The Use of Molecular-Orbital Calculations on Model Systems for the Prediction of Bridging-Bond-Angle Variations in Siloxanes, Silicates, Silicon Nitrides and Silicon Sulfides

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CNDO/2 molecular-orbital calculations are shown to predict trends in bridging angle, $\angle T{-}Y{-}T$, with reasonable accuracy for gas-phase molecules of the type TX_3YTX_3, where Y is an anion ($= O$, OH, S, NH) bridging the tetrahedrally coordinated cations $T (= C$, Si, Al, Be, B) and where X are the nonbridging anions ($=H$, F). For example, calculated equilibrium $\angle T{-}O{-}T$ are 100, 125 and 150° in CH_3OCH_3, SiH_3OCH_3 and SiH_3OSiH_3, respectively, compared to experimental values of 111, 121 and 144°. The equilibrium $\angle Si{-}O{-}Si$ in SiH_3OSiH_3 is also in close agreement with the average value of this angle (148°) in the silica polymorphs. The SiH_3YTH_3 molecule is proposed as a model system for studying bridging bond angles in silicates and is found to give bridging-angle trends in reasonable agreement with those observed in Si-containing solids. In particular, calculations on SiH_3YSiH_3 predict $\angle Si{-}Y{-}Si$ to decrease from 150 to 130 to 109° as Y is changed from O to NH to S, in agreement with observed average angles of 144, 120 and 110°, respectively, in silicates, silicon nitrides and silicon sulfides. For SiH_3OSiH_3 the equilibrium $\angle Si{-}O{-}Si$ is calculated to increase as the Si–O bond distance decreases, at a rate within a factor of two of that observed for the silica polymorphs. Calculations on clusters with Be or B replacing Si invariably lead to predicted equilibrium $\angle Si{-}O{-}T$ values from 125 to 105°, in accord with the small angles that tend to be observed for such bridge bonds in minerals. Since $Si(3d)$ orbitals are excluded in these calculations, it is apparent that the observed angular trends can be explained without invoking $d{-}p\,\pi$ bonding. Inspection of one and two-center energy components of the CNDO/2 total energy also shows that the form of the Si–T interaction is not that of a nonbonded repulsion.

I. Introduction

In the gas-phase molecule CH_3OCH_3, the $\angle C{-}O{-}C$ (C–O–C bridging bond angle) is observed to be 111° (Kimura & Kubo, 1959); in SiH_3OSiH_3, the $\angle Si{-}O{-}Si$ is 144° (Almenningen, Hedberg & Seip, 1963). This difference has been ascribed alternatively to the effect of $Si(3d){-}O(2p)\,\pi$ bonding (Cruickshank, 1961) or to the effect of repulsions between the positively charged Si atoms (Mitchell, 1969). On the other hand, CH_3SCH_3 and SiH_3SSiH_3 have virtually identical bond angles at sulfur of 99 (Pierce & Hayashi, 1961) and 97° (Almenningen, Bastiansen, Ewig, Hedberg & Trætteberg, 1963), respectively, a fact difficult to reconcile in terms of either $d{-}p\,\pi$ bonding or Si–Si repulsions.

In silicate minerals the angles observed at bridging oxygens show a fairly large range of values between ~125 (Hesse, 1977; Petter, Harnick & Keppler, 1971) and 180° (Smolin & Shepelev, 1970; Tossell & Gibbs, 1977). The absence of Si–O–Si angles less than ~125°

has precluded the formation of *einereinfachkette* and *einerdoppelkette* chain silicate structures (Noll, 1968), *e.g.* chain silicates that have one tetrahedron in the repeating unit. Topologically similar chain structures are, however, observed in the germanate $CuGeO_3$ (Liebau, 1962) and in the mineral sillimanite, Al_2SiO_5, in which Si and Al atoms alternate along a chain and the $\angle Si{-}O{-}Al$ along and across the chain are ~115 and ~170° respectively (Burnham, 1963). On the other hand, in Be- and B-bearing silicates the observed $\angle Si{-}O{-}Be$ and $\angle Si{-}O{-}B$ show a small range (115–145°) of values and an even smaller range (110–125°) is observed for Si–N–Si and Si–S–Si angles in silicon nitrides and sulfides. For Si–O–Si linkages in silicates a correlation has been observed between the Si–O bond distance, $d(Si{-}O)$, and $\angle Si{-}O{-}Si$, with shorter Si–O bonds tending to be associated with wider angles (Brown & Gibbs, 1970; Tossell & Gibbs, 1977).

