1340 *Inorg. Chem.* **1994,** *33,* 1340–1343

Isomers of S_7O_2: A Simulated Annealing Study

R. O. Jones

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Received September 9, 1993[*]

Density functional calculations with simulated annealing have been performed for *cyclo*-heptasulfur dioxide, S_7O_2, which is the only stable homocyclic dioxide of sulfur that has been prepared in a pure state. The relatively flat energy surface allows substantial motion of the atoms, and there are numerous structures corresponding to local minima. The calculations show that (1) exocyclic S–O bonds are favored over endocyclic S–O–S bridge bonds, (2) S_7-chair structures are favored over "boat" structures, (3) relative to the S_7 unit, axial SO bonds are favored over equatorial and *cis*-SO bonds are favored over *trans*, and (4) singlet structures are favored over triplet. We discuss the bonding patterns and the consequences for other cyclic sulfur oxides.

I. Introduction

The tendency of the group VI elements S, Se, and Te to form ring and chain structures is well-known, and sulfur, in particular, has a large number of allotropes comprising ringlike molecular units.[1] Sulfur is also the element with the most molecular oxides, of which the homocyclic ones (S_nO, $n = 6$–10) are commonly produced by treating sulfur rings with trifluoroperoxyacetic acid, CF_3CO_3H.[2–4] The oxidation of organic tri- and tetrasulfanes (R_2S_n; R = tBu, 2-$C_{10}H_7$; $n = 3$, 4) using peroxy acid leads to sulfane oxides (R_2S_nO, $R_2S_nO_2$) with a maximum distance between SO groups,[5] indicating that higher oxides of the ring molecules will generally be unstable. It is perhaps not surprising that only one homocyclic dioxide, S_7O_2, has been prepared in the pure state.[6]

S_7O_2 can be obtained by the oxidation of S_7, S_8, S_7O, or S_8O with CF_3CO_3H, yielding dark orange crystals that decompose at 60–62 °C with vigorous evolution of SO_2.[6] The ease of decomposition, which is also complete at 25 °C after 2 h in the dark, means that it is not possible to perform X-ray diffraction studies. Attempts to form stable adducts of the molecule with the Lewis acids $SbCl_5$ and $SnCl_4$ have not been successful to date.[7] The Raman spectrum in CS_2 solution exhibits two IR bands at 1127 and 1138 cm^{-1}.[6] There must then be at least one S atom between the SO groups, since strong vibrational coupling would lead otherwise to a larger separation between the two SO stretching modes.[6] Information about the bond lengths can be derived from the measured Raman spectra, since data on other ring molecules containing sulfur have shown that there is close relationship (see Figure 1) between the bond lengths and vibration frequencies. The number of minima in the energy surfaces associated with the chemical formula S_7O_2 is so great that this information still leaves many possible candidates for the stable isomers. We must consider, for example, seven- and eight-membered rings, the possibility of the SO groups being aligned equatorially/axially or *cis*/*trans* relative to the rings, and singlet and triplet states.

In the present paper, we describe density functional calculations for numerous isomers of S_7O_2. The method incorporates "simulated annealing" by means of molecular dynamics at elevated temperatures. Previous applications of the method have included related systems such as sulfur clusters S_n up to $n = 13$[8] and cycloheptasulfur monoxide S_7O,[9,10] for many of which X-ray structure determinations have been performed. The agreement between calculated and measured structures is generally very satisfactory, and plausible predictions have been made for the most stable isomers of molecules (such as S_5 or S_9) for which X-ray structure determinations have not yet been performed. In S_7O we could follow the transition from an eight-membered-ring structure to the experimental ground state (an S_7 chair with an axial O atom), which is characterized by a relatively flat energy surface and S–S bonds that vary widely in length (1.92–2.28 Å). Similar effects are evident in the dioxide. Molecules for which little is known about the structures of the stable isomers and for which the energy surface contains numerous minima are excellent candidates for study by the MD/DF method or other approaches incorporating simulated annealing.

