

A molecular orbital study of rings in silicates and siloxanes

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Abstract

Ab initio STO-3G molecular orbital theory has been used to calculate energy-optimized geometries for cyclotrisiloxane and cyclotetrasiloxane. The resulting SiOSi angles are in close correspondence with experimental SiOSi angle frequency distributions for tetrahedral rings in silicates and siloxanes. Experimental correlations between SiO bond length and bridging SiOSi angle for rings in silicates and siloxanes are reproduced by the theory. The stable configurations of 4-membered tetrahedral rings are predicted to have the exact reverse sequence to that indicated by previous electrostatic potential energy calculations. The observed configurations of the tetrahedral sheets in gillespite and apophyllite conform with the calculated stable configurations of 4-membered rings with C_{nv} point symmetry. Ascribing the configuration of the silicate sheets to the constitution of the interlayer ions does not appear to be necessary. CNDO/2 calculations for D_{nh} and C_{nv} hydroxycyclosiloxane molecules were used to compare the relative stability of different size silicate rings. The 3-membered ring is indicated to be unstable relative to larger rings due to strained SiOSi angles $\sim 130^\circ$, consistent with its breakdown during a trimethylsilylation reaction. Its presence in silicate glasses and melts must also be infrequent. Larger rings assume nonplanar configurations to achieve minimum-energy SiOSi angles averaging 147° .

Introduction

In an attempt to account for the relative frequencies of n -membered tetrahedral rings in silicate minerals, Zoltai and Buerger (1960) undertook a calculation of the electrostatic energies of model ring structures (D_{nh} point symmetry) as a function of the number of tetrahedra in the ring. Each ring was constructed from a loop of alternating Si^{4+} and O^{2-} ions and from F^{1-} ions replacing the nonbridging oxide ions to achieve tetrahedral coordination of Si^{4+} and electrostatic neutrality of the final unit. Using Coulomb's law, the potential energy per $SiOF_2$ unit was calculated by summing the electro-

static interactions between the ions in the ring, assuming regular tetrahedra. By constraining the symmetry of each ring to be D_{nh} , the SiOSi angle is completely determined by the number of tetrahedra, n , in the ring (Fig. 1). Upon calculating the electrostatic energy as a function of n , they found that a 5-membered ring possessed the lowest energy. This led to the assertion that a silicate tetrahedral structure composed of 5-membered rings should be more stable than one composed, for example, of 4- or 6-membered rings. Nevertheless, an examination of the SiOSi angles calculated for the n -membered rings (Fig. 1) shows that the 5-

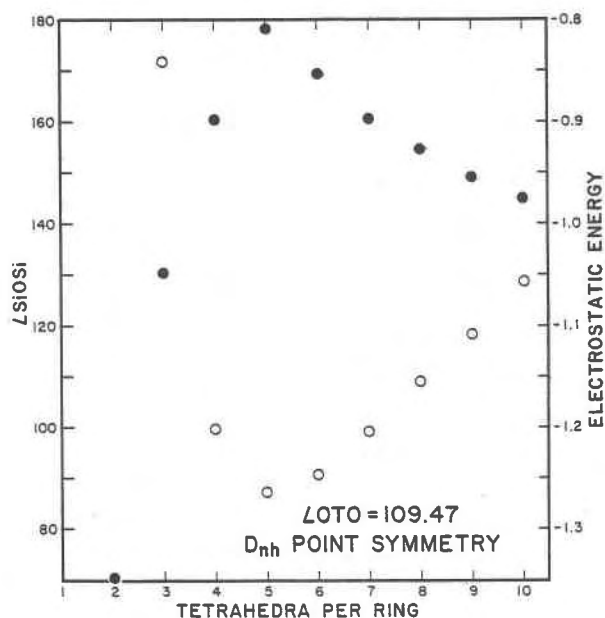


Fig 1. The SiOSi angle variation for different size D_{nh} symmetry rings (solid points using the left-hand scale) and the corresponding electrostatic energies per SiOF_2 unit (open points using the right-hand scale) (after Zoltai and Buerger, 1960). Note that the energy units were not reported. The minimum energy ring occurs for five tetrahedra with a SiOSi angle of 178.5° . For $n \leq 5$, $\text{SiOSi} = 250.53^\circ - 360^\circ/n$ and for $n > 5$, $\text{SiOSi} = 109.47^\circ + 360^\circ/n$.

membered ring possesses a SiOSi angle nearest 180° , where adjacent highly charged Si^{4+} cations comprising the angle are at maximum separation. In fact, each of the remaining rings is indicated to be destabilized relative to the 5-membered ring because of the closer contacts made in these rings between the Si^{4+} cations. Other silicate rings, departing from D_{nh} symmetry, were also examined by Zoltai and Buerger. When the rings were distorted within the constraints of C_{nv} point symmetry where all tetrahedral apices point up (or down), a 6-membered ring was found to possess the lowest energy. For even-membered rings having apices pointing alternatively up and down, again a six-membered ring was found to be most stable. For $4n$ -membered rings having alternating pairs of tetrahedra up and down, the most stable ring was found to have eight tetrahedra. Similarly for each of these distortions, the minimum energy ring was found to be the one in which the SiOSi angle is the widest and the separation between the highly charged Si^{4+} cations is maximal. For the rings having more than one of these distortions, the D_{nh} configuration where the Si^{4+} are at maximum separation was

always indicated to be the most stable whereas the one with C_{nv} configuration where the cations are in closer contact was indicated to be the least stable.

Inasmuch as the SiO bond possesses significant covalent character (Newton and Gibbs, 1980), we undertook a series of molecular orbital (MO) calculations for a variety of siloxane and silicate rings to explore their energetics and to determine whether the optimized geometries conform with those obtained by Zoltai and Buerger (1960). In addition, the optimized SiO bond lengths and SiOSi angles are compared with experimental values for cyclosiloxanes and silicates.

Molecular ring models and methods of calculation

Suitable molecular models to represent silicate tetrahedral rings should be neutral and small enough to make the calculations feasible, yet still retain the stereochemistry which is to be represented. Ring molecules with the compositions $(\text{SiO}_3)_n^{-2n}$, $n \geq 3$ are not suitable because of their unrealistic large negative charge. The compositions $[(\text{OH})_2\text{SiO}]_n$ are among the best conceivable models, however their large size greatly restricts the level of the MO method. Less suitable, but more tractable, are the compositions $(\text{F}_2\text{SiO})_n$ and $(\text{H}_2\text{SiO})_n$.

