AN M.O. STUDY OF THE STEREOCHEMISTRY AND ENERGY OF
THREE-REPEAT SINGLE SILICATE CHAINS

by

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ABSTRACT

Hypothetical three—repeat single chains consisting of regular SiO_4 tetrahedra were generated with a computer program to study the possible conformations and their total potential energy by the CNDO/2 molecular orbital method. Calculations were restricted to those chains with $\angle$Si—O—Si between 110° and 180° with an average of 140° and $\angle(O—O—O)_{br}$ between 90° and 180°. In addition, successive pairs of tetrahedra in each chain were restricted to either single or double—eclipsed or staggered conformation. Those chains with the largest d(Si—Si) and at least one staggered pair of tetrahedra have a lower energy. These are not, as yet, observed in nature presumably because their packing does not accomodate the interstial cations.

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I. INTRODUCTION

Only one type of three-repeat single silicate chain is found in nature in the minerals wollastonite, bustamite, the pectolite-serandite series, schizolite and sorensonite. From a study of the role of octahedral cations in the packing of tetrahedral chains in each of the above minerals, except sorensonite, Ohashi and Finger (1978) found that only small changes in the comformation of the chains occur as a function of chemical variations.

The purpose of this study is to define the different types of three-repeat single chains which are stereochemically possible and to determine their relative energy. Earlier work on two-repeat chains by Meagher (1980) has shown that the potential energy of those chains with bridging Si–O–Si angles, $\angle$Si–O–Si, between 125° and 150° and bridging oxygen angles, $\angle$(O–O–O)$_{br}$, between 125° and 180° is lower than that of chains with any oter conformations. Meagher found that the chains of lowest energy are those with both $\angle$Si–O–Si approaching 135°. The $\angle$(O–O–O)$_{br}$ is apparently less important in determining the energy of these chains. This study was therefore limited to those three-repeat single silicate chains with $\angle$Si–O–Si between 110° and 180° with an average of 140° and $\angle$(O–O–O)$_{br}$ between 90° and 180°, thus reducing the number of chains to be considered. To further reduce the number of chains and to facilitate their identification each was looked upon as composed of three pairs of tetrahedra that were either single or double-eclipsed or

staggered.

II. THE CNDO/2 METHOD

1. Theory

The total energy E of an atomic cluster is given by the Schrodinger equation

$$H\psi = E\psi \tag{1}$$

where H is the Hamiltonian Operator and ψ is the total wave function. This equation cannot be solved for many—electron problems.

The Hartree—Fock Operator, F, (Hartree, 1928 and Fock, 1930) is an appproximation of the Hamiltonian given by

$$F = H_i + J_{ij} - 1/2K_{ij} \tag{2}$$

where H is called the one—center or core Hamiltonian and represents the attraction between an electron in the i—th molecular orbital and the nuclei in the cluster. The terms J_{ij} and K_{ij} describe the two—electron interactions. J_{ij} is the coulomb integral representing the repulsion between two electrons in the i—th and j—th molecular orbitals respectively. K_{ij} is the exchange integral representing the decrease in energy associated with two electrons having the same spin.

The total wave function is an antisymmetrized product of molecular orbitals which Roothan (1951) represents by a linear combination of n atomic orbitals, ϕ_p , (LCAO)

$$\psi_i = \sum_{p=1}^{n} \phi_p c_{ip} \tag{3}$$

For orthonormal atomic orbitals ϕ_p, ϕ_q the overlap matrix S_{pq} is given by

$$S_{pq} = \int \phi_p^* (s) \, \phi_q (s) \, d\tau(s) \tag{4}$$

where $d\tau$ is the volume element associated with electron s.

The best approximation of the energy of an atomic cluster, $\mathcal{E}$, is given by the Variation Theorem.

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \leq \mathcal{E} \tag{5}$$

the coefficients c_{ip} that correspond to the minimun energy must satisfy the set of simultaneous equations

$$\sum_{i=1}^{N} c_{ip} \, (F_{pq} - \mathcal{E} S_{pq}) = 0 \tag{6}$$

where $\mathcal{E}$ is a solution to the secular equation

$$|\, F_{pq} - E S_{pq} \,| = 0 \tag{7}$$

2. CNDO/2 Approximation

The Complete Neglect of Differential Overlap (CNDO) method was introduced by Pople, Santry and Segal in 1965. The overlap associated with the electron repulsion between molecular orbitals with different principal quantum number is assumed to be negligable, i.e.,

$$\iint \psi_i^* (s) \, \psi_j (s) \, r_{st}^{-1} \, \psi_k^* (t) \, \psi_l (t) \, d\tau_s \, d\tau_t = 0 \tag{8}$$

for $i \neq j$ and $k \neq 1$

In addition the corresponding overlap integrals are neglected in the normalization of the molecular orbitals. The remaining

electron–repulsion integrals of the form

$$\iint \phi_{(a)}^2 (s) \; r_{st}^{-1} \; \phi_{(b)}^2 (t) \; d\tau_s \; d\tau_t = \gamma_{ab}$$

(9)

are evaluated. This term represent the average interaction between valence electrons assumed to belong to a s–type orbital on atoms a and b respectively

3. CNDO/2 Parametrization

Each diagonal matrix element H cn be separated into a one–center and a two–center contributions of the form

$$H_{ii} = U_{ii} - \sum_{b \neq a} V_{ab} \qquad \phi_p \text{on a}$$

(10)

where

$$U_{ii} = -1/2 \; (I_i + A_i) - (Z_a - \tfrac{1}{2}) \gamma_{aa}$$

(11)

and $1/2 \; (I_i + A_i)$ is the Mulliken definition of electronegativity, where I is the ionization potential and A is the electronic affinity associated with ϕ_p . Z_a is the core charge of atom a. U_{ii} represents the total energy of an electron belonging to the atomic orbital ϕ_p centered on atom a. The term V_{ab} given by

$$V_{ab} = Z_b \gamma_{ab}$$

(12)

which represents the interaction of any valence electron on atom a with the core of atom b.

For two atomic orbital $\phi_p \neq \phi_\gamma$ on atoms a and b respectively the off–diagonal matrix element H_{ij} becomes

$$H_{ij} = \beta_{ij} = \beta_{ab} S_{ab} \tag{13}$$

where β_{ij} is called the resonnance integral. The bonding parameter β_{ab} is given by

$$\beta_{ab} = 1/2K(\beta_a + \beta_b) \tag{14}$$

where $K = 0.75$ if either a or b is a second row element . β_a and β_b are found by best-fitting to full SCF calculations for small molecules.

