

zation. This basis gives a nearly unchanged MCSCF barrier of 36.8 kcal/mol. A second-order CI wave function, containing all double excitations from this MCSCF wave function, but keeping the bonds to hydrogen doubly occupied, gives a barrier of 36.9 kcal/mol. Unless correlation in the CH and SiH bonds has an effect, this barrier is remarkably insensitive to both the basis set and correlation effects beyond those included in the simple MCSCF wave function.

Summary

We have presented three improvements for the original IRC determination method.¹⁴ These improvements are (1) basing the step size taken on the norm of the gradient at the current IRC point, (2) using a gradient which must be calculated in any case to reduce the linear search time, and (3) taking a harmonically chosen step size away from the saddle point.

A relatively simple split valence MCSCF wave function was used to trace the IRC for the rotation of the prototypical silicon-carbon double bond. The IRC for the rotation of silaethylene shows that for the most part the coordinates vary smoothly during the rotation from the planar to twisted form. For example, the SiC bond length increases smoothly by about 0.15 Å as this bond loses its multiple character. However, the carbon atom is slightly

pyramidalized during the rotation although it is planar at the rotational transition state. As expected for a radical silicon center, the silicon atom is greatly pyramidalized during the rotation. The rotation barrier on the S_0 surface is about 37 kcal/mol. Thus the SiC π bond strength as estimated by the rotational barrier is intermediate to that found for the CC bond (65 kcal/mol⁴²) and the recently calculated SiSi π bond strength (22 kcal/mol⁵⁰). The SiC rotational barrier is very insensitive to calculational improvements such as heavy-atom polarization or extended correlation treatments. The calculated rotational barrier agrees very well with the experimental estimates of the π bond strength. Triplet silaethylene has a geometry very similar to the rotated singlet and lies about 1 kcal/mol below it.

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Theoretical Study on the Dimerization of Silanone and the Properties of the Polymeric Products $(H_2SiO)_n$ ($n = 2, 3,$ and 4). Comparison with Dimers $(H_2SiS)_2$ and $(H_2CO)_2$

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Abstract: In an attempt to extend knowledge of the reactivity of silicon-oxygen doubly bonded compounds (silanones), the potential energy surface of the dimerization of $H_2Si=O$ was investigated by means of ab initio molecular orbital calculations. The dimerization is found to proceed with no barrier to yield the cyclic product $(H_2SiO)_2$ by forming stepwise two new bonds. The structure, vibrational frequencies, and dimerization energy for the dimeric product $(H_2SiO)_2$ are compared with those for the similar cyclic dimers $(H_2SiS)_2$ and $(H_2CO)_2$ at the same level of theory. All these dimers have a planar four-membered ring with D_{2h} symmetry. The unusually short Si-Si distance in $(H_2SiO)_2$ is explained in terms of the greater affinity of silicon for oxygen. Also discussed are the structures and stability of the cyclic trimer $(H_2SiO)_3$ and tetramer $(H_2SiO)_4$.

There has currently been considerable interest in the possible existence of silicon-oxygen doubly bonded compounds, silanones.^{1,2} Experimental evidence for the transient existence has accumulated in the last few years.³ Since, however, most of the evidence is rather indirect, we have recently undertaken the theoretical studies of the thermodynamic and kinetic stability of the parent compound, $H_2Si=O$.^{2,4} In an attempt to extend knowledge of the reactivity, we report here the first ab initio calculations of the reaction of two $H_2Si=O$ molecules to form the dimeric product cyclodisiloxane $(H_2SiO)_2$.

There has been active work on polymeric cyclosiloxanes $(R_2SiO)_n$, because of the practical importance. However, the lowest member ($n = 2$) of the series is almost unknown, and its chemistry is only recently starting to develop.⁵ In view of the situation we tried to explore the structure, vibrational frequencies,

and dimerization energy for the cyclic dimer $(H_2SiO)_2$ from a theoretical point of view. To characterize the properties of $(H_2SiO)_2$, we compared these results with those calculated for the similar cyclic dimers $(H_2SiS)_2$ and $(H_2CO)_2$ at the same level of theory. Also examined were the properties of the cyclic trimer $(H_2SiO)_3$ and tetramer $(H_2SiO)_4$.

Computational Details

All calculations were carried out for closed-shell singlets. Geometries were fully optimized at the Hartree-Fock (HF) level with the split-valence 3-21G⁶ and polarized 6-31G*⁷ basis sets by using the analytical energy gradient technique. The harmonic vibrational frequencies obtained at the HF/3-21G level were used to compute zero-point vibrational energies. The effects of electron correlation were calculated by means of second-order Møller-Plesset perturbation (MP2) theory,⁸ with

(1) For a review, see: Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* 1979, 79, 529.

(2) Kudo, T.; Nagase, S. *J. Phys. Chem.* 1984, 88, 2833.

(3) See a number of references summarized in ref 1 and 2.

(4) Kudo, T.; Nagase, S. *J. Organomet. Chem.* 1983, 253, C23. See also: Gordon, M. S.; George, C. *J. Am. Chem. Soc.* 1984, 106, 609.

(5) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* 1984, 106, 822.

(6) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, 102, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* 1982, 104, 2797.

(7) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta (Berlin)* 1973, 28, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* 1982, 77, 3654.

(8) Møller, C.; Plesset, M. S. *Phys. Rev.* 1934, 46, 618. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* 1976, 10, 1.

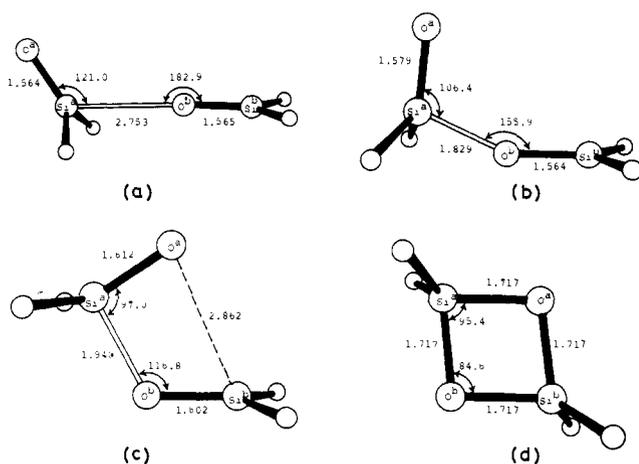
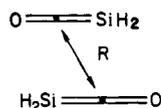


Figure 1. ORTEP drawings of the dimerization $2\text{H}_2\text{Si}=\text{O} \rightarrow (\text{H}_2\text{SiO})_2$ in angstroms and degrees, obtained at the HF/3-21G level: (a) $R = 4.0$ Å, (b) $R = 2.8$ Å, (c) $R = 2.4$ Å, and (d) $R = 1.717$ Å (product).

all orbitals included except the corelike orbitals (1s, 2s, and 2p for Si and S, and 1s for C and O in character). In this paper, notations like MP2/6-31G**/6-31G* denote a single-point calculation at the MP2/6-31G* level on the HF/6-31G* optimized geometry.