The molecules cyclotrisiloxane $(\text{H}_2\text{SiO})_3$ and cyclotetrasiloxane $(\text{H}_2\text{SiO})_4$ were chosen to represent 3- and 4-membered tetrahedral rings, respectively (Fig. 2). To our knowledge, only the tetramer has been isolated as a volatile gas-phase species (Campbell-Ferguson, 1965), the structure of which has been determined by electron diffraction methods (Glidewell *et al.*, 1970). The MO calculations for these two molecules were made by *ab initio* methods (Richards and Horsley, 1970) using the computer program GAUSSIAN 70 (Pople *et al.*, QCPE 11, 236, 1973), employing a minimal STO-3G basis set (Hehre *et al.*, 1969, 1970).

In choosing the most appropriate set of basis functions to do MO calculations for siloxanes and silicic acid molecules, considerable discussion has been devoted to the extent of involvement of Si d-orbitals in the SiO bond (Cruickshank, 1961; Baur, 1971; Collins *et al.*, 1972, 1976; Sauer and Zurawski, 1979; Meier and Ha, 1980; Newton and Gibbs, 1979, 1980). The consensus is that a STO-3G* basis which includes the d-type basis functions, reproduces accurate bond angles, energy barriers and dipole moments whereas the minimal STO-3G basis yields moderately accurate bond lengths (Newton and Gibbs, 1980). However, using available computer

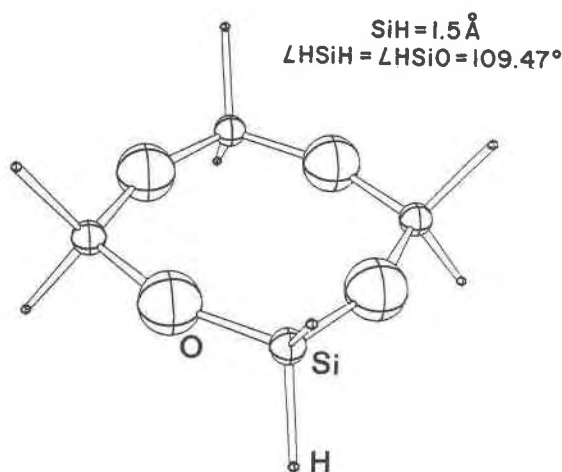


Fig. 2. Cyclotetrasiloxane molecule, $(\text{H}_2\text{SiO})_4$, D_{4h} configuration with $d(\text{SiH})$ fixed at 1.5 \AA and angles $\text{HSiH} = \text{HSiO} = 109.47^\circ$. The larger spheres represent oxygen, the smaller spheres represent hydrogen and the intermediate-sized spheres represent silicon. No particular physical significance is ascribed to these sphere sizes.

programs, the additional five d-orbitals on each Si in molecules of this size precludes *ab initio* calculations for $(\text{H}_2\text{SiO})_n$ rings larger than the trimer. To make the calculations tractable, the SiH distance was fixed at 1.5 \AA and the angles $\text{OSiH} = \text{HSiH}$ set equal to 109.47° .

Since the GAUSSIAN 70 computer program as currently dimensioned cannot accommodate the number of orbitals required for similar molecules with five or more tetrahedra, approximate molecular orbital calculations were made for larger rings. For these calculations, molecules of the composition $[(\text{OH})_2\text{SiO}]_n$, where $n = 3$ through 10, were used. The calculations were made with the CNDO/2 method (Pople and Beveridge, 1970) using the computer program CNINDO (Pople and Beveridge, 1970, p. 163–205). A minimum-valence *sp* basis was used for O and Si and an *s* basis was used for H. For the ensuing calculations the geometries were fixed: $d(\text{SiO}) = 1.62 \text{ \AA}$, $d(\text{OH}) = 1.0 \text{ \AA}$, $\text{OSiH} = 180^\circ$, $\text{OSiO} = 109.47^\circ$ (Fig. 3).

To obtain comparable energies for different-sized rings, the total energy calculated for each molecule was divided by n , the number of tetrahedra in the ring. Direct comparison of *ab initio* and CNDO/2 energies cannot be readily made inasmuch as only the valence electrons are used in the latter. Total energies are reported in atomic units (a.u.) often called the Hartree, which is defined as twice the

energy of the hydrogen atom, 2625.46 kJ/mole , 27.21 eV , or 627.50 kcal/mole .

Ab initio calculations for $(\text{H}_2\text{SiO})_3$ and $(\text{H}_2\text{SiO})_4$ cyclosiloxanes

The Si–O bond lengths, $d(\text{SiO})$, and the angles, SiOSi and OSiO , were optimized for the 3-membered ring in $(\text{H}_2\text{SiO})_3$ while maintaining D_{3h} point symmetry. Subsequently, the tetrahedra were kept rigid but allowed to tilt about their bridging oxygen edges while preserving C_{3v} symmetry. This tilting, for any size ring, can be described by γ , the angle between the HH vector within each tetrahedron and the n -fold symmetry axis of the ring (Peterson *et al.*, 1979). For rings with D_{nh} symmetry, $\gamma = 0^\circ$ (Figs. 2, 3), and when lateral faces of tetrahedra in the ring are coplanar, $\gamma = \pm 35.3^\circ$. The variation of the energy per tetrahedron with γ is presented in Figure 4. Since $d(\text{SiO})$ correlates inversely with SiOSi angle (Brown *et al.*, 1969), the tetrahedra should not be expected to remain rigid during the tilting and the distortion of the SiOSi angle. Re-optimizing the bond lengths and angles indicates this to be the case with the SiO bonds lengthening as the SiOSi angles narrow. Table 1 summarizes the features of the final optimized configuration, which occurs when $\gamma = \pm 17^\circ$. The calculated barrier to tilting is very small, 4 kJ/mole ;

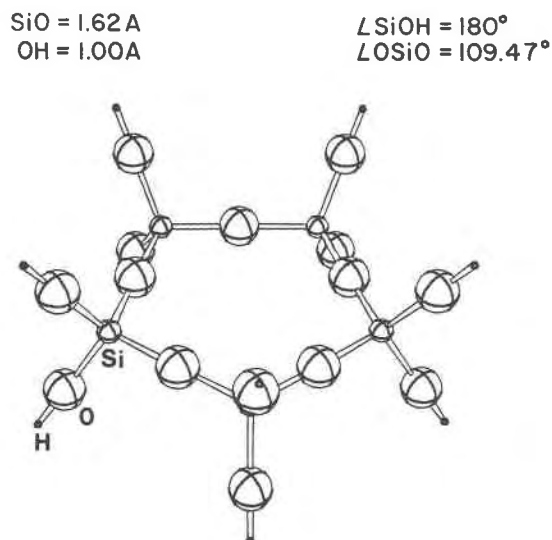


Fig. 3. Hydroxycyclopentasiloxane molecule, $[(\text{OH})_2\text{SiO}]_5$, D_{5h} configuration with fixed geometry: $d(\text{SiO}) = 1.62 \text{ \AA}$, $d(\text{OH}) = 1.0 \text{ \AA}$, $\text{SiOH} = 180^\circ$ and $\text{OSiO} = 109.49^\circ$. The nearly straight SiOSi angles are conspicuous in the 5-membered ring, purported by Zoltai and Buerger to be most stable. Sphere size assignments are the same as in Figure 2.