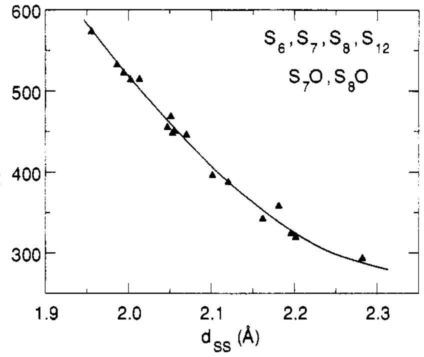


Figure 1. Relationship between the S–S stretching vibration ν_{SS} of a bond in homocyclic sulfur rings and the corresponding bond length d_{SS}. The data for the compounds shown were taken from ref 2.

In section II we outline those aspects of the calculations needed in the present context and the strategy used to determine the isomer structures, which are presented in section III. The structural trends are discussed in section IV, where the relationship between vibration frequency and bond length has proved to be useful. We also discuss the implications for other homocyclic sulfur oxides.

II. Computational Details

The method[11] uses a combination of density functional (DF) calculations with molecular dynamics (MD). For a given geometry, the energy

---

[*] Abstract published in *Advance ACS Abstracts,* March 1, 1994.

(1) Donohue, J. *The Structures of the Elements*; Wiley: New York, 1974; Chapter 9.

(2) Steudel, R. *Comments Inorg. Chem.* **1982,** *1,* 313.

(3) Steudel, R. In *Studies in Inorganic Chemistry*; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984; Vol. 5, p 3.

(4) Steudel, R. *Phosphorus Sulfur* **1985,** *23,* 44.

(5) Steudel, R.; Latte, J. *Chem. Ber.* **1977,** *110,* 423.

(6) Steudel, R.; Sandow, T. *Angew. Chem.* **1978,** *90,* 644; *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 611.

(7) Steudel, R. Private communication.

(8) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *J. Chem. Phys.* **1989,** *89,* 6823.

(9) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *J. Am. Chem. Soc.* **1989,** *111,* 825.

(10) Jones, R. O.; Hohl, D. *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1990,** *24,* 141.

0020-1669/94/1333-1340$04.50/0

and forces are calculated using the DF formalism,[12] with a local density approximation for the exchange-correlation energy. This approach gives a generally reliable description of molecular geometries, and the combination with finite temperature MD means that the energetically unfavorable local minima in the energy surface can be avoided.

In the present calculations, we use periodic boundary conditions with a large unit cell (constant volume 1000 Å^3; fcc lattice constant 15.9 Å with a single point $k = 0$ in the Brillouin zone) to minimize the interaction between the molecular units. The electron–ion interaction in S and O atoms is described by a pseudopotential

$$V_{\text{ext}}(\mathbf{r}) = \sum_I v_{\text{ps}}(\mathbf{r} - \mathbf{R}_I); \qquad v_{\text{ps}}(\mathbf{r}) = \sum_{l=0}^{\infty} v_l(\mathbf{r})\, \hat{P}_l, \tag{1}$$

where $\hat{P}_l$ is the angular momentum projection operator. We have set $v_l = v_{l_{\max}}$ for $l \geq l_{\max}$ ($l_{\max} = 2$) and used the parameters of Bachelet *et al.*[13] for $v_l(\mathbf{r})$. The orbital eigenfunctions are expanded in plane waves, with an energy cutoff of 22.5 au (36 000 plane waves). This expansion is well converged for the sulfur atoms. While the rapid spatial variation of the oxygen pseudopotential means that the expansion does not lead to full convergence of the total energy, the S_7O calculations[10] showed that the difference in total energy between different isomers is given reliably with this cutoff. The parameters used here are the same as those used in the monoxide calculation, so that the calculated structures should be as reliable as those found in that work (bond lengths generally better than 2%; bond and dihedral angles to within 3°).

For each starting geometry, the electrons are brought into their ground state by a two-step procedure: (1) First, we diagonalize the eigenvalue problem using a minimal plane wave basis set (energy cutoff 1 au). (2) With the full plane wave basis set, we then use steepest descents (SD) on the electronic degrees of freedom to bring the electrons onto the Born–Oppenheimer surface. The minimum in the energy surface closest to the starting geometry is then found by using SD on both the ionic and electronic degrees of freedom. For this purpose, we use a time step $\Delta t = 7.2 \times 10^{-16}$ s and an effective "mass" for the electronic degrees of freedom μ_i = 50 000 au. This procedure usually leads to a shallow minimum in the energy surface, and it is in general essential to alternate SD calculations with MD runs at elevated temperatures. In the latter, we use a mean kinetic energy of the ions ("temperature") of 300 K, a time step $\Delta t = 1.2 \times 10^{-16}$ s, and an electronic "mass" of 300 au. We follow the simulation until the energy passes through a (lower) minimum and then optimize the geometry again with a SD calculation on electrons and ions. This cycle is repeated until it produces a negligible energy lowering. The energy surface in the neighborhood of each minimum is probed for possibly more stable structures by a longer MD run, typically at least 500Δt at T = 300–500 K.