Results and Discussion

The Process of Dimerization. Our primary concern is how the dimerization of $\text{H}_2\text{Si}=\text{O}$ proceeds and whether there is a significant barrier or not. For these purposes, we chose the parameter R which specifies the distance between the midpoints of two SiO bonds and defined this as the reaction coordinate. For the selected



values of R the energy was minimized with respect to all other geometrical parameters by using the 3-21G analytical energy gradients at the Hartree-Fock (HF) level.

Figure 1 shows the representative optimized geometries thus obtained along the reaction coordinate. As expected from the strongly polarized Si^+-O^- bond, at a large R the reaction path involves a "head-to-tail" coplanar-like approach of two $\text{H}_2\text{Si}=\text{O}$ molecules, $\text{O}^a=\text{Si}^a\text{H}_2 \cdots \text{O}^b=\text{Si}^b\text{H}_2$. As the distance R decreases, the first molecule $\text{H}_2\text{Si}^a=\text{O}^a$ begins to rotate around the Si^a atom on the Si^b-O^b axis so as to cause a favorable overlap between the π^* orbital of $\text{H}_2\text{Si}^a=\text{O}^a$ localized strongly around Si^a and one of the lone-pair orbitals of the second $\text{H}_2\text{Si}^b=\text{O}^b$ molecule (Figure 1a), resulting in the formation of a new Si^aO^b bond. With the further decrease of R , $\text{H}_2\text{Si}^a=\text{O}^a$ next rotates around the atom O^b in the vertical bisector plane of $\text{H}_2\text{Si}^b=\text{O}^b$ to develop a new bond between the atoms O^a (carrying negative charge) and Si^b (carrying positive charge) (Figures 1,b and c), which leads to the cyclic product (Figure 1d). Thus, the dimerization involves the stepwise formation of two new bonds.

The changes in the potential energy along the reaction path are shown in Figure 2 as a function of R . Upon going from two $\text{H}_2\text{Si}=\text{O}$ monomers to the dimeric product, the energy decreases monotonously,⁹ there being no appreciable barrier to dimerization. To confirm this, we have carried out the larger 6-31G* basis set calculation at the 3-21G optimized geometries. As Figure 2 shows, the improvement of the basis set provides a more smooth energy decreasing, and again it indicates that the dimerization proceeds without a barrier.¹⁰ At this point, it is of interest to note that

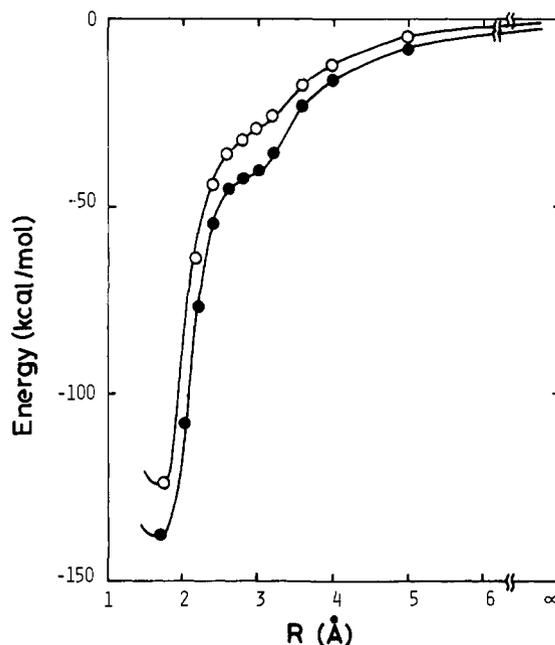
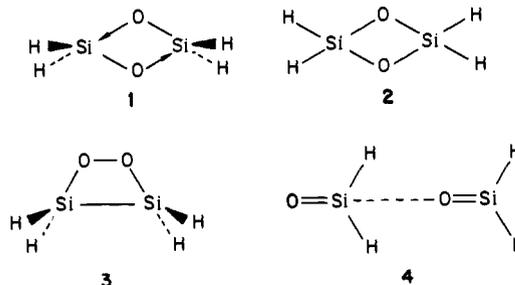


Figure 2. Potential energy curves for the dimerization of $\text{H}_2\text{Si}=\text{O}$ along the reaction path as a function of R , obtained at the HF/3-21G (●) and HF/6-31G**/3-21G (○) levels.

the reaction of two silicon monoxides to form the cyclic dimer ($\text{SiO})_2$ has recently been calculated to proceed with no barrier.¹¹ This suggests that the two hydrogen atoms in $\text{H}_2\text{Si}=\text{O}$ have no significant effect on the barrier to dimerization.

For comparison with the carbon analogue, we have calculated the reaction of two $\text{H}_2\text{C}=\text{O}$ molecules to form the cyclic dimer ($\text{H}_2\text{CO})_2$ but found that it involves a high energy barrier due to orbital crossing at $R \approx 2.0$ Å. The dimerization is formally a $2s + 2s$ forbidden reaction in terms of the Woodward-Hoffmann rule,¹² though symmetry allowed. It is to be noted that the much more polarized frontier orbitals π (strongly localized around O) and π^* (strongly localized around Si) of $\text{H}_2\text{Si}=\text{O}$ can relieve the symmetry restriction in the "head-to-tail" dimerization via a non-least-motion path shown in Figure 1.

Although we already found that the dimerization of $\text{H}_2\text{Si}=\text{O}$ proceeds with no barrier to yield the D_{2h} cyclic product, other structural alternatives were explored at the HF/3-21G level to answer the following questions: (i) are the SiO distances equal, (ii) what are the preferred orientations of the SiH_2 groups, (iii) is a "head-to-head" interaction between two SiO units possible, and (iv) is there a linear complex?



To answer question i, a C_{2h} structure **1** was adopted as a starting geometry. However, the geometrical optimization resulted in giving the more symmetrical D_{2h} structure (shown in Figure 1d)

(9) One sees that the HF/3-21G energy curve changes somewhat irregularly at the distances of $R = 2.8$ – 3.2 Å. In fact, in the region we managed to locate a complex and a transition state whose structure were very similar to each other, at the HF/STO-3G level. The transition state was calculated to be only 0.3 kcal/mol as unstable as the complex. However, the complex and transition state are found to be quite artificial for the use of the minimal basis set and disappear at the HF/3-21G as well as HF/6-31G* levels.

(10) The choice of the midpoint-to-midpoint distance (R) as the reaction coordinate clearly establishes the lack of a barrier in the dimerization. Since, however, the choice is somewhat arbitrary, there may be other purely downhill paths, and the interpretation of Figure 1 may be just one possible picture.

(11) Snyder, L. C.; Raghavachari, K. *J. Chem. Phys.* **1984**, *80*, 5076.

(12) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1969.

