	
	<i>r</i> <sub>7</sub>	219.4		$\alpha_{6,7}$	106.8		$\tau_7$	0.0	

<sup>a</sup>For numbering of atoms and bonds, see Fig. 2. <sup>b</sup>The signs of the torsion angles in different conformations when proceeding clockwise around the ring and starting from atom 1 are as follows [(+) clockwise, (-) anticlockwise]: (a) chair (*C*<sub>s</sub>) -+-+--+, (b) twist (*C*<sub>2</sub>) -+-+--+, (c) boat (*C*<sub>s</sub>) +-+0+--. <sup>c</sup>Ref. 18.

Table 3. Total energies of the conformations of  $S_6$  and  $S_7$ .

Molecule	Conformation	HF/3-21G*	MP2/3-21G*
$S_6$	Chair ( $D_{3d}$ )	-2373.989 01	-2374.732 07
	Twist ( $C_2$ )	-2373.939 27	-2374.681 94
	Twist ( $D_2$ )	-2373.966 42	-2374.710 19
	Boat ( $C_{2v}$ )	-2373.962 25	-2374.707 96
	Semi-plane ( $C_s$ )	-2373.937 59	-2374.679 93
$S_7$	Chair ( $C_s$ )	-2769.650 97	-2770.525 90
	Twist ( $C_2$ )	-2769.650 57	-2770.523 40
	Boat ( $C_s$ )	-2769.639 00	-2770.519 02

perimental values are in excellent agreement. While there is no experimental information available for other conformations, the bond parameters show reasonable values for each geometry. The total energies of all conformations of  $S_6$  and  $S_7$  are shown in Table 3. These values can be used to discuss the energetics of the interconversion between the various conformations. The relative energies of the different conformations of  $S_6$  and  $S_7$  are presented in Table 4 with comparisons to other related molecular systems. In the case of  $S_6$  the relative energy values at the HF and MP2 levels of theory are well in agreement, but for  $S_7$  there are significant differences. It has previously been shown that for the correct prediction of the energetics of the sulfur species the electron correlation needs to be taken into account.<sup>58</sup> Therefore a discussion on the energy barriers in the interconversion between the different conformations is restricted to the MP2 level of theory.

*Cyclohexasulfur,  $S_6$ .* The chair conformation with molecular symmetry  $D_{3d}$  has expectedly the lowest energy. The

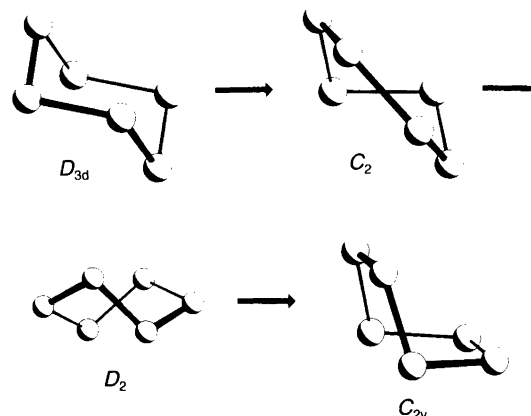


Fig. 3. The pseudorotation in  $S_6$  leading to the inversion of the chair conformation to a boat conformation.

inversion of the chair conformation to form the boat conformation can be thought to proceed by two routes: by direct inversion or by pseudorotation about any bond of the molecule (Fig. 3).

Direct inversion involves the semi-planar conformation ( $C_s$ ) as an intermediate. This conformation constitutes a transition state and lies  $136.9 \text{ kJ mol}^{-1}$  above the chair conformation and  $73.6 \text{ kJ mol}^{-1}$  above the boat conformation at the MP2 level of theory (Table 4). These high barriers have also been indicated by earlier CNDO calculations.<sup>35</sup>

Inversion can also be accomplished upon pseudorotation about any of the six equivalent bonds of the molecule in its ground state. As shown in Fig. 3, a twist conformation with  $C_2$  molecular symmetry is the first intermediate formed during the pseudorotation. This transition state lies

Table 4. Relative energies of the various conformations of  $S_6$  and  $S_7$  (in  $\text{kJ mol}^{-1}$ ).