To summerize, diagonal elements of the Hartree-Fock matrix take the form

$$F_{ii} = U_{ii}(P_{AA} - 1/2 P_{ii})\gamma_{aa} + \sum_{b \neq a}[-Q_b\gamma_{ab} + (Z_b\gamma_{ab} - V_{ab})] \tag{15}$$

The net charge, Q_b, is given by

$$Q_b = Z_b - P_{bb} \tag{16}$$

where the gross electronic population on atom b, P_{bb}, is given by

$$P_{bb} = \sum_p^{atom\ a} P_{pp} \tag{17}$$

and the density matrix, P_{pq}, is given by

$$P_{pq} = 2 \sum_i^{occ} c_{pi} c_{qi} \tag{18}$$

The quantity $-Q_b \gamma_{ab}$ represents the effect of the potential due to the total charge on atom b. The penetration integral, $Z_b \gamma_{ab} - V_{ab}$ represents the difference between the potentials due to the valence electrons on the core of the neutral atom b. The off-diagonal elements take the form

$$F_{ij} = \beta_{ab} S_{pq} - 1/2 P_{pq} \gamma_{ab} \tag{19}$$

All calculations were carried out with the program CNINDO (Dobash, 1974) with the parametrization of Pople and Segal (1965) for the first row elements and that of Santry and Segal

(1967) for the second row elements.

III. MODELS OF THREE—REPEAT CHAINS

1. Description of chain construction

A computer program was written that calculates any four—membered, three—repeat chain starting with the coordinates of three tetrahedra expressed as a function of the Si—O bond length, d(Si—O). In the original configuration, both $\angle$Si—O—Si equal 180° and the cluster has the point symmetry 2/m. Fig 1 shows an atomic cluster before and after rotation including reference and rotation axes. The first tetrahedron remains fixed at all times. The second tetrahedron is free to rotate about the y—axis by an angle ρ_2. A counterclockwise rotation by an angle ρ_2 brings the four non—bridging oxygen atoms on the first and second tetrahedra into a double—eclipsed pair, a clockwise rotation brings them into a single—eclipsed pair. Either a clockwise or a counterclockwise rotation about the Si—O bonds by angle ϕ_2 and θ_2 respectively create a staggered pair. The third tetrahedron is also rotated by an angle ρ_3 about y'—axis which is the previously rotated y—axis and by angles ϕ_3 and θ_3 about its own Si—O bonds. The fourth tetrahedron is added by translating the first tetrahedron along a vector connecting the non—bridging oxygen atoms on the first and third tetrahedra.

2. Description of the fixed pairs

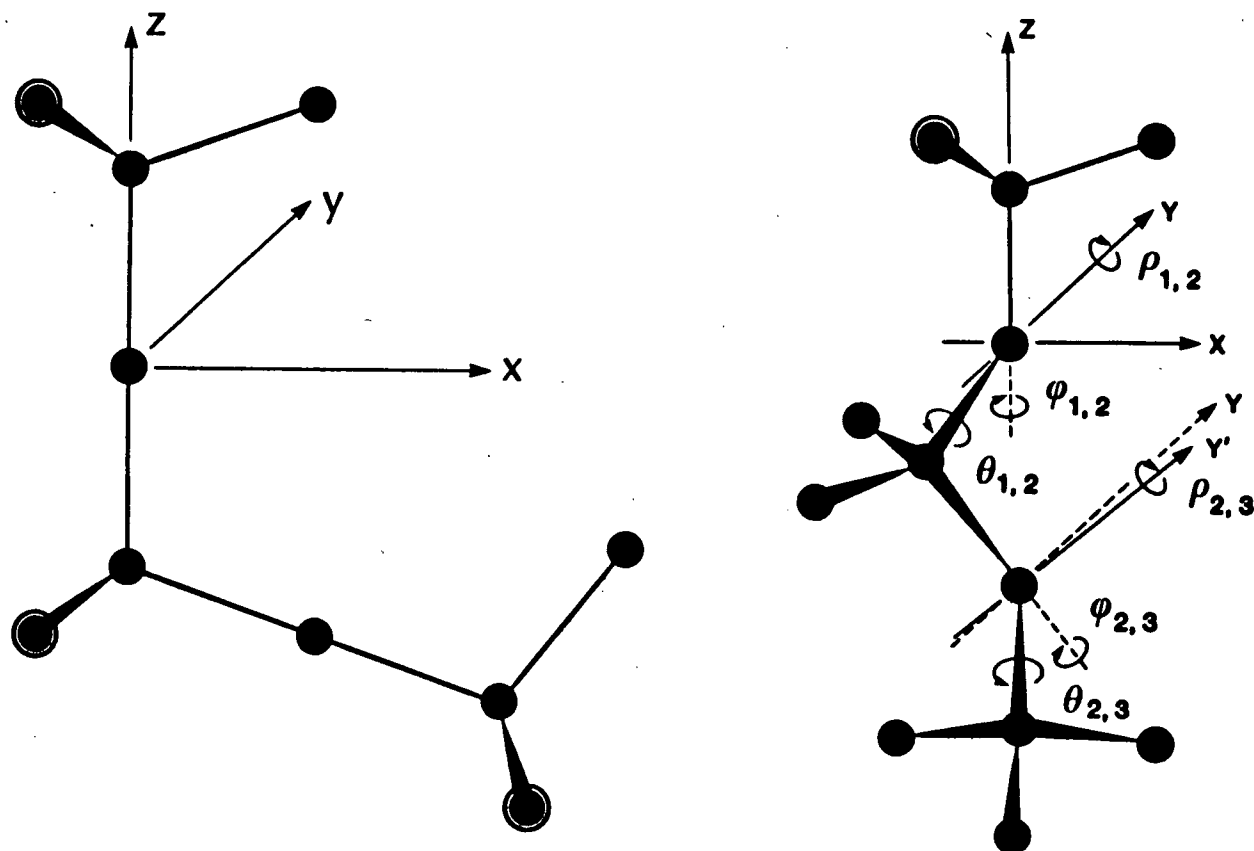Figure 1. Original configuration of the three—repeat chain showing the 2/m point group symmetry and the same cluster after rotation by angles $\varrho_2 = 40°$, $\phi_2 = 35°$, $\theta_2 = 30°$, $\varrho_3 = 40°$, $\phi_3 = 10°$ and $\theta_3 = 45°$.