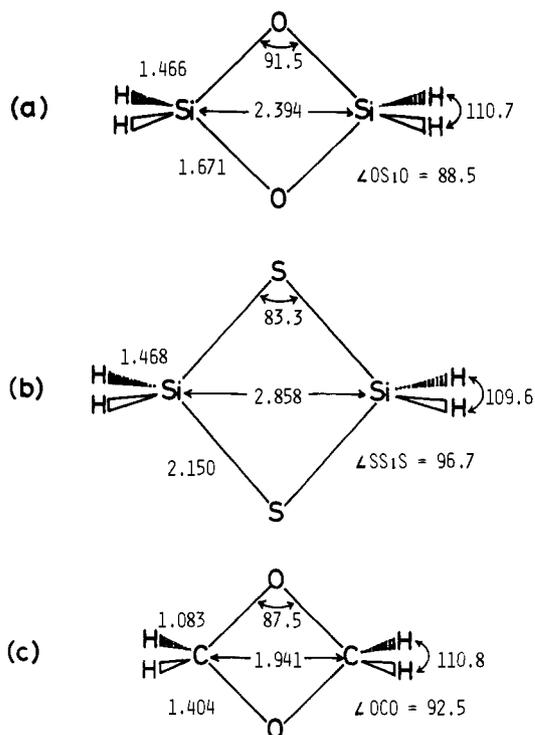


Figure 3. HF/6-31G* optimized structures of the cyclic dimers $(H_2SiO)_2$, $(H_2SiS)_2$, and $(H_2CO)_2$ in angstroms and degrees.

with all SiO distances equal. The same was true for the geometrical optimization at the HF/6-31G* level. To answer question ii, we have optimized an all-planar D_{2h} structure **2** and found it to be a stationary point. However, the force constant matrix for the stationary point gave rise to two negative eigenvalues. That is, **2** was a maximum with respect to the conrotatory and disrotatory motions of two SiH_2 groups, leading to the perpendicular arrangement shown in Figure 1d. As expected from the fact that **2** has eight π electrons (antiaromaticity), it was calculated to be 119.0 kcal/mol more unstable than the structure in Figure 1d. As for question iii, we have undertaken a C_{2v} "head-to-head" structure **3**. As characterized by all positive eigenvalues, the structure was indeed a minimum with the distances of O-O = 1.489 Å, Si-Si = 2.351 Å, and Si-O = 1.752 Å. However, it was found to be 127.2 (141.2 kcal/mol at the HF/6-31G**/3-21G level) kcal/mol more unstable than the structure in Figure 1d. In addition, **3** lies 16.9 kcal/mol above two separated $H_2Si=O$ molecules at the HF/6-31G**/3-21G level. This suggests that the "head-to-head" dimerization must undergo a considerable barrier. Finally, in order to answer question iv as well as check if there is a true coplanar approach at the early stage of the "head-to-tail" dimerization, we have examined a C_{2v} structure **4**. By imposing C_{2v} symmetry, we found a stationary point at an intermolecular SiO distance of 3.1 Å, which was 7.1 kcal/mol more stable than two separated $H_2Si=O$ molecules. However, the force constant matrix revealed that the stationary point was a maximum which led to a non-coplanar structure shown in Figure 1a. This indicates that the "head-to-tail" dimerization involves a "coplanar-like" approach at the early stage but never takes an "exact" coplanar conformation.

Structures and Bonding The structure of the dimeric product $(H_2SiO)_2$ optimized at the HF/6-31G* level is shown in Figure 3. For comparison, the HF/6-31G* optimized structures of the cyclic dimers $(H_2SiS)_2$ and $(H_2CO)_2$ are also included in this figure. In the equilibrium structure of the dimer $(H_2SiO)_2$, the Si and O atoms alternate to make a planar four-membered ring with D_{2h} symmetry. It is not surprising that the Si-O bond length of 1.671 Å is comparable to the normal Si-O single bond length of 1.647 Å in silanol. However, the Si-O-Si and O-Si-O bond angles in the dimer are calculated to be highly strained to 91.5 and 88.5°, respectively, compared with the siloxane bond angle

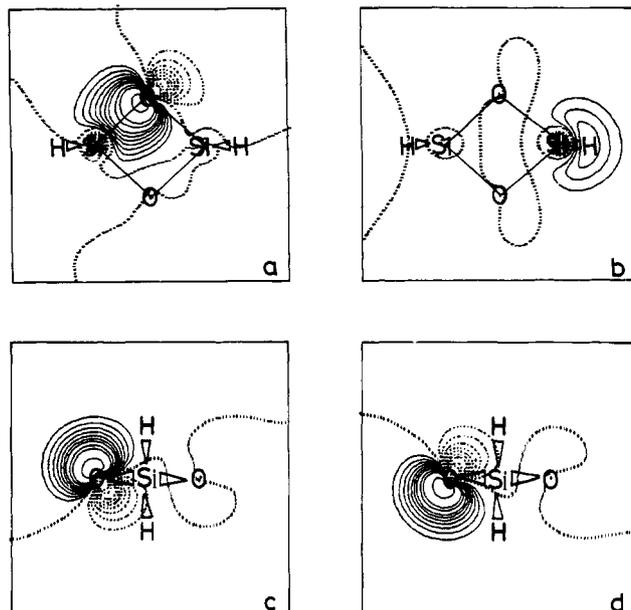


Figure 4. Contour plots of the localized molecular orbitals for the SiO bond (a), SiH bond (b), and lone-pair orbitals (c and d) in $(H_2SiO)_2$ obtained by the HF/3-21G Foster-Boys method.

of 143–149°¹³ in $H_3SiOSiH_3$ and the O-Si-O angle of 112.5°² in $HOSiH_2OH$. More interesting is the Si-Si distance¹⁴ of 2.394 Å in the cyclic dimer that is only 0.041 Å longer than the Si-Si single bond length of 2.353 Å in disilane. The unusually short Si-Si distance seems to be characteristic of silicon compounds, as is apparent from the fact that the C-C distance in the cyclic dimer $(H_2CO)_2$ is calculated to be 0.414 Å longer at the HF/6-31G* level, as shown in Figure 3c, than the C-C single bond length in ethane.

Very recently a stable cyclodisiloxane, tetramesitylcyclodisiloxane $[(Mes_2SiO)_2]$, has been produced from the reaction of tetramesityldisilene with atmospheric oxygen, and its structure has been determined by X-ray diffraction.⁵ The four-membered ring in the X-ray crystal structure is not exactly planar but with a small dihedral angle of $\angle O-Si-Si-O = 6^\circ$. In addition, the SiO distances are not all equal in the crystal structure; two of them are 1.66 Å (very close to our calculated value of 1.671 Å in $(H_2SiO)_2$), but the remaining two distances slightly lengthen to 1.72 Å most probably due to the bulky substituents. Interestingly, the Si-Si distance of 2.31 Å in $(Mes_2SiO)_2$ is further shorter by 0.084 Å than that in $(H_2SiO)_2$, and it is 0.159 Å shorter than the HF/6-31G* value of 2.469 Å¹¹ in the cyclic dimer $(SiO)_2$. This may suggest that substituents on silicon atoms are in part responsible for shortening of the Si-Si distance in the cyclic dimer.¹⁵ Accompanied by the shortening of the Si-Si distance, the O-O distance increases: 2.289 Å for $(SiO)_2$, 2.333 Å for $(H_2SiO)_2$, and 2.47 Å for $(Mes_2SiO)_2$. The increase in the O-O distance may be ascribed to the steric repulsion between the lone-pair orbitals on the oxygen atoms and the substituents on the silicon

(13) For the experimental values of 144.1 and 149°, see: Almendingen, A.; Bastian, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chim. Scand.* **1963**, *17*, 2455. Durig, J. R.; Flanigan, M. J.; Kalasinsky, V. F. *J. Chem. Phys.* **1977**, *66*, 2775. For the calculated value of 143.3°, see: Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7241.

