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An ab Initio Study of the Silicon−Oxygen−Sulfur Oligomers $(SiOS)_n$ ($n \leq 6$)

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Compounds containing silicon, oxygen, and sulfur are promising agents to link anorganic and organic phases in nanostructured hybrid materials. The oligomers $(SiOS)_n$ represent reasonable models for said linking compounds. We present the results of corresponding ab initio calculations at the MP2 level of theory. The energetically lowest isomers consist of chains of four-membered rings which are twisted toward one another. The oligomers are found to be stable with respect to dissociation and disproportionation processes. Because of their distinct polarity, reactions with both electrophilic and nucleophilic agents occur quite readily, leading, in the case of an attack by H_2O, to the cleavage of the respective ring system. Optical excitations have been calculated using CIS, TD-HF, and CASPT2. It turns out that the S_1 state is located about 5.0 eV above the ground state. This excitation corresponds to a forbidden $n \rightarrow \pi^*$ transition.

1. Introduction

Nanoscience, combining the approaches of chemistry, physics, and biology on the scale of molecular dimensions, is the essential tool for the technological revolution, the beginning of which we are just now witnessing. One of the fascinating fields of research is the development of new hybrid materials consisting of both anorganic and organic, and sometimes even biological, components. The crucial point in creating these hybrid materials is the stable linkage of the single parts.

In rubber applications, for example, two-phase fillers made up of silica and carbon black are widely used to reduce the rolling resistance and improve other properties of tires (passenger tread compounds).[1,2] The performance of these mixtures of anorganic and organic particles, however, depends significantly on the way they are connected by adsorption or chemical bonds. One of the coupling agents used to connect the two phases is 1,4-bis(3-triethoxysilylpropyl)tetrasulfane, $((C_2H_5O)_3\text{-}Si{-}(CH_2)_3{-}S{-}S{-})_2$, which reacts both with wetted silica surfaces and with the surface of carbon black particles, thereby establishing a complex chemical linkage between the anorganic and the organic phases, showing a wide variety of bond types.

The triatomic system SiOS is the most simple molecule combining both the reactivity of sulfur and the functionality of Si−O bonds. It has been synthesized in an argon matrix by reaction of SiS with oxygen atoms.[3] The cocondensation of SiO and SiS with argon yields, among several other products, the molecule Si_2OS, which could be characterized by IR spectroscopy.[4] Up to now, however, larger $Si_xO_yS_z$ compounds have not been found experimentally.

While over the years the silicon oxides have stimulated considerable research activity, the silicon sulfides have attracted much less interest. By means of a reaction between the high-temperature molecule SiS and S atoms within a methane matrix, SiS_2 could be obtained.[5] Its Raman and IR frequencies meet earlier quantum-chemical predictions,[6] thereby confirming the linear structure and the double-bond character of SiS_2.

Quite recently, neutral, cationic, and anionic oligomers of SiS_2 have been investigated theoretically by use of the well-known density functional B3LYP and the standard basis sets 6-31G* and 6-31+G*.[7−9] Clusters of SiS_2 have been calculated at the Hartree−Fock level of theory, employing a nearly minimal basis set.[10]

Theoretical results on silicon oxide sulfides, however, have not been published so far. It is the aim of this paper to close this gap, especially because said compounds are model systems for linking agents between anorganic and organic constituents of hybrid materials. We will present information on the geometrical and energetical properties, charge distributions, dipole moments, vibrational spectra, and excitation energies of SiOS oligomers consisting of up to six units. Neither frequencies nor energies have been scaled.

A reliable knowledge of the oligomers' $S_0 \rightarrow S_1$ gap is necessary to estimate whether the corresponding polymers will generate conducting or isolating links between the phases of a hybrid material.

2. Computational Details

We performed our calculations at the MP2 (frozen core) level of theory throughout, using the *Gaussian98* program package.[11] To take care of a good transferability and consistency of the results, we decided to make use of *one* basis set only for all of the oligomers up to $(SiOS)_6$. The optimal basis set was selected among a group of four where the deviation of the calculated vibrational frequencies (at the respective minimum) from the experimental values for the monomer SiOS was taken as the decisive criterion. The reason for this procedure is that the vibrational spectrum is the only available source of experimental data for the so far known Si−O−S compounds. The results can be found in Table 1.