In order to simplify the identification of the types of three—repeat chains each is looked upon as composed of three pairs of tetrahera. Fig 2 shows three standard orientations between the members of a pair. It is double—eclipsed if two oxygen atoms on each tetrahedron in an eclipsed conformation move closer to each other with narrowing $\angle$Si—O—Si or single—eclipsed if only one oxygen atom on each tetrahedron moves similarly. The pair is staggered if one tetrahedron is rotated so that one oxygen atom resides on the plane bisecting one of the $\angle$O—Si—O on the other tetrahedron and these three oxygen atoms move toward each other with narrowing $\angle$Si—O—Si. No variation of the above types are considered for the first and second pairs of tetrahedra in a chain since these can be fixed by keeping the rotation angles ℓ_2, ϕ_2, ϕ_3 and Θ_3 constant. Table I shows the choice of unique settings for the rotation angles ϕ_2, Θ_2, ϕ_3 and Θ_3 that yields double or single—eclised and staggered pairs. The third pair of tetrahedra in a chain depends on the translation of the first tetrahedron so intermediate types are possible.

IV. CLASSIFICATION OF CHAINS

1. Definition of symbols

Each of the pairs of tetrahedra described in the previous chapter is identified by a letter; D for double—eclipsed, S for single—eclipsed and St for staggered. Furthermore the
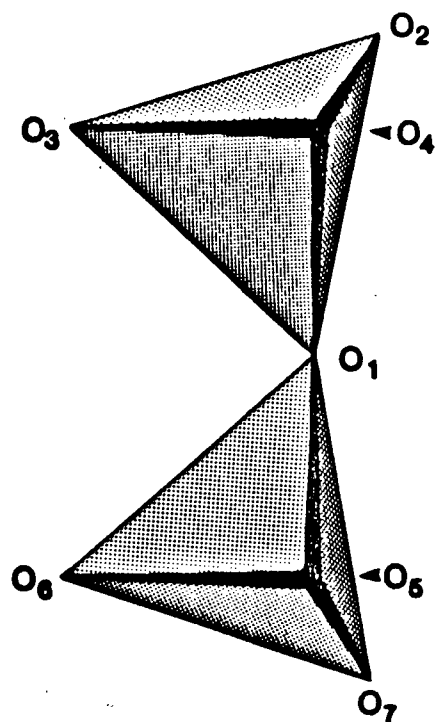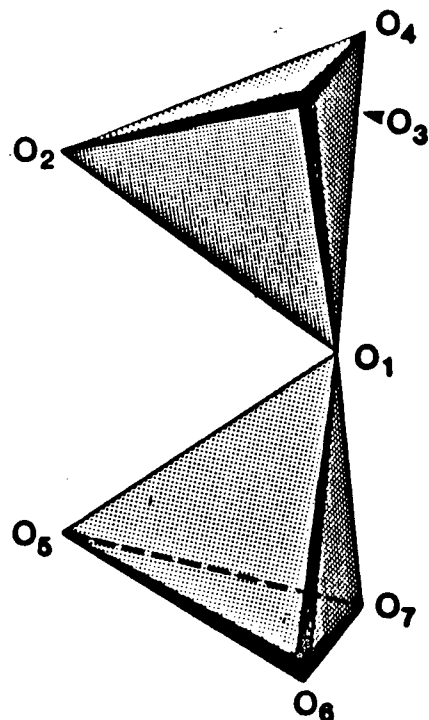
DOUBLE ECLIPSED PAIR   **SINGLE ECLIPSED PAIR**   **STAGGERED PAIR**
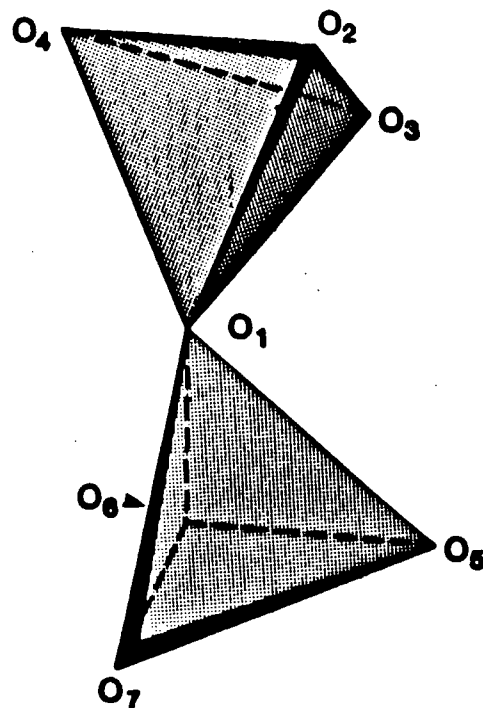
Figure 2. Double-eclipsed, single-eclipsed and staggered pairs of tetrahedra with energies -137.9974, -137.9977 and -137.9983 A.U respectively.

Table I. Unique settings for the rotation angles ϕ_2, θ_2, ϕ_3 and θ_3 that yield double or single-eclipsed and staggered pairs.

First pair		Second pair	
ϕ_2	θ_2	ϕ_3	θ_3

Double-eclipsed pairs

ϕ_2	θ_2	ϕ_3	θ_3
0°	0°	0°	0°
0°	120°	120°	0°

Single-eclipsed pairs

ϕ_2	θ_2	ϕ_3	θ_3
60°	60°	60°	60°
60°	180°	180°	60°

Staggered pairs

ϕ_2	θ_2	ϕ_3	θ_3
0°	60°	60°	0°
60°	0°	0°	60°
0°	180°	180°	0°

relationship of the bridging oxygen atoms from which the chain will be extended, i.e., all oxygen atoms other than O_1 on Figure 2, with respect to the Si–O–Si plane of the pair is described by a number. On Figure 2 O_{br}^{Pair} is always oxygen atom O_1. These symbols are summerized in Table II.

These symbols can be grouped into four categories, as follows. The symbols D_1, S_1 and St_1 represent the case where both bridging oxygen atoms are in the Si–O–Si plane of a given pair. The symbols D_2, S_2, St_2 and St_5 refer to the case where one of the bridging oxygen atom is not in the Si–O–Si plane of a given pair. The last two categories include the pairs in which both bridging oxygen atoms are off the Si–O–Si plane of a given pair. The symbols D_3, S_3 and St_3 designate the case where the bridging oxygen atoms are both on the same side of the Si–O–Si plane while the symbols D_4, S_4 and St_4 refer to the case where the bridging oxygen atoms are on either side of this plane.

2. Representative chains

The work of Meagher (1980) and Newton and Gibbs (1980) indicates that nearest neighbour interactions are most important in determining the comformation of bridging silicate tetrahedra. Accordingly, to decrease the number of chains to be considered only those chains with adjacent tetrahedra having $\angle$Si–O–Si and $\angle$(O–O–O)$_{br}$ which fall into the region of minimum energy as defined by these authors will be computed. The following restrictions were imposed on the chains. The $\angle$Si–O–Si are

Table II. Summary of symbols used in describing three—repeat single chains. These represent all the possible comformations of the double or single—eclipsed and staggered pairs of tetrahedra in a chain.