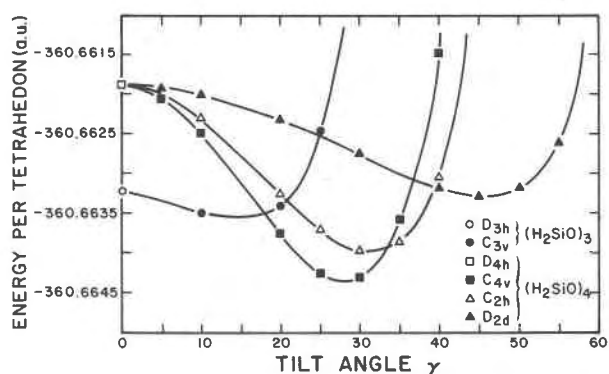


Fig. 4. Potential energy curves (Hartree units) calculated as a function of tilt angle for the C_{3v} distortion of planar $(H_2SiO)_3$ and D_{2d} , C_{2h} and C_{4v} distortions of planar $(H_2SiO)_4$. Here, rigid tetrahedra are assumed, whereas for the data in Table 1 this condition is not imposed. For symmetry reasons, the curves are symmetrical about $\gamma = 0^\circ$.

consequently, the 3-membered ring is indicated to be very flexible to this distortion over a range of γ -values from -20° to $+20^\circ$.

The bond lengths and angles of the 4-membered ring in cyclotetrasiloxane $(H_2SiO)_4$ were similarly optimized, but several configurations are possible, depending upon the signs of γ for each tetrahedron. When γ -angles of the tetrahedra in the 4-membered ring have the signs $++++$ the point symmetry of the ring is C_{nv} , when they have the signs $+-+-$ the ring has D_{2d} point symmetry, and when they have the signs $+- - -$ the ring has C_{2h} symmetry.

Table 1 summarizes the features of the optimized geometries. The order of increasing stability is D_{4h} , D_{2d} , C_{2h} , C_{4v} (Fig. 5), the exact opposite to the sequence indicated by the electrostatic calculations of Zoltai and Buerger (1960). These later three configurations comprise three local minima on the energy hypersurface of $(H_2SiO)_4$, but to assure that the lowest energy configuration has been obtained would require complete relaxation of the symmetry constraints. In fact, the electron diffraction profile of the gas-phase tetramer has been suggested to be consistent with S_4 point symmetry (Glidewell *et al.*, 1970). The proposed structure (Fig. 6) is similar to the D_{2d} configuration, but the bridging oxygens alternate up and down in the ring. Even so, the calculated bond lengths and angles for the D_{2d} tetramer compare well with those observed (\circ) for the gas phase molecule: $d(Si-O) = 1.61(1.628\text{\AA})$, $SiOSi = 142(148.6 \pm 1.2^\circ)$, $OSiO = 111(112.0 \pm 0.9^\circ)$, adjacent $d(O \dots O) = 2.66(2.70\text{\AA})$ and adjacent $d(Si \dots Si) = 3.05(3.13\text{\AA})$. Note, however, that the D_{2d} tetramer is not the lowest energy configuration calculated.

Interactions governing the ring geometries of $(H_2SiO)_3$ and $(H_2SiO)_4$

The frequency distribution of observed $SiOSi$ angles in silicates spans a range of values from 120° to 180° with an average of $\sim 145^\circ$ (Tossell and Gibbs, 1978) so that the inherent tendency of the $SiOSi$ angle to adopt a bent bond configuration is clearly

Table 1. Summary of silicate ring calculations using a STO-3G basis

molecule ^a	$(H_2SiO)_2$	$(H_2SiO)_3$		$(H_2SiO)_4$			$[(OH)_2SiO]_6^c$	
tetrahedra per ring	2	3		4			6	
point symmetry	D_{2h}	D_{3h}	C_{3v}	D_{4h}	D_{2d}	C_{2h}	C_{4v}	C_{6v}
total energy (a.u.)	-720.99238	-1081.98970	-1081.99133	-1442.64762	-1442.65511	-1442.65789	-1442.66145	-354.92145 ^d
energy per tetrahedron (a.u.)	-360.49619	-360.66323	-360.66377	-360.66190	-360.66377	-360.66447	-360.66536	-59.15359 ^d
$d(SiO)$ (\AA)	1.71	1.640	1.644	1.600	1.613	1.613	1.619	1.62 ^e
$d(Si \dots Si)$ (\AA) adjacent	2.630	2.972	2.916	3.141	3.054	3.123	2.990	3.045
$d(O \dots O)$ (\AA) adjacent	2.162	2.687	2.683	2.655	2.665	2.660	2.662	2.645 ^e
$\angle SiOSi$ ($^\circ$)	101.2	130.0	124.9	157.9	142.3	150.9, 132.3	134.7	140
$\angle OSiO$ ($^\circ$)	78.8	110.0	109.4	112.1	111.4	111.1	110.5	109.5
tilt angle γ ($^\circ$)	0	0	17	0	49	34	32	37
barrier to planarity (kJ/mole) ^b	0	0	4.26	0	19.66	26.96	36.31	50.80
$SiOSi$ bending force constant f_α (N/m)	-	-	8.83	-	6.91	10.32	20.48	16.99

^a for the first three molecules $d(SiH) = 1.50 \text{\AA}$, $OSiH = HSiH = 109.47^\circ$

^c CNDO/2 calculation (Peterson *et al.*, 1979)

^b energy differences with respect to the D_{nh} configuration

^d valence electrons only

^e fixed value

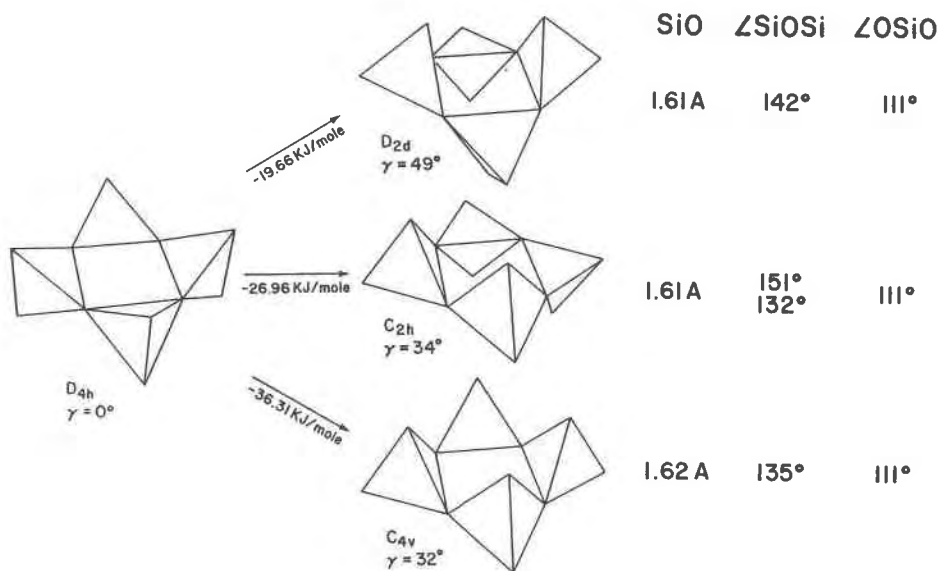


Fig. 5. Final optimized geometries for $(\text{H}_2\text{SiO})_4$ with the enthalpy changes for the distortions from planar symmetry, with the calculated bond lengths and angles.