On the basis of these results, we choose cc-pVDZ, that is, Dunning's correlation consistent double-ζ plus polarization basis set.[12,13]

Excited states have been calculated by means of the single-excitation configuration-interaction (CIS) method[14] as well as of the time-dependent Hartree−Fock scheme. For the small systems the results have been checked using MP2 on the basis of a CASSCF wave function (CASPT2).

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TABLE 1: Vibrational Spectrum of Linear S−Si−O[a]

basis set	E_1	E_2	E_3	error
6-31G*	211	656	1281	14.5
cc-pVDZ	236	645	1251	8.0
AUG-cc-pVDZ	235	632	1217	29.5
cc-pVTZ	241	649	1276	8.5
experiment		643	1265	

[a] The energies are given in inverse centimeters. The error is the mean absolute frequency deviation. Entry 1 refers to the bending mode, whereas entries 2 and 3 refer to the SiS and SiO stretching modes, respectively.

TABLE 2: Dissociation Behavior of Si_2OS

reaction	ΔE (kJ/mol)
$Si_2OS \rightarrow Si_2 + SO$	+859.6
$Si_2OS \rightarrow SiS + SiO$	+116.0
$Si_2OS \rightarrow SSiO + Si$	+553.5

TABLE 3: Vibrations of Si_2OS

symmetry	E(exp) (cm^{-1})	rel int	E(calc) (cm^{-1})	rel int
b_2	350	medium	341	24
a_1	507	medium	521	26
b_2	770	strong	736	100

3. Results

3.1. The Monomer. The linear S−Si−O arrangement is the most stable of the three possible isomers. The molecule in its $^1\Sigma_g$ ground state is characterized by the following parameters:

$$R(\mathrm{S{-}Si}) = 1.949\ \text{Å},\quad R(\mathrm{Si{-}O}) = 1.553\ \text{Å}$$

$$E_{\mathrm{tot}} = -761.742\ 154\ \mathrm{H}$$

$$\mu = 1.42\ \mathrm{D}$$

Also, the silicon sulfoxide isomer Si−S−O is linear, and it forms a minimum on the potential energy hypersurface as well. The Si−S distance is slightly elongated (2.008 Å). The S−O distance amounts to 1.509 Å. Energetically, however, it is located 334.1 kJ/mol above the S−Si−O isomer. Its vibrational spectrum shows an absorption at 535 cm^{-1} which is not present in the experimental findings.

Even the cyclic atom arrangement represents a minimum on the hypersurface. With respect to the linear isomers, all bond lengths are enlarged (Si−S to 2.150 Å, Si−O to 1.696 Å, and S−O to 1.893 Å). The Si−S−O angle adopts a value of 49.1°, and the energy difference to SSiO amounts to 155.7 kJ/mol. The vibrations at 521 and 864 cm^{-1} have no experimental counterpart.

From the energetics we conclude that the formation of SSiO is favored enormously with respect to the formation of the other isomers, which corresponds to the fact that Schnöckel found SSiO only.

Moreover, it seems that SSiO is stable with respect to certain kinds of water attack as well. The reaction $SSiO + H_2O \rightarrow SiO_2 + H_2S$ is endothermic by 69.9 kJ/mol. Employing the MP4(DQ) correlation level and taking into account the zero-point correction, a value of 69.1 kJ/mol is obtained. By use of the larger triple-ζ basis set cc-pVTZ instead of cc-pVDZ, the zero-point-corrected MP2 energy difference shrinks to 45.2 kJ/mol, and with MP4(DQ) instead of MP2, the value still amounts to 54.4 kJ/mol, thereby indicating that this reaction is prohibited. On the other hand, however, SSiO is able to add a molecule of H_2O, thereby yielding $S{=}Si(OH)_2$ with a considerable energy gain (240.1 kJ/mol).