<u>Symbols</u>	<u>Choice of</u> $\underline{O}_{br}$ <u>it represents</u>

<u>Double—eclipsed</u> <u>pairs</u>

D_1		O_2 and O_7
D_2	(a)	O_7 and either O_3 or O_4
D_2	(b)	O_2 and either O_6 or O_7
D_3	(a)	O_4 and O_5
D_3	(b)	O_3 and O_6
D_4	(a)	O_3 and O_5
D_4	(b)	O_4 and O_6

<u>Single—eclipsed</u> <u>pairs</u>

S_1		O_2 and O_5
S_2	(a)	O_5 and either O_3 or O_4
S_2	(b)	O_2 and either O_6 or O_7
S_3	(a)	O_3 and O_6
S_3	(b)	O_4 and O_7
S_4	(a)	O_3 and O_7
S_4	(b)	O_4 and O_6

<u>Staggered</u> <u>pairs</u>

St_1		O_4 and O_5
St_2		O_5 and either O_2 or O_3
St_3	(a)	O_2 and O_7
St_3	(b)	O_3 and O_6
St_4	(a)	O_2 and O_6
St_4	(b)	O_3 and O_7
St_5		O_4 and either O_6 or O_7

between 110° and 180° with an average of 140°. The $\angle(O-O-O)_{br}$ vary between 90° and 180°. The shortest $d(O-O)_{nbr}$ is 2.63 A i.e., the $d(O-O)$ in a regular tetrahedron where the Si-O bonds are equal to the sum of ionic radii (Shannon and Prewitt, 1969). A list of three-repeat chains composed of two fixed pairs as described above is given on Table III.

Table IV shows a list of $\angle$Si-O-Si and $\angle(O-O-O)_{br}$ for wollastonite (Buerger and Prewitt, 1961) and bustamite (Peacor and Buerger, 1962). The series pectolite($Ca_2NaHSi_3O_9$)-serandite($Mn_2NaHSi_3O_9$) (Prewitt, 1967; Takeuchi, Kudoh and Yamanska, 1976) and schizolite, a manganoan pectolite, (Ohashi and Finger, 1978) are not included because of the presence of OH^- group in the chain. The presence of a water molecule forming a hydrogen bridge with oxygen atoms bonded to the silicon atom precludes taking sorensonite, $Na_4SnBe_2(Si_3O_9).2H_2O$, (Metcalf-Johansen and Hazell, 1976) into account as well. All of these compounds have a very narrow range of $\angle$Si-O-Si and $\angle(O-O-O)_{br}$. The $\angle$Si-O-Si are between 135° and 160° with an average between 142° and 145°. The $\angle(O-O-O)_{br}$ are between 121° and 156° with an average between 140° and 149°.

V. DISCUSSION OF ENERGY CALCULATIONS

1. Single chain selection

To select the possible chains the computer program steps through C values for predetermined values of ϕ and θ. The

Table III. List of three—repeat chains composed of two fixed pairs of tetrahedra. The pair quoted in parentheses represents the closest approximation to the standard orientation of the third and fourth tetrahedra. The $\angle$Si—O—Si vary between 120° and 180° with an average of 140°. The $\angle$(O—O—O)$_{br}$ vary between 90° and 180°.

	$\angle$Si—O—Si			$\angle$(O—O—O)$_{br}$		
$D_1-D_2-(St_4)$	145.00	150.00	122.53	144.47	147.09	143.78
$D_2-D_2-(D_2)$	140.00	140.00	138.82	142.17	142.18	143.56
$D_2-D_4-(D_2)$	145.00	145.00	131.57	117.22	144.87	150.27
$D_1-S_2-(St_4)$	150.00	145.00	123.08	139.47	123.19	122.62
$D_2-S_1-(S_2)'$	120.00	179.88	121.16	128.37	109.47	140.92
$D_2-S_2-(St_3)$	130.00	140.00	152.32	135.74	119.33	161.33
$D_2-S_3-(D_2)$	145.00	140.00	133.01	144.87	119.99	149.78
$D_2-S_4-(D_2)$	145.00	145.00	130.67	144.87	176.61	148.27
$D_4-S_4-(D_2)$	145.00	145.00	130.96	117.22	176.61	119.44
$D_1-St_1-(St_1)$	135.00	130.00	155.53	135.00	159.47	155.53
$D_1-St_4-(S_2)$	130.00	125.00	166.87	137.06	164.47	147.32
$D_2-St_1-(D_1)$	135.00	150.00	132.23	139.11	150.36	166.83
$D_2-St_2-(S_2)$	125.00	145.00	151.47	132.11	90.23	136.62

Table III. (continued)

$\angle Si\!-\!O\!-\!Si$			$\angle (O\!-\!O\!-\!O)_{br}$		
$D_2\!-\!St_3\!-\!(St_1)$					
145.00	135.00	139.71	144.87	106.28	139.81
$D_2\!-\!St_4\!-\!(St_5)$					
135.00	160.00	124.05	141.29	149.74	167.55
$D_2\!-\!St_5\!-\!(S_2)$					
150.00	135.00	135.94	147.09	148.50	132.66
$D_3\!-\!St_1\!-\!(St_1)$					
135.00	150.00	137.79	135.00	91.18	133.12
$D_4\!-\!St_5\!-\!(D_4)$					
130.00	130.00	161.00	105.30	149.67	133.87
$S_2\!-\!S_2\!-\!(St_5)$					
140.00	140.00	140.53	119.13	119.13	146.45
$S_2\!-\!S_4\!-\!(D_2)$					
150.00	150.00	122.67	172.26	127.15	134.16
$S_2\!-\!St_3\!-\!(St_3)$					
145.00	150.00	124.85	123.19	113.55	110.72
$S_2\!-\!St_4\!-\!(D_1)$					
135.00	165.00	119.97	115.00	167.03	115.56
$S_2\!-\!St_5\!-\!(S_2)$					
140.00	140.00	141.06	119.13	146.88	120.00
$S_3\!-\!St_4\!-\!(S_2)$					
140.00	140.00	141.57	119.19	145.55	119.41
$S_4\!-\!St_1\!-\!(St_5)$					
135.00	140.00	147.45	135.00	179.14	135.53
$S_4\!-\!St_3\!-\!(St_1)$					
165.00	135.00	119.34	159.30	106.30	120.33
$S_4\!-\!St_4\!-\!(D_1)$					
135.00	165.00	120.14	174.75	167.03	161.73
$S_4\!-\!St_5\!-\!(St_5)$					
135.00	140.00	143.93	174.75	146.88	144.04