To explain the above observations we report here quantum-mechanical calculations using the CNDO/2 method for a number of molecular clusters having the

general formula $TX_3YT'X'_3$, where T and T' are tetra-hedrally coordinated atoms, X and X' are three nonbridging ligands attached to them and Y is a bridging ligand connecting the two tetrahedral groups (Fig. 1).

It is sometimes asserted that studies on molecules can reveal little about the geometries of solids. However, we believe that the chemical interactions are essentially identical in gas-phase molecules and solids and that carefully chosen molecules can therefore be useful as model systems for describing bond angles in solids. Differences between the model system and the real system will of course lead to differences in detail between calculated and observed angles, but we will demonstrate that qualitative trends are reproduced correctly.

An advantage of using a molecular model system approach is that we can vary the composition and geometry of a model system in almost any way desired and examine the effect of these variations on the bridging angle. An empirical approach can establish a correlation between two quantities but cannot establish a cause and effect relation, since there are invariably other quantities besides the ones considered that change from one material to another. For example, we cannot experimentally substitute Be for Si in a silicate to form a Si—O—Be bridge bond without at the same time increasing the coordination number of the bridging oxygen. Hence, we cannot discern whether the accompanying reduction in Si—O—Be bridge angle is due to the replacement of Si by Be, to the increased coordination number of O, or to both effects. Using a model system we can easily distinguish these two effects, as will be shown.

Our objectives in this paper are: (1) to obtain semi-quantitative predictions of $\angle T-Y-T'$ for gas-phase molecules with the CNDO/2 method, (2) to use the molecular clusters as model systems for predicting average values and ranges of bridging bond angles in silicates and related solids, (3) to explain the observed angles and their ranges in terms of specific chemical interactions between atoms, and (4) to assess the validity of qualitative bonding concepts previously proposed for explaining bridging angles. In § II we discuss the application of the CNDO/2 method to this

problem while our fulfillment of objectives (1), (2), (3) and (4) above are discussed in §§ III, IV, V and VI respectively.

II. Application of the CNDO/2 method to bond-angle studies

The CNDO/2 method (Pople, Santry & Segal, 1965; Pople & Beveridge, 1970) has been widely used in organic chemistry and has more recently been applied to inorganic chemistry and mineralogy (Santry, 1968; Gordon, 1969; deJong & Brown, 1975; Tossell & Gibbs, 1976). A comprehensive study of the ability of the method to predict bond angles for molecules containing third-period elements has been made by Marsh & Gordon (1976). Although agreement of results was poorer than that for corresponding second-period molecules, most bond-angle trends were reproduced reasonably well. Our recent study (Tossell & Gibbs, 1976) of the distortion of edge-sharing SiO_4^{4-} and SiS_4^{4-} polyhedra showed that molecular-orbital cluster calculations could provide semiquantitative predictions of bridging-bond angles in the tetrahedral edge-sharing compounds SiO_2 (silica–W) and SiS_2. The Si—Y—Si angles observed are 87 and 80°, respectively, much smaller than those observed in corner-sharing linkages, while those predicted were 96 and 88°. The variation in equilibrium $\angle O-Si-O$ when a silicate tetrahedron shares an edge with another silicate tetrahedron, a Mg-containing octahedron or a Li-containing tetrahedron was also predicted with reasonable accuracy. These results supported our belief in the efficacy of a molecular model systems approach to solids and encouraged the present study. On the other hand, the CNDO/2 method has been found to fail to describe accurately nonbonded repulsions between H atoms or lone pairs (Gregory & Paddon-Row, 1976). We apparently encounter a problem of this type in a CH_3SCH_3 calculation described herein.