The disproportionation of two SSiO into SiO_2 and SiS_2 needs an energy *input* (zero-point corrected) of 5.8 kJ/mol, which increases by 0.1 kJ/mol if the situation is considered at room temperature. The reaction probability can hardly be estimated because of the lack of any knowledge about the transition state, but in view of the energetics, it seems to be a reaction path of minor importance only.

3.2. Si_2OS. Si_2OS is a four-membered ring system with a *planar* ground state of C_{2v} symmetry; that is, the sequence of atoms is Si−O−Si−S. The atomic distances are as follows: Si−Si = 2.703 Å, Si−O = 1.737 Å, and Si−S = 2.219 Å. Neither the bent nor the planar C_s arrangement (with a direct Si−Si bond) represents a minimum on the potential hypersurface. The molecule is thermodynamically stable with respect to all possible dissociation reactions (Table 2).

A comparison of the experimental[4] and the calculated vibrational frequencies and relative intensities demonstrates the reliability of our MP2/cc-pVDZ approach (Table 3).

3.3. The Oligomers. *3.3.1. The Dimer.* We have investigated eight different structures of the dimer $(SiOS)_2$. The results are summarized in Table 4.

The energetically lowest isomer I has a linear S−Si···Si−S axis. The Si−Si distance amounts to 2.460 Å only, so that the 4-ring looks like a system of two annealed Si−O−Si 3-rings with a Si−O bond length of 1.721 Å. The Si−S bond length is 1.940 Å. The compound is stable with respect to *both* dissociation into two SSiO (ΔE = 329.9 kJ/mol) *and* dissociation into SiO_2 and SiS_2 (ΔE = 335.8 kJ/mol). Among its 12 normal modes, only the five shown in Table 5 possess a nonzero IR intensity. Only the line at 394 cm^{-1} represents an out-of-plane vibration. The two Si═S stretching vibrations can be found at 358 and 988 cm^{-1}.

The three lowest excited singlet states of isomer I have been investigated by means of CIS and time-dependent Hartree−Fock theory. The results are presented in Table 6.

The predictions of the two methods agree remarkably well. *All* transitions correspond to excitations from the lone electron pairs of the two sulfur atoms into antibonding Si−S π orbitals ($n \rightarrow \pi^*$). They are forbidden throughout, as can be seen from the extremely small oscillator strengths. To check the reliability

TABLE 4: Isomers of $(SiOS)_2$[a]

no.	description	symmetry	type	E_{relative}
I	S−(Si_2O_2)−S, alternating 4-ring, planar	D_{2h}	minimum	0.0
II	S−(Si_2OS)−O, alternating 4-ring, planar	C_s	minimum	40.2
III	O−(Si_2S_2)−O, alternating 4-ring, planar	D_{2h}	minimum	103.4
IV	O−Si−S−S−Si−O, linear	$D_{\infty h}$	vdW complex	326.6
V	O−S−Si−Si−S−O, linear	$D_{\infty h}$	vdW complex	995.6
VI	O−(Si−S−S−Si)−O, nonalternating 4-ring, planar	C_{2v}	minimum	299.8
VII	(Si−S−O−Si−S−O), alternating 6-ring, planar	C_{2h}	minimum	486.5
VIII	nonalternating S_2Si_2 ring with 2 S−O−S bridges	C_{2v}	transition state	972.6

[a] The energies are given in kilojoules per mole. The entry "vdW complex" means that the species is a *very* weakly bound van der Waals associate ($\Delta E \approx$ 3 kJ/mol).