Table III. (continued)

$\angle\text{Si}-\text{O}-\text{Si}$			$\angle(\text{O}-\text{O}-\text{O})_{br}$		
$\text{St}_1-\text{St}_1-(\text{D}_2)$					
155.00	130.00	134.47	155.00	130.00	155.00
$\text{St}_1-\text{St}_2-(\text{D}_2)$					
130.00	165.00	122.92	130.00	107.46	144.61
$\text{St}_1-\text{St}_3-(\text{D}_2)$					
135.00	140.00	147.45	135.00	108.94	153.93
$\text{St}_1-\text{St}_4-(\text{D}_1)$					
135.00	150.00	137.79	135.00	154.10	147.82
$\text{St}_1-\text{St}_5-(\text{D}_2)$					
135.00	140.00	142.06	135.00	146.88	167.23
$\text{St}_2-\text{St}_3-(\text{S}_2)$					
145.00	140.00	133.18	90.23	108.94	100.97
$\text{St}_2-\text{St}_4-(\text{D}_2)$					
145.00	125.00	151.37	144.60	132.86	151.76
$\text{St}_2-\text{St}_5-(\text{D}_4)$					
120.00	179.88	120.00	149.58	120.00	137.51
$\text{St}_3-\text{St}_4-(\text{St}_4)$					
120.00	179.88	120.00	128.68	120.00	120.00
$\text{St}_3-\text{St}_5-(\text{St}_4)$					
150.00	150.00	120.72	141.86	113.55	125.16
$\text{St}_4-\text{St}_4-(\text{St}_5)$					
130.00	170.00	121.50	137.06	171.35	145.34
$\text{St}_4-\text{St}_5-(\text{D}_2)$					
125.00	145.00	151.37	132.86	144.60	151.73
$\text{St}_5-\text{St}_5-(\text{D}_2)$					
150.00	150.00	120.00	141.86	141.86	137.51

Table IV. $\angle$Si—O—Si and $\angle$(O—O—O)$_{br}$ for bustamite (B) and wollastonite (W).

	B[1]	Ca—B[1]	Mn—B[1]	Fe—B[2]	
$\angle$Si2—O7—Si3	135.59°	138.15°	139.17°	137.50°	*
$\angle$Si1—O8—Si3	135.80°	136.19°	134.95°	134.01°	**
$\angle$Si1—O9—Si2	160.80°	155.47°	159.91°	162.49°	
AVE$\angle$Si—O—Si	144.06°	143.25°	144.68°	144.67°	
$\angle$O9—O7—O8	153.33°	156.27°	154.30°	155.15°	
$\angle$O9—O8—O7	148.87°	150.17°	148.84°	146.37°	
$\angle$O7—O9—O8	122.74°	126.75°	123.05°	121.94°	
AVE$\angle$(O—O—O)$_{br}$	141.65°	144.40°	142.06°	141.15°	

	W[3]		Mn—W[1]	Fe—W[1]	Para—W[4]
$\angle$Si1—O7—Si3	139.24°		139.37°	139.18°	140.24°
$\angle$Si2—O8—Si3	140.18°		140.08°	139.88°	140.42°
$\angle$Si1—O9—Si2	149.14°		150.54°	151.11°	149.33°
AVE$\angle$Si—O—Si	142.85°		143.33°	143.39°	144.33°
$\angle$O9—O7—O8	155.37°		155.02°	154.72°	156.46°
$\angle$O9—O8—O7	156.67°		156.37°	156.25°	155.84°
$\angle$O7—O9—O8	132.00°		131.41°	130.99°	132.30°
AVE$\angle$(O—O—O)$_{br}$	148.01°		147.60°	147.32°	148.20°

* $\angle$Si1—O7—Si3
** $\angle$Si2—O8—Si3
[1] Osashi and Finger (1978)
[2] Rapoport and Burnham (1973)
[3] Peacor and Prewitt (1963)
[4] Trojer (1968)

steps were usually 5° increments. The chains for each set of angular values was then checked to determine that the $\angle$Si–O–Si and $\angle$(O–O–O)$_{br}$ satisfied the previously mentioned angular restrictions. Energy calculations were then undertaken for 61 out of aproximatively 182,000 chains generated. Over one half of these chains also have the smallest possible difference between their individual $\angle$Si–O–Si and therefore the largest average d(Si–Si).

As shown on Figure 3 an infinite three–repeat chain can be represented by three segments each one consisting of three symmetry non–equivalent tetrahedra. However the fourth tetrahedron was included to more fully describe all the atomic interactions. It is also necessary to ascertain that these three segments have comparable energies; i.e. The second and third neighbour interactions are relatively small. The largest variation in energy between two segments of the same chain shown on Figure 3 is 0.001 %.

In all cases hydrogen atoms were appended to the non–bridging oxygen atoms at a distance of 0.95 A and with $\angle$Si–O–H of 180°. The resulting $Si_4O_{13}H_{10}$ cluster is neutral.