(14) To see the effect of the d-type polarization functions on the Si-Si distance, the structure of $(H_2SiO)_2$ was also optimized by omitting either d(Si) or d(O) functions. The omissions of d(Si) and d(O) functions lengthened the Si-Si distance to 2.470 and 2.440 Å, respectively. This indicates that d(Si) and d(O) functions are equally important.

(15) For instance, the Si-Si distance in $(F_2SiO)_2$ was calculated to be 0.053 Å shorter than that in $(H_2SiO)_2$, accompanied by the Si-O distance shortening of 0.026 Å. On the other hand, the Si-Si distance in $(Me_2SiO)_2$ was calculated to be very slightly longer than that in $(H_2SiO)_2$. It seems that the stronger is the charge separation (or ionic character) in the Si⁺-O⁻ bonds, the shorter is the Si-Si distance. The charge separation strengthens the SiO bond but also may reduce the short-range exchange repulsion between the Si atoms because of the decrease in the electron clouds around the Si atoms.

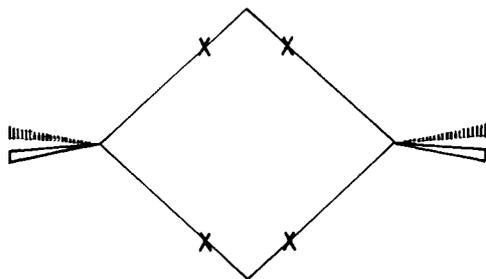
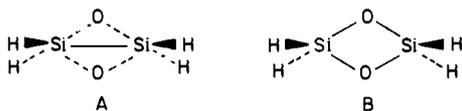


Figure 5. Centroids of the charge distributions of four SiO bond orbitals in $(\text{H}_2\text{SiO})_2$.

atoms. As a result, the cyclic dimer $(\text{Me}_2\text{SiO})_2$ becomes a rhombus where the Si-Si distance is rather shorter than the O-O distance, while the dimers $(\text{SiO})_2$ and $(\text{H}_2\text{SiO})_2$ have a rhomboid structure which is distorted in the opposite sense.

For the nature of bonding in the cyclic siloxane ring, one may consider two models A and B.⁵ In model A there are localized



two-electron bond between the silicon atoms, leading to the short Si-Si distance, and a delocalized four-center six-electron bond about the periphery of the ring. Probably the most convenient procedure for seeing this possibility is the use of localized molecular orbitals since they provide the conventional picture of chemical bonding. The localized orbitals of $(\text{H}_2\text{SiO})_2$ obtained by the Foster-Boys method¹⁶ are shown in Figure 4. There are four equivalent SiH bonds and two equivalent lone-pair orbitals on each oxygen. The lone-pair orbitals are spatially directed above and below the planar ring, respectively, to make an angle of ca. 120° with the ring. Noteworthy is a localized orbital description of bonding in the siloxane ring. Quite unlike model A, no appreciable localized bond orbital is seen between the silicon atoms¹⁷ and the ring is described as the arrangement of four equivalent localized SiO bonds. The centroids of the charge distributions of the localized SiO bond orbitals are shown in Figure 5. Each position of the centroids is much closer to O than to Si, reflecting the strong ionic character in the SiO bonds, but it is almost on the Si-O axis, indicating that there is no appreciable bent character in the SiO bonds. This finding is interesting since the formation of bent bonds has usually been seen in highly strained compounds.¹⁸

We now turn to model B. In this model it is suggested⁵ that severe lone pair-lone pair repulsions between the oxygen atoms are responsible for the short Si-Si distance. If this would be true, one should observe an unusual C-C distance even in $(\text{H}_2\text{CO})_2$. As already pointed out, this is not the case. Although the importance of O-O repulsion cannot be ruled out, we do suggest¹⁹ that the short Si-Si distance in cyclodisiloxane is the result of very strong attraction between the silicon and oxygen atoms. To demonstrate this, we have calculated the dimeric structure for silanethione $(\text{H}_2\text{Si}=\text{S})$ ²⁰ because SiS bonds are less polarized and

(16) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300.

(17) The Mulliken overlap populations between the silicon atoms were calculated to be -0.12 (HF/3-21G) and -0.002 (HF/6-31G*), indicating an antibonding interaction. Since it is well-known that the Mulliken population analysis works much better with minimal basis sets, we calculated the overlap population at the HF/STO-3G level, but again obtained the negative value of -0.11 .

(18) For instance, see: Newton, M. D. In "Modern Theoretical Chemistry"; see Schaefer, H. F. Ed.; Plenum: New York, 1977; Vol. 4, pp 223-268.

(19) If the O-O repulsion would be severe in cyclodisiloxane, one should see a significant increase and decrease in the Si-O-Si angle and Si-O distance, respectively, on going from $(\text{H}_2\text{SiO})_2$ to disilene oxide $\text{H}_2\text{SiSiH}_2\text{O}$ because of the complete absence of the O-O repulsion. However, the angle (81.2°) and distance (1.687 \AA) in the three-membered ring of disilene oxide were calculated to be 10.3° smaller and 0.016 \AA longer, respectively, than those in the four-membered ring of $(\text{H}_2\text{SiO})_2$ at the HF/6-31G* level.

Table I. HF/3-21G Vibrational Frequencies (cm^{-1}) and Zero-Point Energies (kcal/mol) for the Cyclic Dimers

| modes and symmetry ^a | dimers | | |
|---------------------------------|----------------------------|----------------------------|---------------------------|
| | $(\text{H}_2\text{SiO})_2$ | $(\text{H}_2\text{SiS})_2$ | $(\text{H}_2\text{CO})_2$ |
| $\nu_1(\text{b}_{3u})$ | 253 | 109 | 234 |
| $\nu_2(\text{a}_g)$ | 608 | 465 | 1154 |
| $\nu_3(\text{a}_u)$ | 635 | 650 | 1201 |
| $\nu_4(\text{b}_{1g})$ | 649 | 622 | 1164 |
| $\nu_5(\text{b}_{2g})$ | 713 | 566 | 1182 |
| $\nu_6(\text{b}_{3g})$ | 730 | 391 | 1030 |
| $\nu_7(\text{b}_{2u})$ | 749 | 433 | 935 |
| $\nu_8(\text{b}_{3u})$ | 820 | 579 | 1240 |
| $\nu_9(\text{a}_g)$ | 925 | 315 | 946 |
| $\nu_{10}(\text{b}_{1u})$ | 941 | 443 | 1098 |
| $\nu_{11}(\text{b}_{3g})$ | 947 | 768 | 1425 |
| $\nu_{12}(\text{b}_{2u})$ | 1052 | 898 | 1539 |
| $\nu_{13}(\text{b}_{1u})$ | 1074 | 996 | 1711 |
| $\nu_{14}(\text{a}_g)$ | 1118 | 1018 | 1752 |
| $\nu_{15}(\text{b}_{2g})$ | 2365 | 2376 | 3344 |
| $\nu_{16}(\text{b}_{1u})$ | 2370 | 2360 | 3273 |
| $\nu_{17}(\text{b}_{3u})$ | 2370 | 2377 | 3353 |
| $\nu_{18}(\text{a}_g)$ | 2383 | 2364 | 3287 |
| zero point ^b | 29.6 | 25.3 | 42.7 |