an intrinsic and governing feature of the SiOSi disiloxo unit. For the cyclic trimer, $(\text{H}_2\text{SiO})_3$, the curve for total energy *versus* γ -angle is very flat over the range -20° to $+20^\circ$, but at $\pm 17^\circ$ does exhibit a minimum lower in energy by 4 kJ/mole than when $\gamma = 0^\circ$. Moreover, as γ increases from 0° to 17° , the SiOSi angle contracts from 130° to 125° , contrary to the tendency of the SiOSi angle to adopt a wider angle near 145° . A net bonding interaction involving the terminal hydrogens across the ring could stabilize the C_{3v} configuration relative to D_{3h} , but this is apparently not the case. The geminal Mulliken overlap population per tetrahedron, defined to be the sum of the overlap populations between the two hydrogens and the silicon within a tetrahedron and those atoms outside the tetrahedron (Bartell *et al.*, 1970), increases non-linearly as the tilt angle increases. As a result the optimum configuration, when $\gamma = \pm 17^\circ$, exhibits more repulsive interaction than the D_{3h} configuration. Since STO-3G calculations for disiloxane $(\text{H}_3\text{Si})_2\text{O}$ (Sauer and Zurawski, 1979; Newton and Gibbs, 1979; Meier and Ha, 1980) generate an optimum SiOSi angle of 126° , the optimum SiOSi for $(\text{H}_2\text{SiO})_3$ of 125° may not be surprising. If this correspondence is true, then there exists a transferability of the disiloxo configuration in disiloxane to that in cyclotrisiloxane, $(\text{H}_2\text{SiO})_3$. However, the structure of disiloxane examined by electron diffraction (Almenningen *et al.*, 1963) and infrared and Raman spectroscopy (Durig *et al.*, 1977; Durig and Kalasinsky,

1978) is consistent with the SiOSi angle bent to $144.0 \pm 0.8^\circ$ and $149 \pm 2.0^\circ$, respectively, and an SiO distance of $1.634 \pm 0.002 \text{ \AA}$.

Meier and Ha (1979) have investigated basis set dependence by comparing calculations for disiloxane using four different basis sets: STO-3G, STO-3G*, 4-31G and 6-6-31**. The STO-3G and 4-31G calculations most closely reproduce the SiO distance, the 6-6-31** calculation of Newton and Gibbs (1979) and Ernst *et al.* (1981) yields the best SiOSi angle, and overall the 6-6-31** calculation best matches the experimental structure. In general, STO-3G calculations underestimate SiOSi angles

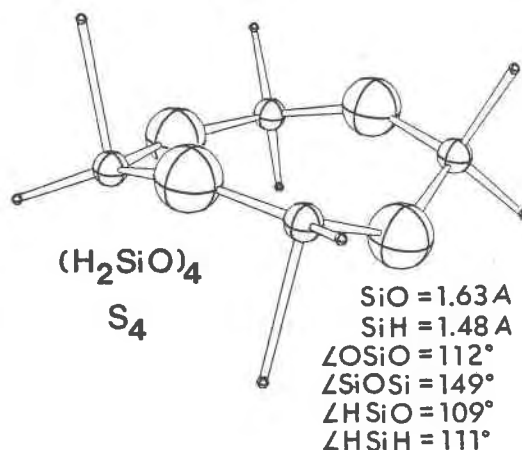


Fig. 6. Structure of cyclotetrasiloxane, $(\text{H}_2\text{SiO})_4$, with S_4 point symmetry, suggested by Glidewell *et al.* (1970) to be consistent with the electron diffraction profile of the gas-phase molecule.

in siloxanes; therefore, they overestimate the stability of small cyclic rings (Sauer and Zurawski, 1979) like cyclotrisiloxane (H_2SiO)₃, in which the SiOSi angles are necessarily restricted to narrow values. Often small rings are strained (unstable) due to the constriction of minimum-energy bond angles (*e.g.*, Newton, 1977), which would be the case for cyclotrisiloxane if the STO-3G basis did yield a minimum-energy SiOSi angle of 145° . The results indicate the D_{3h} 3-membered ring to be more stable than the D_{4h} 4-membered ring, and the C_{3v} 3-membered ring to be as stable as the D_{2d} 4-membered ring (Table 1). For the 4-membered rings, decreasing total energy corresponds to decreasing average SiOSi: D_{4h} , 157.9° ; D_{2d} , 142.3° ; C_{2h} , 141.6° ; C_{4v} , 134.7° . In fact, the depths of the potential energy wells for all four distortions of the D_{nh} configurations correlate linearly ($r^2 = 0.97$) with the change in the SiOSi angle from the D_{nh} configuration. For the 3-membered ring the potential energy curve over the range $\gamma = -20^\circ$ to $+20^\circ$ is very flat because the SiOSi angle is not deformed appreciably. In contrast, the sharper wells in the potential curves for the 4-membered rings reflect the SiOSi angle's tendency to approach 125° , but falling short as the nonbonded repulsions quickly dominate.

Calculations using a STO-3G* basis (d-orbital functions included for Si) were made for the 3-membered ring as a function of γ to see if the total energy curve would exhibit a minimum at $\gamma = 0^\circ$. A planar equilibrium geometry does result, with wider bond angles and shorter bonds. Therefore, we conclude that the similarity in energy of the 3-membered ring to those of the 4-membered rings must be an artifact of the STO-3G basis.

The energy per tetrahedron of the D_{4h} 4-membered ring is 435 kJ/mol lower than that of the 2-membered ring in the dimer (H_2SiO)₂ (Table 1). The SiOSi angle in the dimer, 101.2° , is most assuredly strained, explaining the absence of silicate minerals of 2-membered silicate rings consisting of two tetrahedra sharing a common edge.

These results are consistent only within the STO-3G level of calculation; they must be accepted with caution until better basis sets and models yield similar results.