2. Results of energy calculations

It can be shown that for chains with average $\angle$Si–O–Si equal to a constant those chains with all $\angle$Si–O–Si equal to the average have the largest d(Si–Si). The total energy of chains
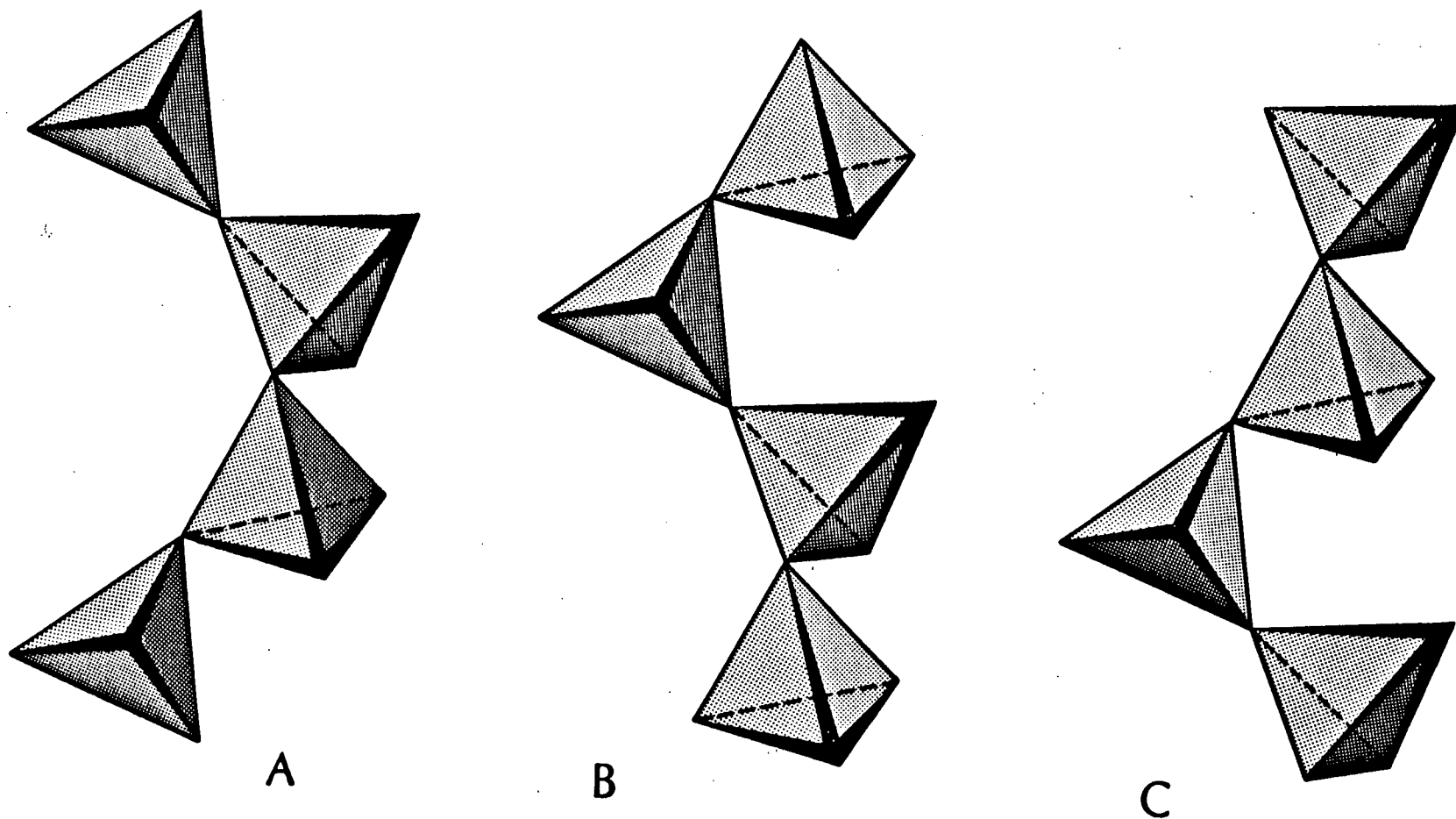
Figure 3. Three segments of the same chain whose energies are -256.172, -256.170 and -256.170 A.U respectively.

can then be related to the $\angle$Si—O—Si through the d(Si—Si).

Figure 4 shows a plot of total energy against the average d(Si—Si) in the cluster. The total energy varies between -256.168 and -256.147 A.U. While the average d(Si—Si) ranges from 2.93 to 3.04 A. A weak negative correlation exists between these two as indicated by the regression equation with regression coefficient 0.63.

$$E = 267 \ (42) - 0.142 \ (14) \ d(Si-Si) \qquad R^2 = .63$$

For this population of chains with average $\angle$Si—O—Si approximatively equal to 140°, those with all three $\angle$Si—O—Si close to the average generally have lower energy than those with $\angle$Si—O—Si covering a wider angle.

Figure 5 shows six plots of total energy vs average d(Si—Si). The top row includes chains with combinations of double and single—eclipsed pairs. Since the spacing between every other bar on the vertical scale is of the same order of magnitude as the discrepancy between calculations on the different segments of the same chain; no statistically significant trend can be observed from the diagram for the chains with a double and a single—eclipsed pair or those with two single—eclipsed pairs. All diagrams in the first row contain very few points reflecting geometry constraints on these chains. The chains composed of double and single—eclipsed pairs and those composed of two single—eclipsed pairs have a narrower range of average d(Si—Si) than the chains composed of two double—eclipsed pairs.

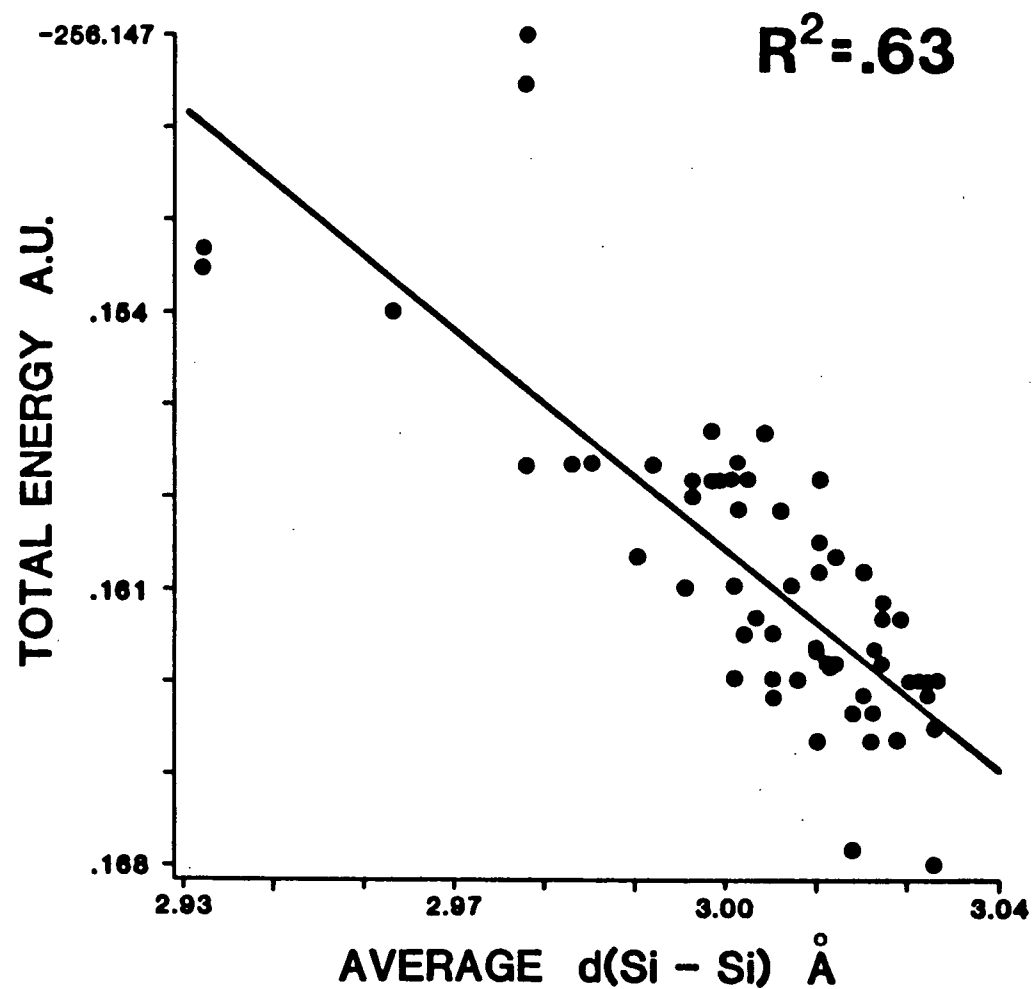The second row includes chains composed of combinations of