III. Results

The calculations were carried out for a large number (>20) of starting geometries. Several were far from a stable local minimum in the energy surface, and annealing led to substantial distortions. In discussing the isomers of S_7O_2, it is natural to relate the structures to the most stable form of S_7, the "chair" form shown in Figure 2(a). This structure and the "boat" form have C_s symmetry, so that one bond has a dihedral angle of 0°. We adopt the cyclic numeration of the atoms shown here, with atom 1 being opposite to this bond. It is important to note that the effect of the added oxygen atoms on the structures is not localized to their immediate neighborhoods. This reflects both the delocalized nature of the molecular orbitals in cumulative S rings and the relations between structural parameters inherent in any closed-ring geometry. Some structures are so distorted that the use of the terms "chair" and "boat" is not really appropriate. Unless otherwise stated, however, we shall denote atom 1 as that opposite the bond with the smallest dihedral angle.

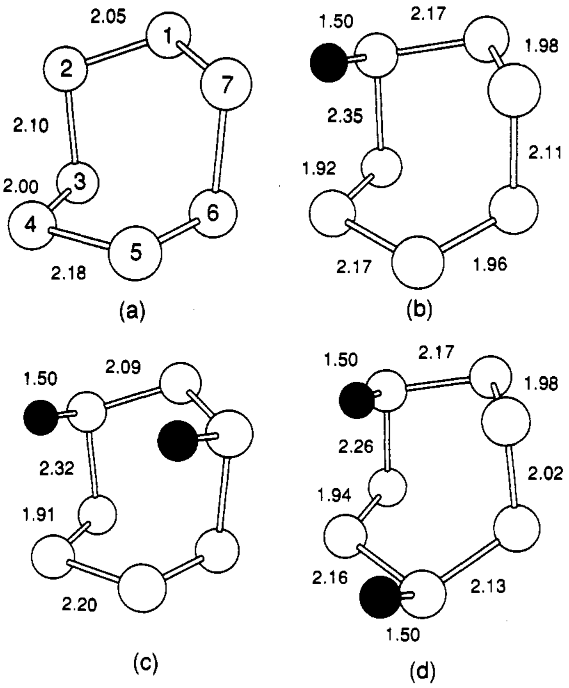


Figure 2. Structures of (a) S_7 "chair", (b) S_7O, and (c,d) the two most stable isomers found in S_7O_2. Distances are in angstroms. Sulfur atoms are white; oxygen atoms, black.

Table 1. Bond Angles (deg) in Structures Related to the S_7 "Chair"

	S_7 [2(a)][a]	S_7O [2(b)][b]	S_7O_2 (C_s) [2(c)]	S_7O_2 (C_1) [2(d)]
α_1	105	103	110	95
α_2	102	99	103	100
α_3	105	95	96	95
α_4	107	108	103	112
α_5		106		105
α_6		104		111
α_7		106		106
α_{128}		107	112	102
α_{328}		102	97	100
α_{659}				116
α_{459}				97

[a] Reference 14. [b] Reference 10.

A. Structures of S_7O_2 Isomers. In Figure 2 we show the (experimental) structure of S_7 (chair),[14] the calculated structures of S_7O,[10] and the two most stable isomers found here for S_7O_2. These isomers are almost degenerate, the C_s form (c) lying less than 0.02 eV below (d) (C_1 symmetry), and the latter is one of the two candidates suggested by Steudel[4] for the most stable isomer. We discuss the identification of the most stable isomer in more detail below. The ease of torsional motion in sulfur ring structures is well-known, so that changes in bond and dihedral angles are often associated with very small energy changes. The bond angles α in Table 1 are therefore given to the nearest degree.