A nagging problem in CNDO/2 calculations for third-period elements is whether or not to include Si($3d$) orbitals in the basis set. Accumulating theoretical evidence indicates that Si($3d$) participation has little effect upon the energies of the MO's of silicates. Both CNDO/2 calculations (see, for example, Jonas, Schweitzer, Grimm & Carlson, 1972) and ab initio SCF Hartree–Fock minimal basis set calculations (Collins, Cruickshank & Breeze, 1972) which include Si($3d$) orbitals invariably lead to erroneously large Si($3d$) participation and to ionization potentials for MO's with Si($3d$) character which are considerably larger than those observed experimentally (Tossell, 1975). Recent band-structure calculations for α-quartz (Chelikowsky & Schluter, 1977) also have found little Si($3d$)-orbital participation, although these calculations did not accurately predict the intensities in the Si L X-

(a)

(b)

Fig. 1. Geometries of TX_3YTX_3 (a) singly eclipsed, and (b) doubly eclipsed.

ray emission spectrum, suggesting that $Si(3d)$ orbital participation may affect spectral intensities more strongly than energies. Since the CNDO/2 method obtains bonding parameters semiempirically, it is conceivable that an s,p,d' atomic orbital basis set with carefully chosen $3d$ parameters (Santry, 1968) could give better results than one using s,p orbitals only. In a previous study (Tossell & Gibbs, 1976) on edge-sharing SiO_4^{4-} and SiS_4^{4-} tetrahedra, we found that trends and interpretations were similar for s,p and s,p,d' basis sets, with the absolute values of $\angle X$–Si–X being more accurate for the s,p,d' basis. Here we find the s,p basis to give more accurate results for corner-sharing tetrahedra. This difference probably results from the fact that the Si–Si separations are larger in the present studies of corner-sharing tetrahedra than in our previous study of edge-sharing tetrahedra and flexibility in the Si basis set is therefore less necessary.

Before describing the corner-shared tetrahedra results we should note that our calculated equilibrium bond distances for the Si_2 molecule are 2·48 without and 2·09 Å with $Si(3d)$ orbitals, compared to an experimental distance of 2·25 Å. All calculations used the CNDO/2 method implemented for a slightly modified version of $QCPE$ 141. Bonding parameters $\frac{1}{2}(I + A)$ and $\beta°$ were taken from the tabulation of Santry (1968) for Si and S and from Santry & Segal (1967) for H, Be, B, C, N, O and F. For Al, the Santry (1968) values were extrapolated to give $-6·8$ for $\beta_{Al}°$ while the value of Santry & Segal (1967) was used for $\frac{1}{2}(I + A)_{Al}$. In the calculations employing only s and p orbitals on third-row elements the Santry (1968) s,p parameters were used without change. A one and two-center energy analysis was completed with the expressions utilized by Gordon (1969).

In our calculations all bond distances were taken from experimental values and all angles within the tetrahedra were set equal to 109·5°. We have assumed the so-called doubly eclipsed conformation for dimethyl ether, dimethylsulfide and methylsilyl ether and the singly eclipsed conformation for disilyl ether and the other compounds (Fig. 1). In the doubly eclipsed conformation four H atoms from the two TH_3 groups become close, while in the singly eclipsed conformation two H atoms become close as $\angle T$–Y–T' is decreased. For molecules with small equilibrium $\angle T$–Y–T', the difference in energy of the two conformations is significant; however, when the equilibrium $\angle T$–Y–T' is large, the two conformations are practically identical in energy. For example, in SiH_3OSiH_3 with $d(Si$–$O) = 1·63$ Å and $\angle Si$–O–Si at its equilibrium value of 144°, the two conformations differ in energy in our calculations by about 2 kcal mol^{-1}, with the singly eclipsed being more stable. These energy differences are considerably smaller than those observed for $\angle Si$–O–Si variation. The calculated equilibrium angles for the two conformations also differ by only a couple of

degrees. Thus, for sake of simplicity, we shall ignore the question of conformation and concentrate upon the variation of energy with $\angle T$–Y–T'. We shall also ignore the possibility of tilting of the TX_3 group axis away from the T–Y bond direction since electron-diffraction studies generally show such tilting to be small.

III. CNDO/2 results

Curves of total energy vs T–O–T' angle are shown in Fig. 2 for s,p CNDO/2 calculations on CH_3OCH_3, CH_3OSiH_3 and SiH_3OSiH_3; clearly, the calculated equilibrium angle widens along this series. The interpolated minimum-energy angles, from three-point parabolic fits to the calculated points, are shown in Table 1 and are seen to be in reasonable agreement with experiment.