Figure 4. Total energy (A.U.) against average d(Si–Si) (A) , those chains with the largest d(Si–Si) have the lowest energy. [the spacing on the horizontal axis is 0.012 A the inaccuracy reflects the round–off error]
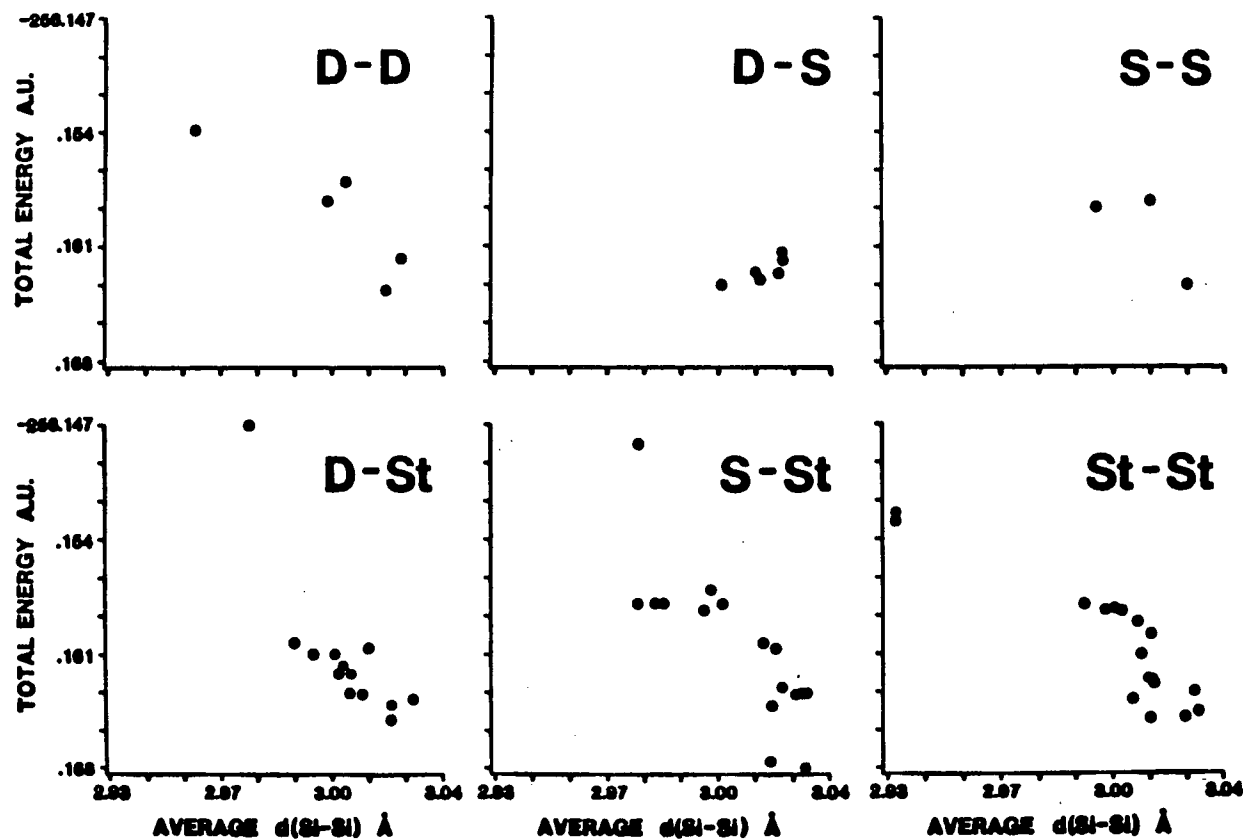
Figure 5. Total energy (A.U.) against average d(Si—Si) (A) , for each
group of chains. [the spacing on the horizontal axis is 0.012 A the
inaccuracy reflects the round—off error]

one staggered pair with either a single or a double—eclipsed pair or another staggered pair. All of these combinations have a larger number of chains. The first two diagrams show a range of d(Si—Si) between 2.97 and 3.03 A. However in the first case the energy varies between -256.163 and -256.147 A.U. While in the second case it varies between -256.168 and -256.147 A.U. Although chains consisting of a staggered pair and either a double or a single—eclipsed pair cover the same range of average d(Si—Si) the latter group has chains with a lower energy. In both cases the chains with the highest energy has one ∠Si—O—Si less than 110°. The last diagram shows a range of average d(Si—Si) between 2.93 and 3.03 A with energy varying between -256.164 and -256.152 A.U. The two chains with the higest energy are those with two ∠Si—O—Si equal to 120°. In this case the range of average d(Si—Si) is wider than in the previous examples.

Although a combination of single and staggered pairs yield chains with the lowest energy i.e. -256.167 A.U. Any combination including at least a staggered pair of tetrahedra tend to have a lower energy than a chain containing no such pair.