CNDO/2 calculations for [(OH)₂SiO]_n n-membered silicate rings

Fixed geometries as described previously were calculated for n-membered rings of compositions [(OH)₂SiO]_n, $n = 3$ through 10. Note that these

molecules differ from the previous ones in that the terminal hydrogens are replaced by OH ligands. Figure 7 presents the energy per tetrahedron as a function of ring size for rings with D_{nh} point symmetry. Note the sharp drop in energy from three to four tetrahedral per ring (the 2-ring is some 105 kcal/mole less stable than the 3-ring), at variance with the *ab initio* results. Figure 7 contrasts markedly with the electrostatic energies (Fig. 1) calculated by Zoltai and Buerger inasmuch as no minimum occurs over this ring size interval. Since OSiO angles were fixed at 109.47° , the SiOSi angles are constrained, and, as the ring size increases, the SiOSi passes a maximum angle of 180° at five tetrahedra and beyond narrows to the limit of 109.47° (*i.e.*, re-entrant SiOSi angles). A minimum should result at some size greater than the interval shown in Figure 7, due to the eventual close approach of the Si atoms. When the ring contains an infinite number of tetrahedra it is equivalent to a chain (*cf.* Meagher, 1980, for a CNDO/2 study of the instability of a silicate chain of this configuration). The slight curvature of the points beyond six tetrahedra per ring projects to a minimum energy ring having 13 tetrahedra. For a D_{nh} ring containing 13 tetrahedra with equal length SiO distances and OSiO angles fixed at 109.47° , the SiOSi angle is constrained to value of 137° . Considering the tendency for the SiOSi angle to be bent near 145° , this result agrees with the

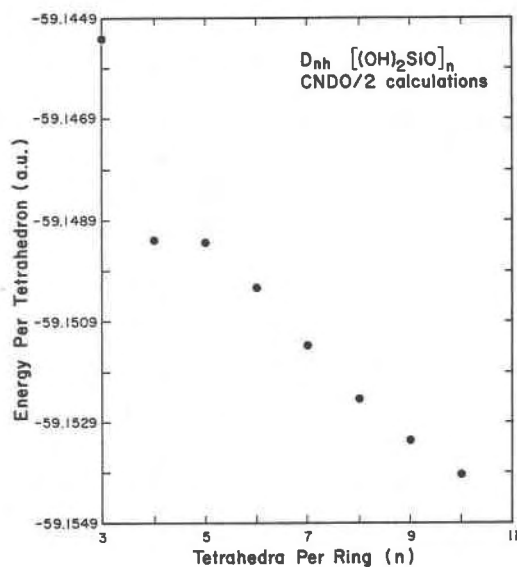


Fig. 7. The energy per tetrahedron (Hartree units) for D_{nh} symmetry [(OH)₂SiO]_n composition rings plotted against ring size, constituting the revision of Figure 1 obtained by Zoltai and Buerger.

observed better than the electrostatic calculations by Zoltai and Buerger (1960). However, for the larger rings, ideal geometries with planar bridging oxygen arrangements would not be expected, therefore comparisons of this kind may not be particularly meaningful.

Since the *ab initio* calculations indicate the C_{nv} configurations for 3- and 4-membered tetrahedral rings to be most stable, the energies for C_{nv} configurations of $[(OH)_2SiO]_n$, $n = 3$ through 8, have been calculated for different tilt angles (Fig. 8). The form of the energy curve for the 3-membered ring differs noticeably from that obtained in the *ab initio* calculations. All of the C_{3v} configurations have energies well above those for the 4-membered ring, consistent with the 3-membered ring being more strained than the 4-membered ring. The minimum energy configuration occurs for a tilt angle of 0° , and the curve is flat over a smaller interval, $\gamma = -10^\circ$ to $+10^\circ$. The CNDO/2 result may be more reasonable than the *ab initio* calculation in this case, probably due to the presence of OH rather than H ligands. Note that when the six terminal H atoms of H_6Si_2O are replaced by OH, the SiOSi angle opens to 140° in a STO-3G calculation (Newton and Gibbs, 1979; Meagher *et al.*, 1980; Gibbs *et al.*, 1981). In fact, an optimization of the cyclic trimer, $[(OH)_2SiO]_3$, with STO-3G methods does yield a γ -value of 0° , in agreement with the CNDO/2 results.

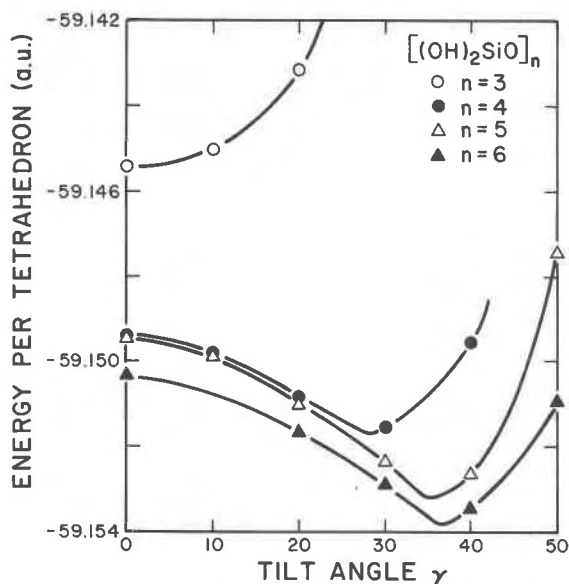


Fig. 8. The energy per tetrahedron (Hartree units) calculated as a function of tilt angle γ for C_{nv} symmetry $[(OH)_2SiO]_n$ rings.

For the 4-membered ring, the form of energy curve is very similar to the one obtained with the *ab initio* method. Compare the minimum energy results with those for the *ab initio* calculation (γ): tilt angle = $27.6(32^\circ)$, barrier to planarity = $7.9(36.3$ kJ/mole), SiOSi = $140(135^\circ)$, and $d(Si \dots Si) = 3.04(2.99\text{\AA})$.