TABLE 5: IR-Active Vibrations of Dimer-I

symmetry	E (cm^{-1})	rel int
b_{2u}	139	1
b_{3u}	394	4
b_{1u}	609	7
b_{2u}	836	14
b_{1u}	934	100

TABLE 6: Vertical Excitations of Dimer-I

	CIS		TD-HF	
symmetry	ΔE (eV)	osc strength	ΔE (eV)	osc strength
$^1B_{1g}$	5.39	$\leq 10^{-4}$	5.31	$\leq 10^{-4}$
^1A_u	5.46	$\leq 10^{-4}$	5.38	$\leq 10^{-4}$
$^1B_{3g}$	5.59	$\leq 10^{-4}$	5.53	$\leq 10^{-4}$

TABLE 7: Selected Vibrations of Dimer-II

symmetry	E (cm^{-1})	rel int
a''	340	15
a'	408	15
a'	701	17
a'	791	63
a'	911	100
a'	1244	39

TABLE 8: Vertical Excitations of Dimer-II

	CIS		TD-HF	
symmetry	ΔE (eV)	osc strength	ΔE (eV)	osc strength
$^1A''$	4.98	$\leq 10^{-4}$	4.91	$\leq 10^{-4}$
$^1A'$	5.72	0.0136	5.65	0.0125
$^1A''$	5.88	0.0274	5.81	0.0246

of these findings, 4 × 4 CASPT2 calculations have been performed using the following Hartree−Fock orbitals, which are suitable to generate the two lowest excited states: HOMO-1 (b_{3g}), HOMO (b_{2u}), LUMO+2 (b_{3u}), and LUMO+3 (b_{2g}). The S_1 state, in fact, turns out to be the predicted $^1B_{1g}$, and the excitation energy amounts to 5.28 eV, in very good agreement with the previous results. The changes in the CIS and TD-HF excitation spectra caused by the use of the larger cc-pVTZ basis set are negligible.

Isomer II, containing the alternating Si−S−Si−O 4-ring, is located energetically 40.2 kJ/mol above isomer I. While the inner ring Si−O as well as the external Si−S bond length are nearly the same as those in the case of I (1.712 and 1.946 Å, respectively), the Si−Si distance is significantly enlarged (by 0.142 Å) because of the two long Si−S bonds of 2.159 Å in the ring. The external Si−O distance adopts a value of 1.547 Å, and the S−Si···Si−O axis is linear. Due to the reduced symmetry versus I, a dipole moment of 1.50 D arises.

The vibrational spectrum of II differs significantly from the one of isomer I, which should allow for a precise identification of the isomers (see Table 7, where the six most intense modes are shown). Note that in the case of a matrix isolation experiment only the in-plane (a') modes can be detected.

The mode at 1244 cm^{-1} can be identified as the Si═O stretching vibration. No explicit Si═S mode has been found.

The lowest vertical excitation of isomer II is a pure HOMO → LUMO transition showing the same characteristics as in the case of I; that is, it is a transition from the external sulfur's lone pair (of a' symmetry) into the corresponding Si−S π^* orbital. The higher excitations involve much more orbitals. For the results see Table 8.

Again, the symmetry and energy of the S_1 state have been checked by a 4 × 4 CASPT2 calculation, confirming the symmetry assignment and yielding an energy of 5.16 eV in really good agreement with the CIS result.

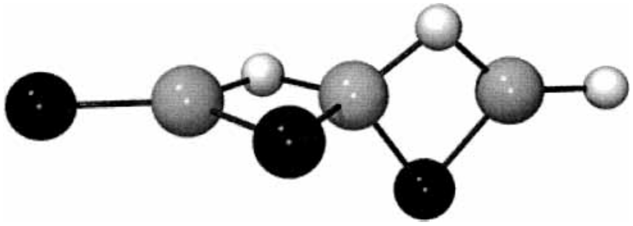

Figure 1. Optimized structure of trimer-I. The silicon atoms are represented by the gray balls, the sulfur atoms by the black balls, and the oxygen atoms by the white ones.

3.3.2. The Trimer. Out of the experience with the several (SiOS)$_2$ isomers, we have confined our attention, in the case of the trimeric molecules, to atom arrangements similar to the dimer isomers I−III. Trimer-I (see Figure 1) consists of two alternating planar Si−S−Si−O 4-rings which are connected by one common Si atom. The two other Si atoms are saturated by double bonds to one external O and S atom, respectively, and the two 4-rings are twisted toward one another by a certain dihedral angle (starting value 90°) so that C_1 symmetry is obtained. Two other isomers can be generated if, instead of the two *mixed* 4-rings, one alternating Si$_2$S$_2$ ring and one alternating Si$_2$O$_2$ ring are connected by a common Si atom. Then isomer II is formed by binding the external oxygen atom to the sulfur containing ring and the external sulfur atom to the oxygen containing ring. In the case of isomer III, the opposite is done. Both II and III possess C_{2v} symmetry.