Figure 6 shows the wollastonite chain and the chain generated which is closest in comformation. Figures 7 and 8 illustrate the chains with the lowest energy in each of the six groups of theoretical chains
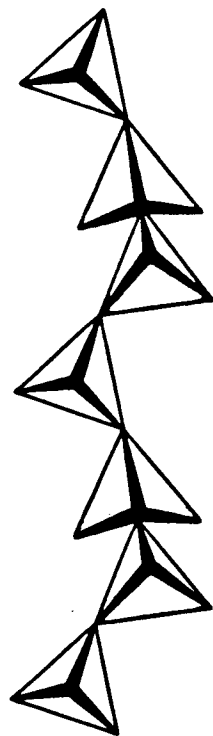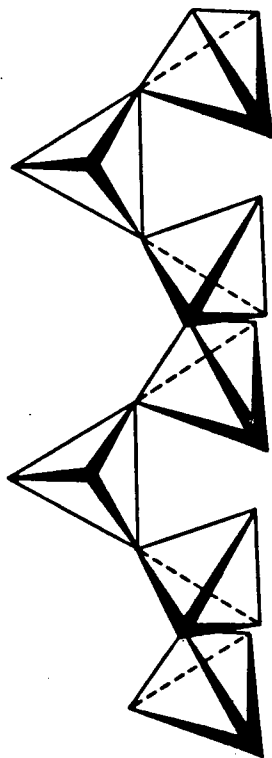
3. Packing of chains
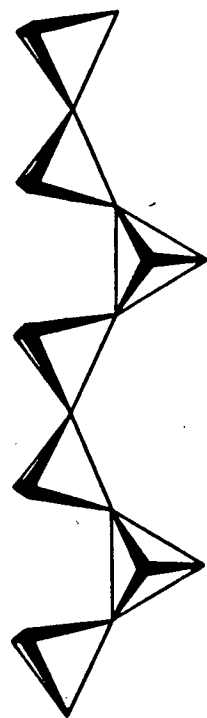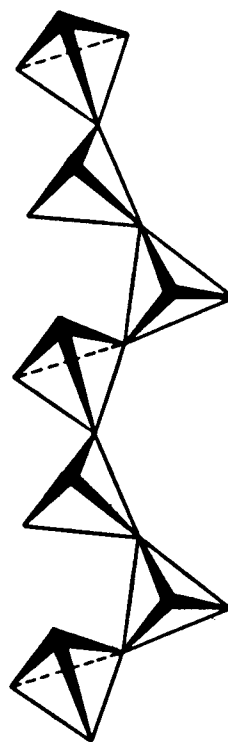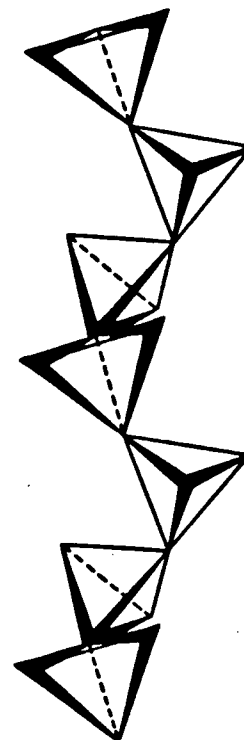
WOLLASTONITE $D_1 - D_2 - St_4$

Figure 6. Wollastonite (Buerger and Prewitt,1961) and its closest approximation with total energy -256.158 A.U.

$D_2-D_2-D_2$ $D_1-S_2-St_4$ $S_2-S_2-St_5$

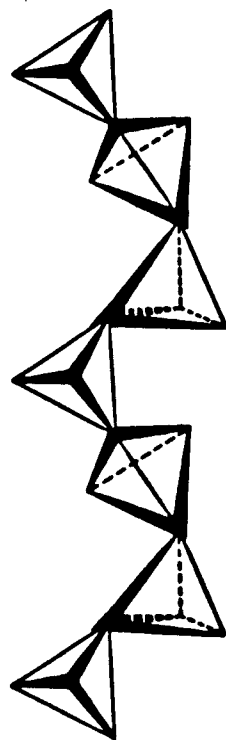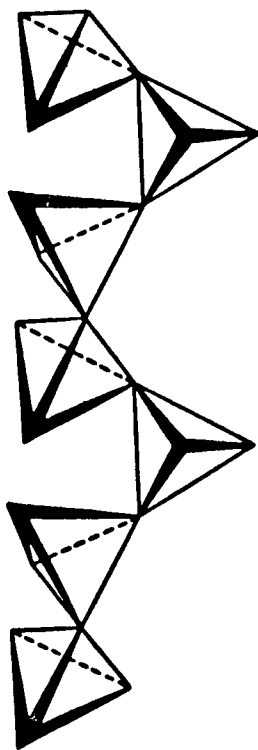Figure 7. Chains containing a combination of double or single—eclipsed pairs with energies -256.164, -256.163 and -256.163 A.U. respectively.

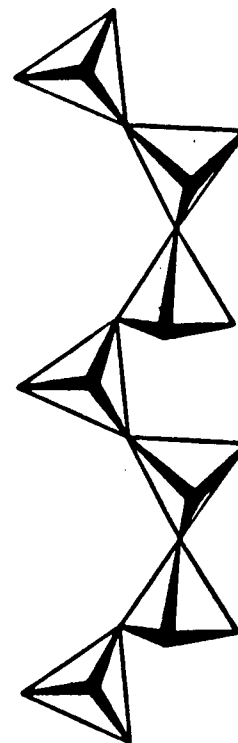$$D_2 - St_3 - St_1 \qquad S_2 - St_4 - D_2 \qquad St_1 - St_3 - D_2$$

Figure 8. Chains containing a staggered pair of tetrahedra with either a double or single eclipsed or another staggered pair. Energies are -256.165, -256.167 and -256.164 A.U. respectively.

Liebau (1980) defined the stretching factor of a chain as

$$f = \frac{I^{chain}}{l_c^{max} \, p}$$

where I^{chain} is the length of the chain, l_c^{max} is the length of the tetrahedral edge and p is the periodicity. The stretching factor of odd repeat chains is larger than that of even repeat chains. It appears to be related to the electronegativity and the radii of the interstitial cations. A regression of total energy against the stretching factor for the theoretical chains gives a regression coefficient of 0.01 showing that no correlation exist i.e., there is no tendency for a straighter chain to have a lower energy. Of those low energy chains generated in this study only the $S_2-St_4-(D_2)$ and $S_3-St_4-(D_2)$ chains appear unlikely to lend themselves to close packing. A further study is required to determine if the remaining chains can be packed such that interstitial cations can be coordinated in a crystal chemically reasonnable manner.

VI. CONCLUSION

The total energy of three-repeat chains is influenced by two factors. First, chains with the largest d(Si-Si), i.e, those with all three $\angle$Si-O-Si equal to 140° have the lowest energy. Secondly, chains with at least a staggered pair of tetrahedra also have a lower energy than those with no such pair. This is

in keeping with the fact that for pairs of tetrahedra with a constant $\angle$Si—O—Si the staggered conformation has a lower energy than either the single or double—eclipsed pairs. It is noteworthy that the two lowest energy two—repeat chains are the sodium silicate type which is composed of two pairs of staggered tetrahedra and the pyroxene type which is composed of two pairs of single—eclipsed tetrahedra.

Under the geometric restrictions of this study there exist three—repeat chains different from the one type found in nature and the energy of a number of these chains is as low or lower than that of the closest approximation to the wollastonite type. In the group of two—repeat chains those of lowest energy happen to pack in such a way as to accommodate interstitial cations. In the three—repeat chains there appear to be many low energy chains which cannot pack together such as to provide suitable sites for interstitial cations. Further investigation is necessary to determine if it is possible to optimize both the average d(Si—Si) and the bonding requirements of the interstitial cations for chains different from the wollastonite type. No correletion was found between the stretching factor and the energy of three—repeat chains indicating no tendency for straighter chains to have lower energy.

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