A minimum energy C_{nv} ring was not found in the interval 3 to 8 tetrahedra per ring as shown by Figure 9. The potential energy curve decreases rapidly to 6 tetrahedra, then flattens, but no minimum occurs at 6 as determined by Zoltai and Buerger. Optimizing the tilt angle γ for the C_{nv} rings enables the SiOSi angle to adopt an equilibrium value. The number of tetrahedra in the ring, the optimum tilt angle and the optimum SiOSi angle were obtained as follows: 3, 0° , 130.5° ; 4, 27.6° , 139.8° ; 5, 35.5° , 139.0° ; 6, 33.9° , 142.5° ; 7, 34.6° , 140.8° ; 8, 33.7° , 139.5° . Zoltai and Buerger had considered only those ring models with γ fixed at 35.3° , which requires all tetrahedral faces to be coplanar. Peterson *et al.* (1979) have demonstrated by methods identical with ours for the same molecules that the C_{6v} 6-membered ring is not only more stable than the D_{6h} ring, but that it is additionally stabilized by a trigonal distortion. To meaningfully compare the stability of different size rings requires completely optimized geometries for each ring determined without symmetry constraints, but as yet these requirements have not been met using *ab initio* STO-NG basis set calculations because of the excessive computer time and the large number of calculations required to accomplish this goal. So-called approximate methods (Halgren *et al.*, 1978;

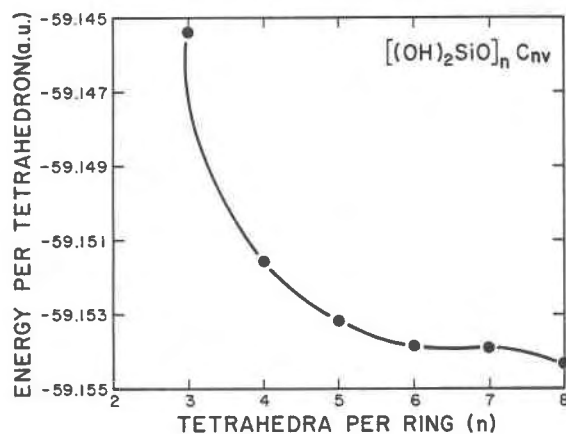


Fig. 9. The energy per tetrahedron (Hartree units) for the minimum energy $C_{nv}[(OH)_2SiO]_n$ rings plotted against ring size.

Dewar and Ford, 1979) are promising alternatives for future research.

A comparison of silicate and siloxane rings

Bond length and angle trends in ring structures

An inverse correlation between the average SiO distance and SiOSi angle has been corroborated by experimental data (Cannillo *et al.*, 1968; Brown *et al.*, 1969; Hill and Gibbs, 1979), semi-empirical MO calculations and *ab initio* MO calculations (Gibbs *et al.*, 1972; Louisnathan and Gibbs, 1972a,b; Cohen *et al.*, 1977; Meagher *et al.*, 1979; Gibbs *et al.*, 1974, 1977, 1981; Newton and Gibbs, 1980). Additional documentation is made here by comparing the variation of average SiO bond length, $\langle d(\text{SiO}) \rangle$, versus the percent fractional *s*-character of the bridging SiO bonds $\%f_s = 100/(1 + \lambda^2)$, where $\lambda^2 = -\sec \text{SiOSi}$, for tetrahedral rings in siloxanes and silicates with that calculated *ab initio* for the following cyclosiloxane molecules: $(\text{H}_2\text{SiO})_3$, D_{3h} , C_{3v} and $(\text{H}_2\text{SiO})_{4h}$, C_{4v} , D_{2d} (Fig. 10). Note that the C_{2h} configuration for $(\text{H}_2\text{SiO})_4$ was omitted because the molecule's symmetry does not necessarily constrain the $d(\text{SiO})$ distances to be equivalent, yet this condition was imposed. Figure 10a is similar to Figure 9b of Newton and Gibbs (1980), differing in

that it possesses more data which are restricted to silicate rings (Chakoumakos, 1981). The significance of this linear correlation is interpreted elsewhere (Newton and Gibbs, 1980; Newton, 1981) using classical hybridization arguments.

SiOSi angle frequency distribution for ring structures

The stereochemistry of the organosiloxanes is remarkably similar to that of the silicates. Noll (1968, p. 246–331) describes this correspondence, noting similar anion configurations and bond length–angle variations. Shklover and Struchkov (1980) review the structural chemistry of the organocyclosiloxanes. As expected, the SiOSi angle frequency distribution for Si-containing tetrahedral rings in siloxanes and silicates are quite similar (Fig. 11). The paucity of data for the hexamers is due to the lack of structure refinements. In contrast, the lack of data for the pentamers of siloxanes and silicates reflects their rare occurrence. In preparing the plots for the silicate data, silicate rings in cyclosilicates and as portions of more condensed anions were used. The true relative abundance of tetrahedral ring sizes for both siloxanes and silicates is not completely represented by the histograms, since structural data are lacking for the larger rings.

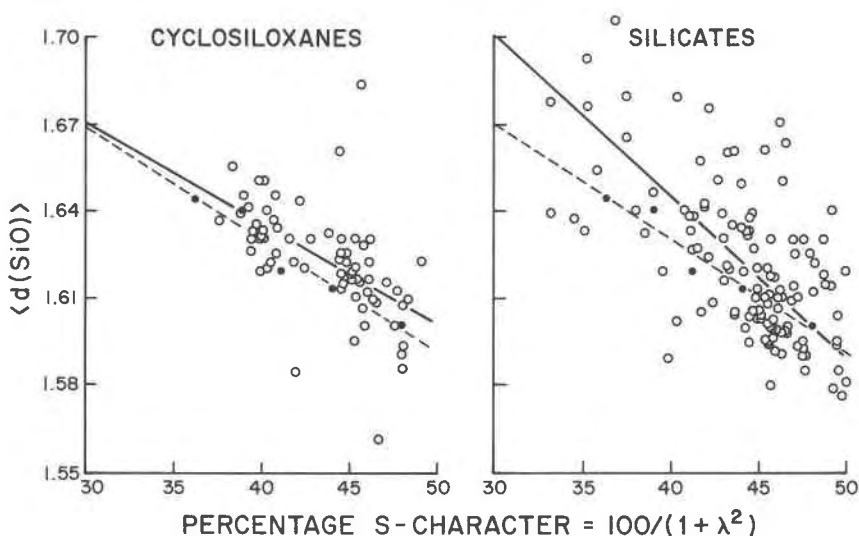


Fig. 10. Scatter diagrams of the average SiO bond length, $\langle d(\text{SiO}) \rangle$, to a bridging oxygen for rings in (a) cyclosiloxane molecules and molecular crystals, and (b) silicates, plotted against the percent fractional *s*-character, $\%f_s = 100/(1 + \lambda^2)$, of the SiOSi bond. The solid lines correspond to the regression equations for the observed data, (a) $\langle d(\text{SiO}) \rangle = -3.5 \times 10^{-3} \%f_s + 1.78$, $r^2 = 0.34$; and (b) $\langle d(\text{SiO}) \rangle = -5.6 \times 10^{-3} \%f_s + 1.87$, $r^2 = 0.64$. The dashed line corresponds to the regression equation $\langle d(\text{SiO}) \rangle = -4.0 \times 10^{-3} \%f_s + 1.79$, $r^2 = 0.94$, calculated for the following molecules (indicated by solid circles): $(\text{H}_2\text{SiO})_3$, D_{3h} , C_{3v} and $(\text{H}_2\text{SiO})_4$, D_{4h} , C_{4v} , D_{2d} , whose geometries were optimized *ab initio*. Note that $\lambda^2 = -\sec \text{SiOSi}$, so that for $f_s = 0.5$, $\text{SiOSi} = 180^\circ$, and for 0.3, $\text{SiOSi} = 115^\circ$.