Geometry optimization shows that, in contrast to the means in the case of the dimer, trimer-I, which contains the mixed rings, is the most stable one. The bond lengths differ only insignificantly from the values obtained for the three lowest (SiOS)$_2$ isomers. The dihedral angle between the two rings shifts to 113.6°, and the Si−Si distances amount to 2.582 and 2.594 Å, respectively. The rings remain essentially planar. In contrast to the cases of dimers-I−III, however, the O−Si···Si···Si−S arrangement is no longer linear. We obtain a Si−Si−Si angle of 166.8°, indicating a certain curving tendency of the line of the Si atoms. The dipole moment has a value of 1.89 D.

Thermodynamically, I is a very stable molecule. The energy balances show that both the dissociation into SiO$_2$ + SiS$_2$ + SSiO and the disproportion into SiO$_2$ and SiS$_2$ are endothermic by 628.4 and 631.4 kJ/mol per (SiOS)$_3$ unit, respectively. These values agree reasonably with what one would expect by extrapolation from the dimer-I results. Also, the hydrolytic reaction to SiO$_2$ and H$_2$S is energetically unfavorable by 832.0 kJ/mol.

The third silicon atom, connecting ring no. 2 and the external oxygen atom, bears a Mulliken charge of +0.65 units. This finding, combined with the fact that said Si$_{(3)}$ is surrounded by two oxygens and one sulfur only, indicates that it should be possible to open the ring by nucleophilic attack of a water molecule, leading to the formation of a −O−Si(═O)−OH group. In fact, it can be shown that the ring opening is favored thermodynamically by 94.2 kJ/mol. The optimized structure of the resulting derivative of the metasilicic acid is given in Figure 2.

It is to be expected that ring no. 2 can also be attacked quite readily by an electrophilic agent such as, for example, H$^+$. The most electron-rich site is the ring's oxygen atom, showing a Mulliken charge of −0.50 units; that is, the proton will be bound to this atom preferentially. The question, however, is whether the ring will ride the attack out or not. Addition of H$^+$ to trimer-I leads to a very stable H−O bond of 0.982 Å length with an enormous energy gain of 732.3 kJ/mol, accompanied by a

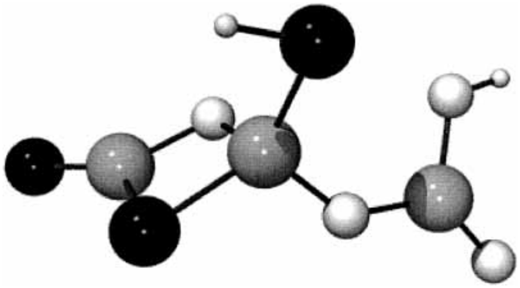

Figure 2. Optimized structure of the derivative of the metasilicic acid obtained by reaction of H_2O with trimer-I.

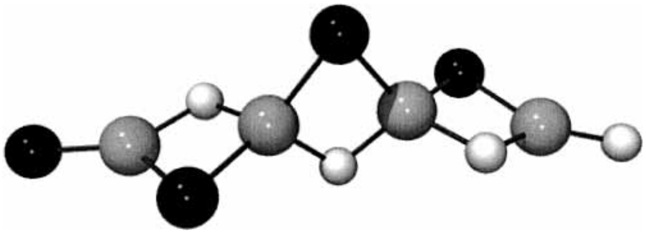

Figure 3. Optimized structure of $(SiOS)_4$.

uniform elongation of the Si−O bonds from about 1.70 to 1.82 Å whereby the coherence of the ring is preserved.

Regarding the electronic excitations, trimer-I behaves in the same way as dimer-I; that is, the S_1 state corresponds to a pure HOMO−LUMO transition from the external sulfur's lone pair into the $Si-S_{external}$ π^* orbital. The CIS (TD-HF) excitation energy amounts to 5.06 (4.98) eV. This transition is forbidden, since the oscillator strength is on the order of 10^{-4}.