In Figures 3 and 4 we show further structures of S_7O_2 that correspond to local minima in the energy surface. The perspective shown has been chosen to relate the structures to the S_7 chair shown in Figure 2, although the bond lengths show that the distortions are sometimes large. An additional measure of this is the deviation from 0° of the dihedral angle γ_{45}. In structure 2(d), for example, γ_{45} is 25°, and in structures 3(b) and 3(d) it is almost 20°. In structures 3(c), 3(e), and 4(b), even larger values of γ_{45} are found (38, 34, and 41°, respectively), so that the description as "chair" or "boat" is perhaps inappropriate. In fact, by choosing a different atom as reference atom "1", we can show relationships with other structures shown. If we take atom 3 in Figure 2(b) as our reference atom 1, for example, the structure is related to 2(d) by torsion of atom 6. In Figure 4(d) γ_{45} is over

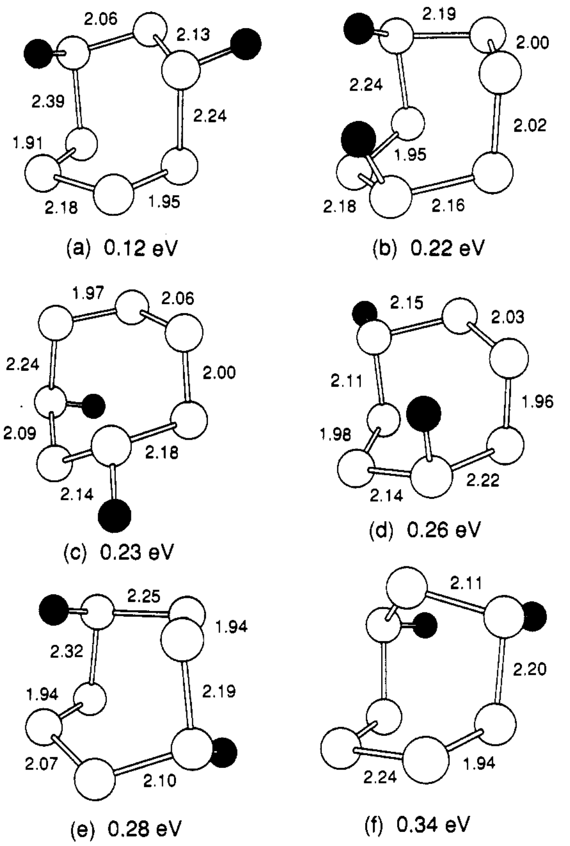
---

(11) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471. For a review of molecular applications, see: Jones, R. O. *Angew. Chem.* **1991**, *103*, 647; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 630.

(12) For a review, see: Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689.

(13) Bachelet, G. B.; Hamann, D. R.; Schlüter, M. *Phys. Rev. B* **1982**, *26*, 4199.

(14) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F.; Reinhardt, R. *Z. Naturforsch., B* **1980**, *35*, 1378.

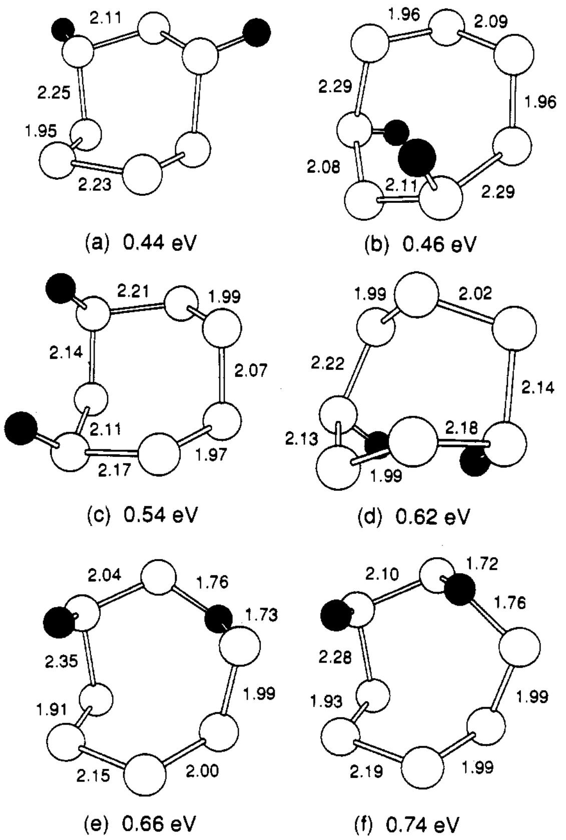


(a) 0.12 eV (b) 0.22 eV

(c) 0.23 eV (d) 0.26 eV

(e) 0.28 eV (f) 0.34 eV

Figure 3. Six isomers of S_7O_2, with energies above the most stable isomer. Distances are in angstroms. Sulfur atoms are white; oxygen atoms, black.