^a See Figure 6. ^b Zero-point energies for the monomers are 12.1 ($\text{H}_2\text{Si}=\text{O}$), 11.1 ($\text{H}_2\text{Si}=\text{S}$), and 18.2 ($\text{H}_2\text{C}=\text{O}$) kcal/mol.

expected to be weaker than SiO bonds. As seen in Figure 3, the Si-Si distance of 2.858 \AA in cyclodisilthiane $(\text{H}_2\text{SiS})_2$ is 0.464 \AA longer than that in $(\text{H}_2\text{SiO})_2$. This results undoubtedly from the fact that sulfur has a much smaller affinity for silicon than does oxygen.²¹

In 1955 an electron diffraction structure was reported for tetramethylcyclodisilthiane $(\text{Me}_2\text{SiS})_2$.²² By using the assumed geometrical parameters for the methyl group parts, the distance of Si-S = $2.18 \pm 0.03 \text{ \AA}$ and bond angles of $\angle\text{SiSSi} = 75^\circ$ and $\angle\text{SSiS} = 105^\circ$ were determined in the electron diffraction study. The determined values for the bond angles differ significantly from our calculated values in $(\text{H}_2\text{SiS})_2$. In addition, the Si-Si distance in the electron diffraction structure seems too short compared to our calculated value in $(\text{H}_2\text{SiS})_2$. However, one should note that the Si-Si distance of 2.65 \AA ²³ in $(\text{Me}_2\text{SiS})_2$ is 0.34 \AA longer than that in $(\text{Me}_2\text{SiO})_2$.

In a very recent report²⁴ on the X-ray structure it is found that the four-membered ring in $(\text{Me}_2\text{SiS})_2$ is planar (D_{2h} symmetry) with the distance of Si-S = 2.152 \AA and bond angles of $\angle\text{SiSSi} = 82.5^\circ$ and $\angle\text{SSiS} = 97.5^\circ$. These are all very close to our calculated results (Si-S = 2.150 \AA , $\angle\text{SiSSi} = 83.3^\circ$, and $\angle\text{SSiS} = 96.7^\circ$) for $(\text{H}_2\text{SiS})_2$. Furthermore, the Si-Si distance of 2.837 \AA in the X-ray structure is in good agreement with our calculated value (2.858 \AA) in $(\text{H}_2\text{SiS})_2$ and 0.527 \AA longer than that in $(\text{Me}_2\text{SiO})_2$.

Vibrational Frequencies. Table I summarizes the HF/3-21G harmonic vibrational frequencies and zero-point energies for the cyclic dimers $(\text{H}_2\text{SiO})_2$, $(\text{H}_2\text{SiS})_2$, and $(\text{H}_2\text{CO})_2$. The vibrational modes are schematically shown in Figure 6. To our knowledge no experimental values are available for comparison, but one may refer to two ring deformation frequencies $439\text{--}443$ (b_{2u}) and $527\text{--}536$ (b_{3u}) cm^{-1} assigned recently for tetramethylcyclodisilthiane.²⁵ These assigned values may be compared with our

(20) For a theoretical study on $\text{H}_2\text{Si}=\text{S}$ in the ground and excited states, see: Kudo, T.; Nagase, S., manuscript in preparation.

(21) One may consider that the longer Si-Si distance in $(\text{H}_2\text{SiS})_2$ is due to the smaller S-S repulsion. However, Figure 3 reveals that the Si-S-Si angle of 83.3° in $(\text{H}_2\text{SiS})_2$ is significantly smaller than the Si-O-Si angle of 91.5° in $(\text{H}_2\text{SiO})_2$. It should be emphasized that the exchange repulsion between the less positive Si atoms in $(\text{H}_2\text{SiS})_2$ is more severe than that between the much more positive Si atoms in $(\text{H}_2\text{SiO})_2$.

(22) Yokoki, M.; Nomura, T.; Yamasaki, K. *J. Am. Chem. Soc.* **1955**, *77*, 4484. Yokoki, M. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 100.

(23) Note that the authors of ref 5 misvaluated the Si-Si distance to be 2.34 \AA when they cited ref 22 and considered that there also was an unusual Si-Si distance in $(\text{Me}_2\text{SiS})_2$; this is a misunderstanding.

(24) Schklower, W. E.; Strutschkow, Yu. T.; Gusel'nikov, L. E.; Wolkowa, W. W.; Awakyan, W. G. *Z. Anorg. Allg. Chem.* **1983**, *501*, 153.

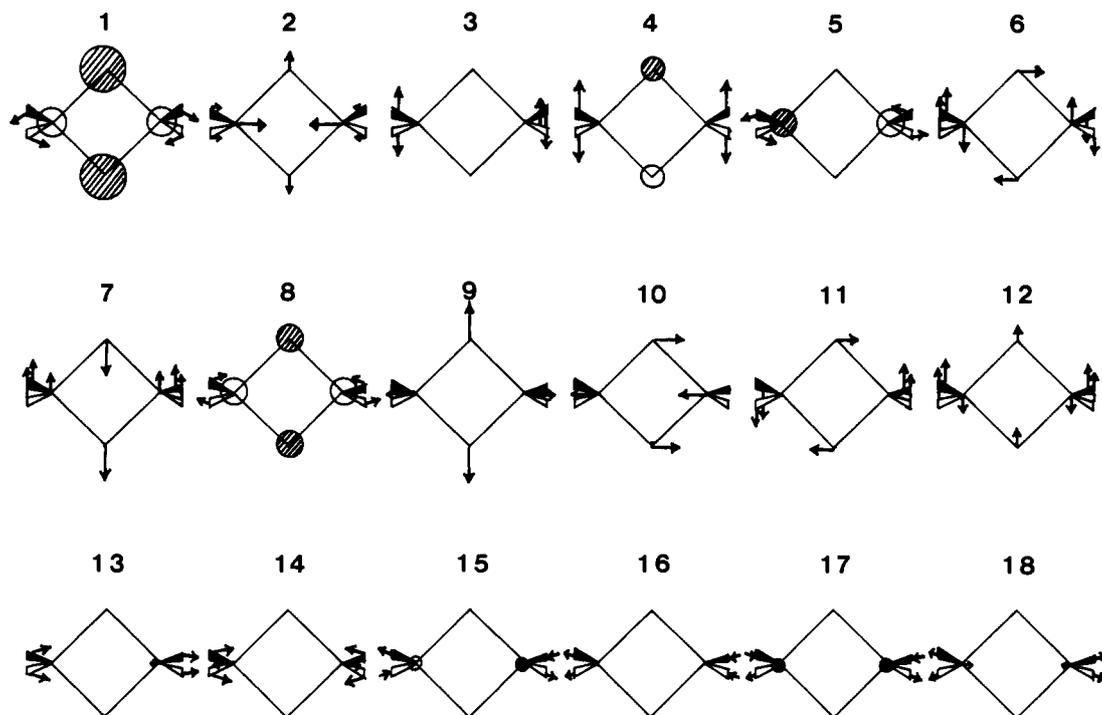


Figure 6. Schematic description of the vibrational modes for cyclic dimers.