Since $Si(3d)$ orbitals were excluded in these calculations, it is clear that the experimental results can be explained, at least semi-quantitatively, without invoking $Si(3d)$–$O(2p)$ π bonding. This is in accord with the results of Bartell, Su & Yow (1970) and Gibbs, Hamil, Louisnathan, Bartell & Yow (1972), who found that trends in bond-overlap populations obtained with extended Hückel calculations were in reasonable agreement with expected bond-length variations in compounds containing third-period elements, whether or not they included $3d$ orbitals in the basis set. If $Si(3d)$ orbitals are included in the basis set, the CNDO/2 results actually deteriorate. The calculated
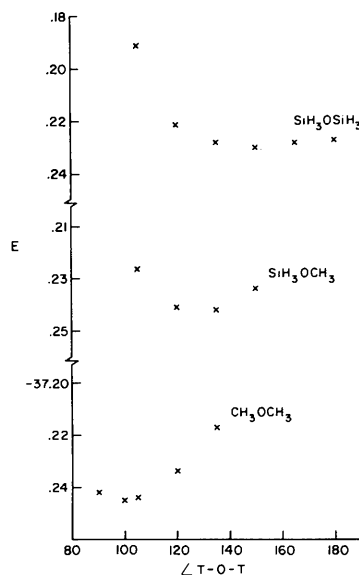

Fig. 2. Calculated total energy vs $\angle T$–O–T for CH_3OCH_3, SiH_3-OCH_3 and SiH_3OSiH_3 [$d(Si$–$O) = 1·63$ Å]; energies in hartrees, 1 hartree $= 627·51$ kcal mol^{-1}.

$\angle$Si—O—Si is too narrow, as shown in Fig. 3. We find that the use of the Santry & Segal (1967) s,p parameter set also leads to an equilibrium angle of about 125°.

We also find reasonable agreement between calculated and observed bridging angles along the series CH_3OCH_3, CH_3OSiF_3, SiF_3OSiF_3, as shown in Table 1, with the fluoride angles being wider than those in the analogous hydrides.

We attribute this partly to the larger F—F nonbonded repulsions and partly to the shorter d(Si—O) in the fluorides, requiring a wider bridging angle to obtain a fixed Si—Si separation. The difference between calculation and experiment for these compounds may well arise from limitations of the CNDO/2 method, although it is conceivable that the results could be

improved by searching for the most stable conformation by varying the angles of tilt and twist on the terminal TX_3 groups. Also, the experimental electron diffraction results for SiF_3OSiF_3 do not preclude the possibility of a straight Si—O—Si angle, although later IR work also suggests a bent angle (Durig, Kalasinsky & Flanagan, 1975; Durig, Flanagan & Kalasinsky, 1975).

Along the series SiH_3OSiH_3, SiH_3NHSiH_3, SiH_3SSiH_3, the CNDO/2 minimum-energy $\angle$Si—Y—Si values decrease in reasonable agreement with experiment (Table 1). For CH_3SCH_3, however, the calculated angle is ~30° too narrow. This is probably a result of the underestimation of the H—H nonbonded repulsions by the CNDO/2 method (Gregory & Paddon-Row, 1976). For the remaining molecules, other factors prevent the H atoms from approaching closely and thus the total energy does not strongly depend on the magnitude of their nonbonded repulsions. For CH_3SCH_3 the C—C interactions are so attractive that the $\angle$C—S—C becomes too small without an adequate accounting of the repulsion between the H atoms on the two CH_3 groups.