(a) 0.44 eV (b) 0.46 eV

(c) 0.54 eV (d) 0.62 eV

(e) 0.66 eV (f) 0.74 eV

Figure 4. Six isomers of S_7O_2, with energies above the most stable isomer. Distances are in angstroms. Sulfur atoms are white; oxygen atoms, black.

50°, and we have chosen the perspective primarily to illustrate the distortions that can result from an initially symmetric (C_s) boat structure.

The lengths of the exocyclic SO bonds (1.49–1.50 Å) show remarkably little variation about the value found in S_7O and are not shown in Figures 3 and 4. The bonds are very close in length to that in the SO diatomic molecule (1.481 Å).[15] It can be seen that structures 2(d) and 3(b) have the same topology and similar bond lengths but different orientations of the O atoms. An additional minimum with the same topology was found 0.31 eV above the energy of the most stable isomer, and the less stable structures would certainly convert to the 2(d) structure if annealing were carried out for a longer time or at a higher temperature. These results show, however, that the number of minima in the energy surface is larger than the number of topologically different structures.

B. Bonding Trends. We now focus on structural trends apparent in Figure 2–4. While certain general principles are apparent, extrapolations to general "rules" must be made with caution. A comparison of the structures shows immediately, however, that the influence of the exocyclic O atoms is not localized to its immediate neighborhood. There is also a clear preference for structures related to the "chair" form of S_7 rather than the "boat" form of similar energy.[8] The most direct comparison is between the C_s structures 2(c) and 3(f), which are separated by 0.34 eV. The "chair" analogy of Figure 4(d) distorted substantially on annealing to give the structure discussed in section IIIA 0.31 eV above the most stable isomer.

In agreement with the conclusions of Steudel and Sandow,[6] structures with O atoms attached to adjacent members of S_7 rings were found to be unstable to annealing at 300 K. In the four most stable structures, oxygen is bonded in an axial position relative to atom 2, as in S_7O [Figure 2(b)]. This is associated with a small dihedral angle γ_{8234} and a long S_2–S_3 bond in each case. It is interesting that such a long bond is associated with relatively stable structures. A comparison of Figure 2(c) with Figures 3(a) and 4(a) shows that equatorial SO bonds, although associated with shorter S(2)–S(3) bonds, are energetically less favorable than axial SO bonds. This is a general trend and indicates that there is a weak bond between the exocyclic O atom and S(4). A comparison of the C_s structures 3(c) and 4(a) indicates an average of 0.22 eV for the energy difference between axial and equatorial conformers, and the difference between the C_1 structures 2(d) and 3(d) gives 0.24 eV for the same energy difference. The energy difference between 2(c) [C_s] and 3(d) [C_1] is only 0.12 eV. The relative stability of the C_1 structure compared with the C_s structures can be related to the lack of symmetry constraints on the former.

The tendency of ring structures to favor exocyclic axial bonds is well-known.[16] An example of a ring structure containing S and O is S_3O_9, where each S atom in the ring has an axial and an equatorial SO bond. The former is on average shorter (1.37 Å), and therefore stronger, than the latter (1.43 Å).[17] This is not always the case, however. The related structures 3(c) and 4(d) differ by the conformation of one exocyclic O atom, but the latter structure with two axial bonds lies higher in energy.

In our earlier study of S_7O using the same method, we found that the eight-membered ring with an endocyclic, bridge O atom also led to a local minimum in the energy surface, with an energy 0.13 eV above the most stable isomer 2(b). Eight-membered rings are also possible in the dioxide, and we have performed calculations for two representative structures shown in Figure 4(e,f). The energies are 0.66 and 0.74 eV, respectively, above the most stable structure, and the lengths of the S–O bonds are very similar to that found in the eight-membered ring of the monoxide (1.75 Å).[10] Several other eight-membered rings can also occur, such as those related to S_8O, which has an oxygen atom bound

---

(15) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

(16) See, for example: Romers, C.; Altona, C.; Buys, H. R.; Havinga, E. *Top. Stereochem.* **1969**, *4*, 39.