Also the isomers II and III represent minima on the trimer potential hypersurface with only small energy gaps of 24.7 and 21.8 kJ/mol, respectively, to trimer-I. Bond lengths and angles are as expected. The mean of the Si−Si distances corresponds to the Si−Si distances in I.

3.3.3. The Tetramer. Taking into account the situation in the trimer case, only one isomer has been investigated. It is the structural analogue of trimer-I and in fact shows (in most cases) very similar geometry parameters (see Figure 3). The chain of the four Si atoms deviates from linearity by an angle of 9.7°. The mean dihedral angle between two adjacent 4-rings, which are essentially planar, amounts to 124.6°; that is, the distortion of two ring planes toward one another is more pronounced than in the trimer case. The dipole moment adopts a value of 1.51 D.

Also, energetically the tetramer behaves as one would extrapolate from the trimer-I results: Thermodynamical stability versus dissociation into four monomers as well as versus disproportionation is guaranteed, and the first excited singlet state is obtained by the already well-known HOMO−LUMO excitation, yielding an $n \rightarrow \pi^*$ transition at 5.07 (CIS) and 5.00 eV (TD-HF), respectively. Also this transition is forbidden (oscillator strength = 10^{-4}).

The terminal $Si_{(4)}$ atom bears a Mulliken charge of +0.63 units, thereby indicating that also the tetramer should be sensitive toward nucleophilic ring opening by water. The ring oxygen atoms have Mulliken charges of about −0.50 units, so that an electrophilic attack is as likely to occur as in the case of trimer-I.

3.3.4. The Hexamer. In analogy to previous findings, five alternating Si−S−Si−O rings are connected by common Si atoms. Now, however, a helical symmetry is realized (see Figure 4); that is, the first and the fifth ring have the same orientation with respect to a laboratory coordinate system. The rings are planar and twisted toward one another by a mean dihedral angle of 90.0°. The chain of the six Si atoms deviates from linearity by an angle of 7.3° only (which is the angle between the two vectors $\overrightarrow{Si_{(1)}Si_{(2)}}$ and $\overrightarrow{Si_{(1)}Si_{(6)}}$). Again the dipole moment amounts to 1.51 D, thereby indicating a constant polarity of the linear oligomers. Also the Mulliken charge of the terminal Si atom does not differ from the value of the tetramer; that is, the possible hydrolytic cleavage of (at least) the terminal ring seems to be a common feature of all larger oligomers. In analogy to the case of the smaller molecules, the hexamer's ring oxygens are sensitive to electrophilic attack as well (Mulliken charge ≈ −0.50 units).

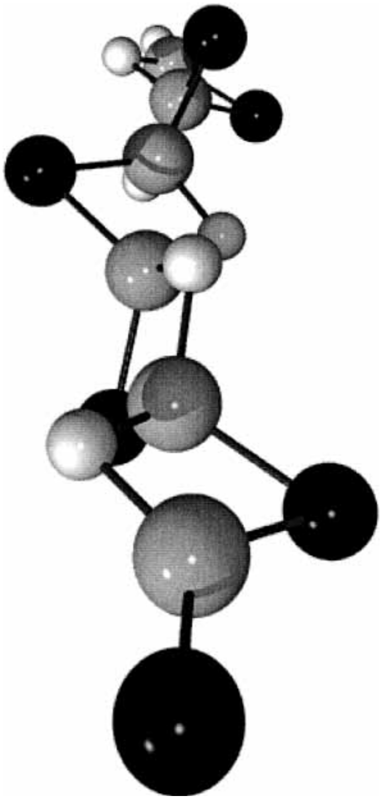

Figure 4. Optimized structure of $(SiOS)_6$.

The orbitals HOMO-1 and HOMO are nearly degenerate and represent the external sulfur's lone electron pairs. Accordingly, the $S_0 \rightarrow S_1$ transition is of $n \rightarrow \pi^*$ type, leading to an occupation of the antibonding $Si-S_{external}$ π orbital. The CIS excitation energy amounts to 5.09 eV (oscillator strength = 10^{-4}).