Table II. Total Energies (hartrees) Calculated at Several Levels of Theory

| species | HF/3-21G//3-21G | HF/6-31G*//3-21G | HF/6-31G*//6-31G* | MP2/6-31G*//6-31G* |
|--------------|-----------------|------------------|-------------------|--------------------|
| $H_2Si=O$ | -362.955 90 | -364.909 95 | -364.914 40 | -365.180 94 |
| $H_2Si=S$ | -684.105 14 | -687.583 46 | -687.587 29 | -687.783 46 |
| $H_2C=O$ | -113.221 83 | -113.865 29 | -113.866 33 | -114.165 25 |
| $(H_2SiO)_2$ | -726.131 71 | -730.017 89 | -730.026 82 | -730.536 22 |
| $(H_2SiS)_2$ | -1368.305 26 | -1375.269 98 | -1375.288 79 | -1375.679 76 |
| $(H_2CO)_2$ | -226.453 74 | -227.721 50 | -227.731 11 | -228.330 88 |
| $(H_2SiO)_3$ | -1089.326 87 | -1095.114 81 | | |
| $(H_2SiO)_4$ | -1452.475 24 | | | |

calculated values of 433 (b_{2u}) and 579 (b_{3u}) cm^{-1} for $(H_2SiS)_2$.

In Table I, the following points are noteworthy. First, the vibrational frequencies of the silicon-containing dimers $(H_2SiO)_2$ and $(H_2SiS)_2$ are generally much lower than those of $(H_2CO)_2$. When comparison is made between $(H_2SiO)_2$ and $(H_2SiS)_2$, ring deformation frequencies are higher in the former than in the latter, as is obvious from the comparison of the frequencies $\nu_5-\nu_{11}$. This suggests that the Si_2O_2 ring is rigid compared with the Si_2S_2 ring. In contrast, $(H_2SiO)_2$ and $(H_2SiS)_2$ have similar values for the frequencies associate with the SiH_2 part. Second, in all the dimers the lowest frequency corresponds to out-of-plane distortion and the values are calculated to be as small as 253 cm^{-1} for $(H_2SiO)_2$, 109 cm^{-1} for $(H_2SiS)_2$, and 234 cm^{-1} for $(H_2CO)_2$. This reveals that the planarity of the cyclic rings is loose. Third, the Si-Si stretching frequency ($\nu_2 = 608 cm^{-1}$) of $(H_2SiO)_2$ is higher than that ($\nu_2 = 465 cm^{-1}$) of $(H_2SiS)_2$, and it is comparable to the Si=Si stretching frequency (621 cm^{-1}) of a planar disilene ($H_2Si=SiH_2$).

Dimerization Energies. The total energies of the monomers and dimers were calculated at several levels of theory. These results are given in Table II. The calculated dimerization energies are listed in Table III where entries are ordered according to the increasing quality of computation. The values with zero-point correction (ZPC) are also given in this table. The dimerization energy for $(H_2SiO)_2$ is relatively sensitive to the level of theory employed, and it is overestimated by the smaller basis set probably due to the basis set superposition error. However, at all levels

Table III. Dimerization Energies (kcal/mol)^a

| level of theory | dimers | | |
|--------------------------------------|--------------|--------------|-------------|
| | $(H_2SiO)_2$ | $(H_2SiS)_2$ | $(H_2CO)_2$ |
| HF/3-21G//3-21G | -138.0 | -59.6 | -6.3 |
| HF/6-31G*//3-21G | -124.2 | -64.7 | 5.7 |
| HF/6-31G*//6-31G* | -124.3 | -71.7 | 1.0 |
| MP2/6-31G*//6-31G* | -109.4 | -70.8 | -0.2 |
| + zero-point correction ^b | -104.0 | -67.7 | 6.1 |

^aNegative (positive) values indicated stabilization (destabilization) relative to two separated monomers. ^bZero-point energies in Table I are used for correction.

of theory there is a remarkable and general trend: the dimerization energies increase dramatically in the order $(H_2CO)_2 < (H_2SiS)_2 < (H_2SiO)_2$, as expected from electrostatic²⁶ and frontier orbital²⁷ interactions.²⁸

At the MP2/6-31G*//6-31G* level²⁹ the dimerization of $H_2Si=O$ is calculated to be 109.4 (104.0 after ZPC) kcal/mol exothermic and that of $H_2Si=S$ is 70.8 (67.7 after ZPC) kcal/mol

(26) The HF/6-31G* dipole moments are 2.67 ($H_2C=O$), 3.70 ($H_2Si=O$), and 4.13 ($H_2Si=S$) D.

(27) At the HF/6-31G* level the frontier orbital π levels are -14.7 ($H_2C=O$), -10.3 ($H_2Si=S$), and -12.3 ($H_2Si=O$) eV while the π^* levels are 4.0, 0.5, and 1.5 eV, respectively.

(28) According to the energy component analysis based on the method by Morokuma (Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294), for instance, in $(H_2SiO)_2$ the attractive term consists of 38% electrostatic, 30% polarization, and 32% charge-transfer interactions at the HF/6-31G* level.

(29) We may need calculations at the more sophisticated levels of theory. However, it is instructive to note that in the dimerization of SiO the exothermicity of 43.3 kcal/mol calculated at the MP2/6-31G*//6-31G* level differs little from that of 43.7 kcal/mol at the MP4/6-31G+2d//6-31G* level.¹¹

(25) Gusel'nikov, L. E.; Volkova, V. V.; Avakyan, V. G.; Nametkin, N. S.; Voronkov, M. G.; Kirpichenko, S. V.; Suslova, E. N. *J. Organomet. Chem.* **1983**, *254*, 173. See also: Krigsmann, H.; Clauss, H. *Z. Anorg. Allg. Chem.* **1959**, *20*, 210.

Table IV. Enthalpy (ΔH) and Entropy (ΔS) Changes for Dimerization

| | dimers | | |
|-------------------------------------------------|-----------------------------------|-----------------------------------|----------------------------------|
| | (H ₂ SiO) ₂ | (H ₂ SiS) ₂ | (H ₂ CO) ₂ |
| ΔH°_{298} (kcal/mol) | -105.7 | -68.5 | 4.2 |
| ΔS°_{298} (cal/mol·K) ^a | -45.6 | -42.7 | -43.4 |
| $\Delta S^\circ_{\text{trans}}$ | -35.3 | -36.2 | -34.1 |
| $\Delta S^\circ_{\text{rot}}$ | -13.6 | -14.6 | -11.7 |
| $\Delta S^\circ_{\text{vib}}$ | 3.3 | 8.1 | 2.4 |

$$^a \Delta S^\circ_{298} = \Delta S^\circ_{\text{trans}} + \Delta S^\circ_{\text{rot}} + \Delta S^\circ_{\text{vib}}$$

exothermic. These high exothermicities result from the greater strength of four single bonds than two double bonds, indicating that silicon is reluctant to form double bonding. The much smaller exothermicity in the H₂Si=S dimerization is the result of the cleavage of stronger SiS π bonds (compared with SiO π bonds)²⁰ as well as the formation of weaker SiS single bonds (compared with SiO single bonds). In contrast, the dimerization of H₂C=O is calculated to be rather endothermic by -0.2 (6.1 after ZPC) kcal/mol, because of the greater advantage in strength of the CO double over single bonds.