(17) McDonald, W. S.; Cruickshank, D. W. J. *Acta Crystallogr.* **1967**, *22*, 48.

axially to an S_8 ring.[18] These structures can be related by bond torsion or the exchange of O and S atoms to the structures 4(e,f) and are unlikely to be among the most stable isomers.

All the structures discussed above are singlets; i.e., the highest occupied molecular orbital is doubly occupied. It is natural to study the triplet states obtained by promoting an electron to the next highest orbital, and we have performed such calculations starting with the two most stable isomers, Figure 2(c,d). In both cases we found a large gap between the eigenvalues of the uppermost (singly occupied) levels, and very large structural distortions occurred during annealing at 300 K. The local minima in the energy surface that resulted had energies 1.50–1.70 eV above the most stable singlet, and the corresponding structures had S–S bonds that were much longer (2.8–2.9 Å) than found in any stable sulfur ring. These results suggest that triplet states of S_7O_2 will have energies well above those of the most stable isomers and will usually be unstable.

IV. Discussion and Conclusions

We have described here an extended series of calculations on isomers of S_7O_2, the only stable homocyclic dioxide of a sulfur-ring molecule yet prepared in a pure state. The calculations use a simulated annealing technique so that the effective kinetic energy of the ions corresponds to an elevated temperature, usually 300 K. This approach shows that many of the local minima in the energy surface are shallow, so that the corresponding structures distort readily into more stable ones. This ease of distortion is consistent with the experimental finding that the molecule decomposes readily, even at 25 °C.

The calculated energies of the isomers show clear tendencies to favor S_7 chair structures over the related boat structures or eight-membered rings, axial SO–bonds over equatorial, and *cis* bonds over *trans*. The energetically most favorable triplet structures have large HOMO–LUMO gaps and lie well above the singlet structures shown in Figures 2–4. These trends are consistent with other findings on the structures of related molecules and give reliable estimates for the energy differences between different structures.

The two most stable isomers found [Figure 2(c,d)] are closely related to the structure of the monoxide S_7O [Figure 2(b)], and both structures were stable to (relatively short) molecular dynamics simulations at 500 K. The difference between the energies of these isomers is very small, so that either could be the most stable isomer. The measured Raman frequencies[6] and the relationship between frequencies and bond lengths in cumulated sulfur rings (Figure 1) provide additional information. Our work on S_7O using the method of calculation underestimated bond lengths by 0.01–0.04 Å, with the exception of d_{23}, which was overestimated by 0.07 Å. If we have similar discrepancies in S_7O_2, we can estimate the bond lengths and, using Figure 1, the corresponding vibration frequencies. We find that the *range* of the frequencies is reproduced better by the C_s structure but the number and the overall distribution are reproduced better by structure 2(d). It is possible, of course, that the two isomers coexist, and it would be interesting to have the results of calculations using other methods. We note that the SO groups are separated by one and two sulfur atoms in structures 2(c) and 2(d), respectively, so that no particular preference for one of these two types is apparent in the present results.

Many of the above bonding trends should transfer to other ring oxides of sulfur, for most of which there will be structures with pronounced local minima. We should note, however, that the S_n-ring structures have different patterns of dihedral angles for odd and even values of *n*, so that differences between the related oxides can be expected. We also note that the existence of a stable local minimum in the calculated energy surface does not imply that the corresponding isomer can be observed in an experiment. In calculations on molecules containing elements of groups V and VI,[19] for example, stable structures were found for molecules such as P_4Te_3 and P_2Te_5, which have not yet been observed.

The present calculations have shown the usefulness of the simulated annealing technique in electronic structure calculations in molecules, particularly in a case where the structures of the most stable isomers are unknown and the energy surfaces are both relatively flat and have a large number of local minima. Finite temperature simulations allow us to avoid many of the shallow, energetically unfavorable minima and to make predictions about S_7O_2 and its related molecules.

Acknowledgment. I thank R. Steudel for suggesting this study and for helpful correspondence. The calculations were performed on Cray computers of the Forschungszentrum Jülich (KFA) and the German Supercomputer Center (HLRZ).

---

(18) Luger, P.; Bradaczek, H.; Steudel, R.; Rebsch, M. *Chem. Ber.* **1976**, *109*, 180.

(19) Jones, R. O.; Seifert, G. *J. Chem. Phys.* **1992**, *96*, 2942.