Molecule	Conformation	HF <sup>a</sup>	MP2 <sup>a</sup>	MM <sup>b</sup>	CNDO <sup>c</sup>	STO-3G <sup>b</sup>	DF/MD <sup>d</sup>	DZP <sup>e</sup>
$S_6$	Chair ( $D_{3d}$ )	0.0	0.0	0.0	0.0	0.0	0.0	
	Twist ( $C_2$ )	130.6	131.6					
	Twist ( $D_2$ )	59.3	57.4	63.2		52.7		
	Boat ( $C_{2v}$ )	70.2	63.3	64.4	15.4	59.4	50.9	
	Semi-plane ( $C_s$ )	135.0	136.9		95.6			
$S_7$	Chair ( $C_s$ )	0.0	0.0	1.3			0.0	
	Twist ( $C_2$ )	1.1	6.6	0.0				
	Boat ( $C_s$ )	31.4	18.1	43.5			10.2	
$O_6$	Chair ( $D_{3d}$ )					0.0		0.0
	Twist ( $D_2$ )					52.8		66.5
	Boat ( $C_{2v}$ )					60.0		73.1
$Se_7$	Chair ( $C_s$ )						0.0	
	Boat ( $C_s$ )						7.1	
$Se_2S_5^f$	Chair ( $C_1$ )						0.0	
	Twist ( $C_1$ )						11.8	

<sup>a</sup>This work. <sup>b</sup>For  $S_6$ , see Ref. 29 and for  $O_6$ , see Ref. 59. <sup>c</sup>Ref. 35. <sup>d</sup>For  $S_6$  and  $S_7$ , see Ref. 48; for  $Se_7$ , see Ref. 49; for  $1,2\text{-Se}_2\text{S}_5$ , see Ref. 50. <sup>e</sup>Ref. 59. <sup>f</sup>The ground-state chair conformation has the two selenium atoms at atomic positions of 4 and 6 (Fig. 1).<sup>19,42</sup> Upon pseudorotation the selenium atom positions shift to positions 6 and 7. (The pseudorotation between two chair conformations is exemplified in Fig. 4.) The twist conformation is the intermediate that has the highest energy along the rotation coordinate.

131.6 kJ mol<sup>-1</sup> above the ground state and represents the energy barrier for this pathway. Upon continued pseudorotation another twist conformation with *D*<sub>2</sub> molecular symmetry is formed. This can be viewed as a distorted boat and lies 57.4 kJ mol<sup>-1</sup> above the energy of the chair conformation. The boat conformation is easily reached from the *D*<sub>2</sub> twist and has a relative energy of 63.3 kJ mol<sup>-1</sup> with respect to the chair conformation.

Since both abovementioned pathways for inversion in S<sub>6</sub> have very high energy barriers, interconversion from the chair conformation to the boat conformation or *vice versa* is very unlikely. These high barriers explain why the boat conformation has not been observed for neutral cyclic six-membered chalcogen molecules. They also indicate, however, that the boat conformation, if formed, should also be relatively stable against inversion to the chair conformation.

It is interesting to note that the distorted boat (twist of symmetry *D*<sub>2</sub>) constitutes a local minimum and is somewhat more stable than the boat (*C*<sub>2v</sub>), which represents a transition state. The small energy difference between the two conformations implies that the boat conformation of S<sub>6</sub> is fluxional, undergoing easy pseudorotation analogous to that in S<sub>7</sub> (Fig. 4 and discussion below). The pseudorotation can be viewed as proceeding from one *D*<sub>2</sub>-twist via the boat conformation to a different, but identical, *D*<sub>2</sub> twist. The barrier for this pseudorotation is only 5.9 kJ mol<sup>-1</sup> (Table 4), indicating that it should be very facile in solution at ambient temperature.

Recent *ab initio* calculations on the chair, *D*<sub>2</sub>-twist and boat conformations of O<sub>6</sub> using a double-zeta quality basis set for oxygen which is augmented by the polarization functions yield very similar relative energies for the three conformations.<sup>59</sup>

*Cycloheptasulfur, S<sub>7</sub>*. The pseudorotation scheme of cycloheptasulfur is shown in Fig. 4. The molecule has the ground-state symmetry of *C*<sub>s</sub> in the chair conformation (Tables 2 and 3) consistent with the crystal structure information.<sup>18</sup> The pseudorotation of 90° about the unique bond (bond 7; Fig. 4) in *C*<sub>s</sub> symmetry, with subsequent adjustment of all bond lengths and angles to accommodate the changed chemical environment of all sulfur atoms, creates a different but identical S<sub>7</sub> molecule. It is easily seen from Fig. 4 that all SS bonds have been shifted from their original positions. An intermediate transition state with *C*<sub>2</sub> symmetry is obtained upon the pseudorotation of 45°. From this intermediate an alternative pathway can also be conceived. It involves pseudorotation about bond 1, which is unique in *C*<sub>2</sub> symmetry. This creates a molecule in the boat conformation with *C*<sub>s</sub> molecular symmetry. Thus the pseudorotation of S<sub>7</sub> produces two series of identical molecules. As the pseudorotation process is repeated, it can be understood that all seven SS bonds can exist in any position in every conformation.