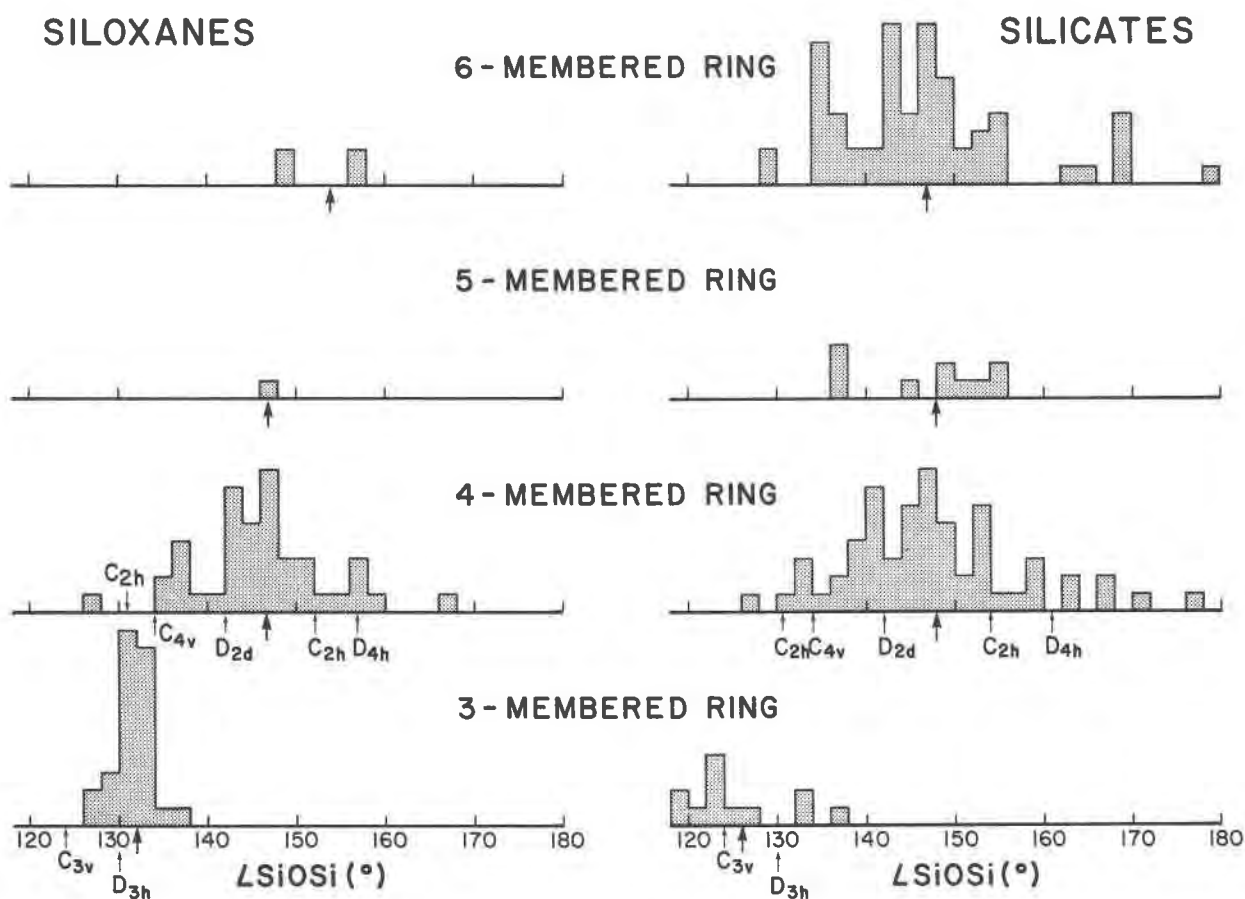


Fig. 11. The SiOSi angle frequency distributions for Si-containing tetrahedral rings observed for silicates and siloxanes (Chakoumakos, 1981). The bold arrows indicate the mean values and the other arrows with Schoenflies notation mark the SiOSi angles calculated for the *ab initio* optimized geometries for cyclotrisiloxane and cyclotetrasiloxane.

Actually the 6-membered rings are more abundant for the silicates and the 4-membered rings for the siloxanes. In general, the SiOSi angles of the 3-membered rings are narrower ($\sim 130^\circ$) and have a more restricted range of values than those for the 4-membered rings. The SiOSi angle distributions for the larger rings are quite broad yet center around 147° .

Occurrence of ring structures

3-membered rings. Occurrence of 3-membered rings in the silicates is restricted almost entirely to cyclosilicates like benitoite, catapleite, margarosanite, walstromite, wadeite and high-pressure CaSiO_3 . Eudialyte is unusual because its structure has discrete 3- and 9-membered rings. Rarely do they occur as portions of more condensed silicate anions except, for instance, as part of the sheet anion of zussmanite. In all cases, configurations

close to D_{3h} and C_{3v} are observed. The 3-membered silicate ring in walstromite (Glasser and Glasser, 1968) is reported to have a configuration close to C_{3v} with $\gamma = \pm 35^\circ$, which requires an average SiOSi angle of 125° . Our MO calculations indicate this configuration to be relatively unstable. Additional minerals, with suspected 3-membered silicate rings, are pabstite (Gross *et al.*, 1965) and bazirite (Young *et al.*, 1978). Three-membered silicate rings are stabilized by replacing one or two of the Si atoms with Be or B, which have narrower minimum-energy TOSi angles to alleviate the ring strain.

Cyclotrisiloxane has yet to be isolated, but the ring structure of hexamethylcyclotrisiloxane has been determined to be consistent with D_{3h} point symmetry, with a flat energy curve for tilting over the range $\gamma = \pm 8^\circ$ (Oberhammer *et al.*, 1973). All cyclotrisiloxane rings are nearly planar. Note that in Figure 11 the SiOSi angles obtained in *ab initio*

optimized $(\text{H}_2\text{SiO})_3$ conform with the observed distributions.

4-membered rings. Many configurations are observed in addition to the D_{4h} , D_{2h} , C_{2h} and C_{4v} configurations examined previously. Hence, it is not possible to directly correlate portions of the frequency distribution with particular configurations. The SiOSi angles, obtained in *ab initio* optimized $(\text{H}_2\text{SiO})_4$, effectively span the range of observed SiOSi angles, and for the siloxanes the observed configurations actually exhibit a preponderance of configurations close to D_{2d} .