Cyclic isomers based on a Si_6 ring do not seem to exist. We have looked for a minimum of the alternating system II (see Figure 5) both in D_{3d} (planar) and in C_{2h} symmetry (chair). The changes during geometry optimization point out that no stationary point on the $(SiOS)_6$ potential energy surface corresponds to isomer II. Instead this structure decomposes into two dimer-I molecules and one dimer-III molecule. Also a Si_6 chair with all oxygen atoms on top and all sulfur atoms below (C_s) decays into fragments.

4. Conclusions

1. Oligomeric silicon oxide sulfides are compounds which are thermodynamically stable with respect to (i) dissociation, (ii) disproportionation, and (iii) reaction with H_2O under formation of SiO_2 and H_2S.

Table 9 presents the increase in the total energy per monomer unit with increasing chain length.

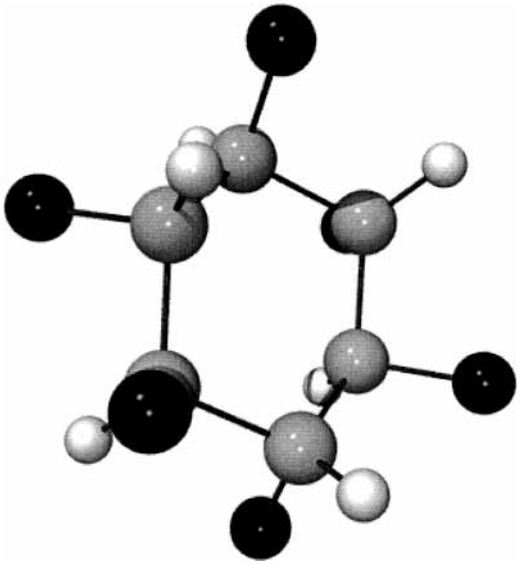

Figure 5. Starting structure of the cyclic $(SiOS)_6$ isomer II.

TABLE 9: Total Energy per Unit in $(SiOS)_n$

n	E_{tot} (H)	$E_n - E_{previous}$ (kJ/mol)
1	−761.742 154	
2	−761.797 301	−144.9
3	−761.821 145	−62.8
4	−761.832 845	−30.6
6	−761.844 530	−30.5

Quite often an analysis of the total energies yields not more than a rough estimate of the thermodynamical stability of the corresponding species. It is therefore suggested, although it is much more costly, to calculate the thermal free energy in addition. Because of limited computer resources, we have done this for the tetramer only. Its thermal free energy at room-temperature amounts to −3047.344 453 H, which corresponds to an energy gain of 198.1 kJ/mol per unit, compared to the free monomer. With respect to $2SiO_2 + 2SiS_2$, the tetramer possesses a thermal free energy which is by 811.0 kJ/mol lower than that of the disproportionation products, thereby showing that $(SiOS)_4$ is a thermodynamically very stable species indeed.

2. They form chains of planar Si−S−Si−O four-membered rings which are connected via common Si occupied vertexes. The rings are twisted toward one another, and since the arrangement of the Si atoms is approximately linear, a helical overall symmetry can be obtained (see Figure 4).

3. The high lying S_1 state ($\Delta E \approx 5.0$ eV) is obtained by excitation of one electron from the external sulfur's two lone pairs into the antibonding $Si-S_{external}$ π orbital. In view of the very small oscillator strength, this transition is very unlikely to occur, so that these compounds should act as isolators.

4. There is, however, a distinct polarity of the oligomers giving rise to a dipole moment of about 1.5 D. The silicon atom of the chain's terminal Si═O group bears a relatively high Mulliken charge of about +0.6 units, so that a nucleophilic attack should be possible which, in the case of H_2O as the reactive agent, will lead to the hydrolytic cleavage of (at least) the corresponding Si−S−Si−O ring. The reaction with H^+ will yield stable cations where the ring systems seem to be preserved.

The geometry data of all molecules described can be obtained upon request.

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