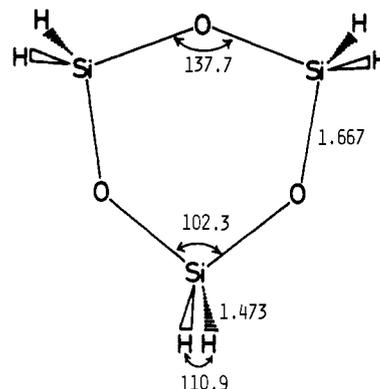
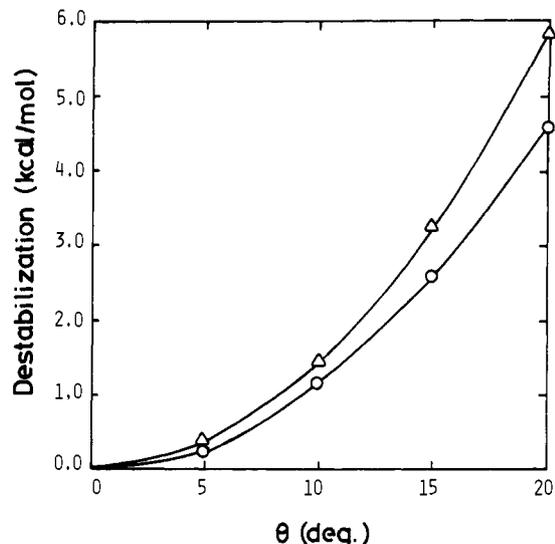
The dimerization energies are likely to be observed in the near future. In an attempt to predict theoretically the values, we have evaluated the thermodynamic quantities such as enthalpies (H), entropies (S), and Gibbs free energies (G) by using the HF/6-31G* geometries, MP2/6-31G*//6-31G* relative energies, and HF/3-21G vibrational frequencies. On the basis of the statistical treatment,³⁰ the molecular partition functions for translational, rotational, and vibrational motions (assumed to be separated) were calculated within the ideal gas, rigid rotor, and harmonic oscillator approximations. The enthalpy (ΔH°) and entropy (ΔS°) changes thus obtained at a standard state (pressure = 1 atm and temperature = 298 K) are given in Table IV where ΔS° is decomposed into translational ($\Delta S^\circ_{\text{trans}}$), rotational ($\Delta S^\circ_{\text{rot}}$), and vibrational ($\Delta S^\circ_{\text{vib}}$) entropies.

It is interesting to note that the enthalpic stabilization and destabilization (ΔH°) for dimerization are close to the zero-point corrected potential energy values given in Table III. This means that the effect of excited vibrational states (accounted for in ΔH°) is rather minor, while zero-point correction is significant. Upon incorporation of two separated monomers into the dimer, the entropy (S°) decreases due to the loss of the translational (S°_{trans}) and rotational (S°_{rot}) entropies. However, the degree of the entropy decrease is essentially the same for all dimerizations, because of the structural resemblance. The silicon-containing dimers can compensate the entropy cost by a large enthalpic stabilization, but (H₂CO)₂ cannot repay it because of the enthalpic destabilization. Finally, the Gibbs free energy changes for the dimerizations are calculated to be

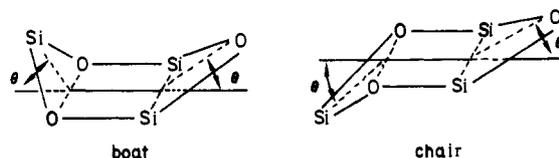


Polymerization. The formation of cyclic polymers is generally typical.³¹ We are now in a position to assess the structures and stability of the trimer (H₂SiO)₃ and the tetramer (H₂SiO)₄ with respect to those of the dimer (H₂SiO)₂. The calculated total energies of the trimer and tetramer are given in Table II. Because of the size of the molecules, our discussion is meant to be qualitative and interpretive rather than quantitative.

Figure 7 shows the HF/3-21G optimized structure of the cyclic trimer (H₂SiO)₃. The optimized structure has D_{3h} symmetry with alternate silicon and oxygen atoms arranged in a planar six-membered ring. The planarity of the Si₃O₃ ring has also been observed in the electron diffraction study of hexamethylcyclo-

**Figure 7.** HF/3-21G optimized structure of the (H₂SiO)₃ trimer in angstroms and degrees.**Figure 8.** Destabilization energies due to the boat (O) and chair (Δ) distortions as a function of θ .

trisiloxane (Me₂SiO)₃.³² However, there also is a report³³ which claims that the Si₃O₃ ring deviates from planarity in the X-ray crystal structure. In order to see the degree of planarity of the ring, distortions to "boat" and "chair" forms were examined.



In both distortions, Si and O atoms on the stern and prow were displaced with the angles of θ from the planar base of the remaining heavy atoms in the same direction for the boat and in the opposite direction for the chair. As Figure 8 shows, the "boat" and "chair" distortions undergo increasing destabilization. The increase in destabilization is smaller in the boat form than in the chair form at all the values of θ . This is ascribed to the more favorable electrostatic attraction between the stern and prow in the boat form. Even at the angle of $\theta = 10^\circ$ the destabilization due to the "boat" distortion is as small as 1.2 kcal/mol. Inclusion of d-type polarization functions on the Si and O atoms (i.e., HF/6-31G*//3-21G calculation) reduces the destabilization to 0.8 kcal/mol. This suggests that the ring is considerably flexible.

The Si-O-Si and O-Si-O angles of 137.7° and 102.3° in the trimer (H₂SiO)₃ are much larger (i.e., less constrained), respec-

(30) Herzberg, G. "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand: New York, 1945; pp 501-530.

(31) For instance, see: ref 1 and Barton (Barton, T. J. *Pure Appl. Chem.* **1980**, 52, 615).

(32) Aggarwal, E. H.; Bauer, S. H. *J. Chem. Phys.* **1950**, 18, 42. Peyronel, G. *Chim. Ind.* **1954**, 36, 441. See also: Peyronel, G. *Atti. Accad. Naz. Lincei., Cl. Sci. Fis., Mat. Nat. Rend.* **1954**, 16, 231.

(33) Hernandez, R. P. *Acta Crystallogr. Sect. A* **1978**, S406.

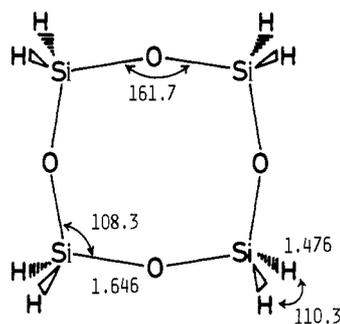


Figure 9. HF/3-21G optimized structure of the $(\text{H}_2\text{SiO})_4$ tetramer in angstroms and degrees, obtained by imposing D_{4h} symmetry.