5-membered rings. These are very uncommon in silicates, but they do occur in frameworks such as keatite (Shropshire *et al.*, 1959) and some synthetic high-silica zeolites (*e.g.*, silicalite, Flanigen *et al.*, 1978) and in the sheet anion of okenite (Mamedov and Belov, 1958) and nekoite (Alberti and Galli, 1980). Five-membered rings with one or more of the Si atoms replaced by other cations (Li, Be, B, Al, Fe^{3+}) are more frequent.

In siloxanes 5-membered tetrahedral rings are also uncommon. They occur in decamethylcyclopentasiloxane (Oberhammer *et al.*, 1973) and as part of the $\text{Si}_{12}\text{O}_{18}^{12-}$ cage of dodeca(phenylsilasesquioxane) (Clegg *et al.*, 1980). Discrete double 5-membered rings occur in decamethylsilasesquioxane (Baidina *et al.*, 1980) and they have been isolated from crystalline mixtures in the systems $\text{N}(\text{n-C}_4\text{H}_9)_4\text{OH-SiO}_2\text{-H}_2\text{O}$ and $\text{N}(\text{i-C}_5\text{H}_{11})_4\text{OH-SiO}_2\text{-H}_2\text{O}$ (Hoebbel *et al.*, 1975).

Silicate rings in glasses and melts. Rings of tetrahedra in the silicate anions of glasses and melts conform with popular models for those vitreous states; however, quantitative structural studies are as yet not possible. Discrete 4-membered silicate rings in some lead orthosilicate glasses have been detected by combined mass spectroscopy and chromatography applied to trimethylsilyl derivatives (Götz *et al.*, 1972, 1976). Improvements of this method (Masson, 1977; Sharma and Hoering, 1977) now allow semi-quantitative determination of the anionic constitution in silicate structures; however, the silylation techniques are applicable only to silicate structures with small anions with easily replaceable metallic ions. A common problem encountered in the silylation process is that side reactions give rise to new anions not present in the original structure (Lenz, 1964, 1966; Masson, 1977). In particular, the trimethylated cyclic trimer is very difficult to recover in high yields inasmuch as it undergoes cleavage during trimethylsilylation,

transforming to the linear trimer (Masson, 1977). This experimental observation is not surprising because the cyclotrisiloxane ring is unstable due to strained SiOSi angles. In contrast, the linear tetramer, $\text{Si}_4\text{O}_{13}^{10-}$, undergoes cyclisation to the cyclic tetramer, $\text{Si}_4\text{O}_{12}^{8-}$, during trimethylsilylation of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ (Calhoun *et al.*, 1980).

Raman spectra of trimethylsilyl derivative mixtures are not easily deciphered since the major frequency shifts are insensitive to the size of the polymer (Sharma and Hoering, 1977). In contrast, Raman spectroscopy applied directly to glasses and quenched melts may provide a means of identifying specific anion structures (Mysen *et al.*, 1980; Virgo *et al.*, 1980). Moreover, unique sets of anionic species in equilibrium in silicate melts may be identified for specific ranges of nonbridging oxygen to silicon ratios. Our MO calculations suggest that the 3-membered tetrahedral ring should be rare, if not totally absent.

Inherent stability of silicate anions

The silicate anions in gillespite (Pabst, 1943) and apophyllite (Chao, 1971) are $\text{Si}_8\text{O}_{20}^{8-}$ sheets that can be viewed as tessellations of C_{4v} 4-membered silicate rings (Liebau, 1968) (Fig. 12). In gillespite the apices of the C_{4v} rings point at each other whereas in apophyllite the tetrahedral bases of the C_{4v} rings face each other. Of the 4-membered ring distortions examined by MO calculations, the C_{4v} configuration is indicated to be the most stable, so the sheets in gillespite and apophyllite are simply two possible stable condensations of the C_{4v} ring. Attributing the configuration of the apophyllite sheet to the constitution of the interlayer ions (Liebau, 1968; Chao, 1971) is not necessary. The distortions in the layer structures mica, kaolinite and serpentine and those of single and multiple chain structures are also indicated to be inherently stable configurations (Peterson *et al.*, 1979, Meagher, 1980).

Conclusions

Over-estimation of the stability of cyclotrisiloxane results from using a STO-3G basis set. The hexahydroxycyclosiloxane molecule is a better model for the 3-membered ring as evinced by the STO-3G and CNDO/2 calculations. The 3-membered ring is less stable than larger rings, since the SiOSi angles are strained, and their optimum configurations are necessarily restricted to be nearly planar. Their instability is consistent with their rarity in silicate structures and their breakdown

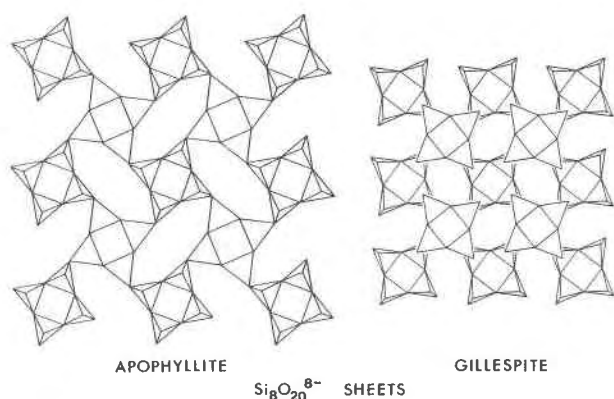


Fig. 12. Silicate sheet anions, $\text{Si}_8\text{O}_{20}^{8-}$, in gillespite and apophyllite can be viewed as two different tessellations of the C_{4v} ring (Liebau, 1968).

during a trimethylsilylation reaction, but they may be stabilized by high pressure. Their presence in silicate glasses and melts must also be infrequent.

Larger rings are indicated to assume nonplanar configurations in order to achieve minimum energy SiOSi angles averaging 147° . For 4-membered tetrahedral rings, three local minima on the energy hypersurface of $(\text{H}_2\text{SiO})_4$ have been determined to be associated with the configurations D_{2d} , C_{2h} , C_{4v} , in order of increasing stability. For C_{nv} rings, a minimum energy ring does not occur at 4 or 6 tetrahedra, in disagreement with the frequency distribution of ring sizes in siloxanes and silicates. The relative stability of different size silicate rings can only be meaningfully compared using completely optimized geometries for each ring. As larger calculations become more feasible, they should be carried out for $[(\text{OH})_2\text{SiO}]_n$ ring molecules using a larger basis set than STO-3G or STO-3G.*

Frequency distributions of SiOSi angles and $\langle d(\text{SiO}) \rangle$ versus their percentage s -character in tetrahedral rings containing only Si are very similar for siloxanes and silicates, further substantiating the correspondence between these two chemical groups.

A premise of the conceptual framework used to describe the stability and structure of silicate anions and siloxanes must be that observed structures are inherently stable, and not solely consequent of the interaction with their local crystal field (Noll, 1968, p. 246–331).

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