The relative energies of the different conformations are shown in Table 4. The situation is clearly different from S<sub>6</sub>. At the MP2 level of theory the *C*<sub>2</sub> intermediate lies only 6.6 kJ mol<sup>-1</sup> above the ground-state chair conformation. This energy difference is comparable to the barrier for pseudorotation in the boat conformation of S<sub>6</sub>. Also the difference in energies of the boat and chair conformations is only 18.1 kJ mol<sup>-1</sup>. These values are in excellent agreement with the predicted barrier of pseudorotation, which from vapour-phase thermodynamic data was estimated to be ≤24 kJ mol<sup>-1</sup>.<sup>25</sup> The results of Hohl and Jones<sup>48</sup> are also consistent with this estimate. The various calculations for S<sub>7</sub>, Se<sub>5</sub>S<sub>2</sub> and Se<sub>7</sub> shown in Table 4 clearly indicate that all seven-membered chalcogen ring molecules behave in an analogous manner.

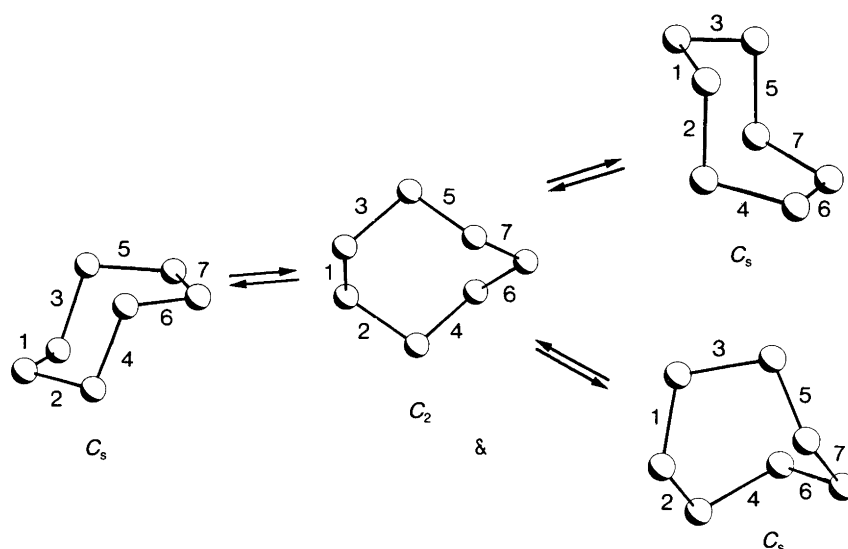


Fig. 4. The pseudorotation in S<sub>7</sub>. The two pathways lead either to another chair conformation or result in the inversion of the chair conformation to a boat conformation.

## Conclusions

The present MO study of  $S_6$  and  $S_7$  shows that *ab initio* techniques can be used to predict the small energy differences between the various conformations of both molecules. The basis set of sulfur, however, has to be augmented with 3d-polarization functions, and electron correlation has to be taken into account. Both the geometries of the different conformations and their relative energies are in good agreement with experimental evidence where available. The high barriers for both the direct inversion via the semiplanar intermediate and the pseudorotation via the  $C_2$  intermediate explain why the chair conformation of  $S_6$  is rigid and undergoes no interconversion into the boat conformation. Our calculations, however, predict that a twisted boat conformation of  $S_6$ , once formed, could also be relatively stable against the inversion into the chair conformation. In contrast to this behaviour  $S_7$  is fluxional, undergoing facile pseudorotation. It could be expected that all possible conformations of  $S_7$  can coexist in solution or in the molten state.

*Acknowledgements.* Financial support from the Academy of Finland is gratefully acknowledged.

*Note added in proof.* It has recently come to our attention that Raghavachari *et al.*<sup>60</sup> have performed an *ab initio* MO study on sulfur molecules  $S_2$ – $S_{12}$  involving 3-216\* basis set in geometry optimization and a 6-316\* basis set in energy calculations, and taking electron correlation into account applying Møller–Plesset perturbation theory. Our results, where they overlap, are in good agreement with theirs, as expected.

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