Table V. Comparison in the Net Atomic Charges and Frontier Orbital Energies of $\text{H}_2\text{Si}=\text{O}$ and $(\text{H}_2\text{SiO})_n$ ($n = 2-4$) at the HF/3-21G Level

| species | atomic charge | | energy level (eV) | |
|--------------------------------|---------------|-------|-------------------|------|
| | Si | O | HOMO | LUMO |
| $\text{H}_2\text{Si}=\text{O}$ | 1.12 | -0.70 | -11.6 | 1.5 |
| $(\text{H}_2\text{SiO})_2$ | 1.46 | -0.97 | -11.9 | 3.2 |
| $(\text{H}_2\text{SiO})_3$ | 1.61 | -1.06 | -11.6 | 4.7 |
| $(\text{H}_2\text{SiO})_4$ | 1.66 | -1.10 | -11.4 | 5.0 |

tively, than those in the dimer $(\text{H}_2\text{SiO})_2$. Reflecting this, the disproportion energies for $3(\text{H}_2\text{SiO})_2 \rightarrow 2(\text{H}_2\text{SiO})_3$ are calculated to be -162.3 kcal/mol at the HF/3-21G level and -110.4 kcal/mol at the HF/6-31G**/3-21G level. These large negative values clearly favor the trimer over the dimer.³⁴ Furthermore, the insertion of $\text{H}_2\text{Si}=\text{O}$ into the SiO bond of $(\text{H}_2\text{SiO})_2$, $(\text{H}_2\text{SiO})_2 + \text{H}_2\text{Si}=\text{O} \rightarrow (\text{H}_2\text{SiO})_3$, is calculated to be 150.1 (HF/3-21G) and 117.3 (HF/6-31G**/3-21G) kcal/mol exothermic. These high exothermicities suggest that the ring expansion proceeds rapidly with no significant barrier.³⁵

Figure 9 shows the HF/3-21G optimized structure of the tetramer $(\text{H}_2\text{SiO})_4$ obtained by imposing D_{4h} symmetry.³⁶ The energy released upon going from $4(\text{H}_2\text{SiO})_3$ to $3(\text{H}_2\text{SiO})_4$ is calculated to be 74.2 kcal/mol. At the HF/3-21G level this energy is 88.1 kcal/mol smaller than that from $3(\text{H}_2\text{SiO})_2$ to $2(\text{H}_2\text{SiO})_3$, suggesting that the formation of the tetramer is less favorable than

(34) In contrast, the disproportion energy for $3(\text{H}_2\text{SiS})_2 \rightarrow 2(\text{H}_3\text{SiS})_3$ is calculated to be much less negative (-30.3 kcal/mol). The details will be discussed elsewhere.

(35) In fact, our preliminary calculations at the HF/STO-2G level show that the ring expansion proceeds with no appreciable barrier via a path similar to that shown in Figure 1.

(36) For a puckered Si_4O_4 ring in cyclotetrasiloxanes, see: Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr., Sect. B* 1979, B35, 522 and references cited therein. Since the Si_4O_4 ring is supposed to be unusually flat, we did not carry out the optimization of the puckered structure for the present purpose.

the formation of the trimer. However, the tetramerization is likely to occur readily, as expected from the fact that the reactions $(\text{H}_2\text{SiO})_3 + \text{H}_2\text{Si}=\text{O} \rightarrow (\text{H}_2\text{SiO})_4$ and $(\text{H}_2\text{SiO})_2 + (\text{H}_2\text{SiO})_2 \rightarrow (\text{H}_2\text{SiO})_4$ are calculated to be 120.8 and 132.9 kcal/mol exothermic, respectively, at the HF/3-21G level. To the extent that the difference in the exothermicity is meaningful, the tetramer may be produced more favorably by the reaction of two dimers than by the insertion of $\text{H}_2\text{Si}=\text{O}$ into the SiO bond of the trimer.³⁷

Finally, it may be interesting to mention the net atomic charges and frontier orbital energies of $\text{H}_2\text{Si}=\text{O}$ and $(\text{H}_2\text{SiO})_n$ ($n = 2-4$). As Table V shows, with increasing "n" the silicon and oxygen atoms in $(\text{H}_2\text{SiO})_n$ carry more positive and negative charges, respectively, than those in $\text{H}_2\text{Si}=\text{O}$. Accompanied by the increase in ionic character, the Si-O single bond distances in $(\text{H}_2\text{SiO})_n$ decrease in the order 1.717 ($n = 2$) $>$ 1.667 ($n = 3$) $>$ 1.646 ($n = 4$) Å. This may suggest that the strength of the Si-O single bond increases with the increase in "n", as far as bond energy-bond length relationships are valid. As shown in Table V, the HOMO energy levels of $\text{H}_2\text{Si}=\text{O}$ and $(\text{H}_2\text{SiO})_n$ are essentially the same. With increasing "n", however, the LUMO levels of $(\text{H}_2\text{SiO})_n$ become much higher than that of $\text{H}_2\text{Si}=\text{O}$. This indicates that $(\text{H}_2\text{SiO})_n$ becomes less reactive toward nucleophiles³⁸ with the increase in the size of the ring in terms of frontier orbital theory.

Concluding Remarks

The dimerization of $\text{H}_2\text{Si}=\text{O}$ proceeds with no barrier along a non-least-motion path to yield the cyclic "head-to-tail" dimer $(\text{H}_2\text{SiO})_2$ by forming stepwise two new bonds. The equilibrium structure of the dimeric product has D_{2h} symmetry with alternate silicon and oxygen atoms in a planar four-membered ring. The unusually short Si-Si distance in the ring is explained in terms of the strength of the SiO bonds and the less severe exchange repulsion between the Si atoms. The dimerization energy for $(\text{H}_2\text{SiO})_2$ is calculated to be much larger than those for the similar cyclic dimers $(\text{H}_2\text{SiS})_2$ and $(\text{H}_2\text{CO})_2$. Finally, it is found that trimerization and tetramerization are both more favorable than dimerization and very likely to proceed with no appreciable barrier.

Acknowledgment. We are grateful to Professor R. West for bringing the unusual structure of cyclodisiloxane to our attention and for making ref 5 available prior to publication. All calculations were carried out at the Computer Center of the Institute for Molecular Science with the IMPAK(WF10-8)³⁹ and GAUSSIAN80-(WF10-24)⁴⁰ programs in the IMS Computer Center library program package.

(37) For a related experiment, see: Tomadze, A. V.; Yablokova, N. V.; Yablokov, V. A.; Razuvaev, G. A. *J. Organomet. Chem.* 1981, 212, 43.

(38) For the high reactivity of $\text{H}_2\text{Si}=\text{O}$ toward nucleophiles, see ref 2.

(39) Coded by: Morokuma, K.; Kato, S.; Kitaura, K.; Ohmine, I.; Sakai, S.; Obara, S.

(40) An IMS version of the GAUSSIAN80 series of programs by: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* 1981, 13, 406.