We have also calculated equilibrium $\angle$Si—O—T' for the molecular clusters $(SiH_3OAlH_3)^{1-}$, SiH_3OAlH_3 (doublet state from open-shell CNDO/2 calculation), $(SiH_3OBeH_3)^{2-}$, $(SiH_3OHBeH_3)^{1-}$ and $(SiH_3OBH_3)^{1-}$ as shown in Table 2. For singly eclipsed conformations the Al-containing clusters have calculated equilibrium angles of about 150°, while the two Be-containing clusters have angles of 124° for $(SiH_3OBeH_3)^{2-}$ with

Table 1. *Calculated and experimental T—Y—T' angles (°)*

Compound	Calculated angle	Experimental angle
CH_3OCH_3	100	111[a]
CH_3OSiH_3	125	121[b]
SiH_3OSiH_3	150	144[c]
CH_3OSiF_3	139	131[d]
SiF_3OSiF_3	180	156[e]
CH_3SCH_3	70	99[f]
SiH_3SSiH_3	109	97[g]
SiH_3NHSiH_3	130	128[h]

References: (a) Kimura & Kubo (1959). (b) Glidewell, Rankin, Robiette, Sheldrick, Beagley & Freeman (1970). (c) Almenningen, Hedberg & Seip (1963). (d) Airey, Glidewell, Robiette & Sheldrick (1971). (e) Airey, Glidewell, Rankin, Robiette, Sheldrick & Cruickshank (1970). (f) Pierce & Hayashi (1961). (g) Almenningen, Bastiansen, Ewig, Hedeberg & Trætteberg (1963). (h) Rankin et al. (1969).

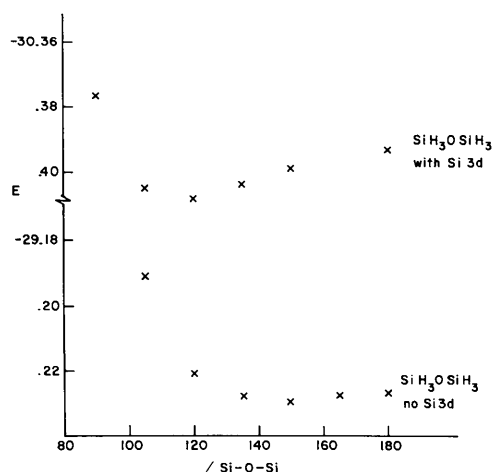Table 2. *Calculated and experimental $\angle$Si—O—T for molecular clusters containing Al, Be or B*

	$\angle$Si—O—T	
Cluster	Calculated	Average experimental
$(SiH_3OAlH_3)^{1-}$	150°	137°
$(SiH_3OBeH_3)^{2-}$	124[a], 114[b]	125
$(SiH_3OHBeH_3)^{1-}$	114[a], 104[b]	
$(SiH_3OBH_3)^{1-}$	127	128

(a) Singly eclipsed. (b) Doubly eclipsed.

Table 3. *$\angle$Si—O—Si and d(Si—Si) as a function of d(Si—O) for SiH_3OSiH_3, singly eclipsed*

d(Si—O)	$\angle$Si—O—Si (calculated)	d(Si—Si) (calculated)
1·58 Å	167°	3·14 Å
1·61	155	3·14
1·63	150	3·15
1·66	142	3·14
1·70	136	3·15

Fig. 3. Calculated total energy vs $\angle$Si—O—Si for SiH_3OSiH_3 with and without Si(3d) orbitals in basis set.

a bridging oxygen and 114° for $(SiH_3OHBeH_3)^{1-}$ with an OH bridging group and the B-containing cluster shows an equilibrium angle of 127°.

Calculations for SiH_3OSiH_3 with d(Si—O) from 1·70 to 1·58 Å also show that the equilibrium $\angle$Si—O—Si increases as d(Si—O) decreases (Table 3 and Fig. 4). Although force constants are known for only a few siloxanes, it is observed that in general the Si—O—Si bending force constant decreases and the Si—O stretching force constant increases as the $\angle$Si—O—Si increases (Lazarev, Poiker & Tenisheva, 1967). Such a reduction in bending force constant at large angle is in accord with the flatness of the energy minimum in SiH_3OSiH_3 [d(Si—O) = 1·58 Å] and in SiF_3OSiF_3 [d(Si—O) = 1·58]. The Si—O stretching force constant correlates directly with $\angle$Si—O—Si, both because larger bridging angles are associated with shorter and thus stronger bridge bonds and because widening the $\angle$Si—O—Si (at constant Si—O) itself leads to a stronger bond, as indicated by a more negative value of the Si—O two-center energy.

IV. Application of CNDO/2 gas-phase molecule results to minerals

The observed $\angle$Si—O—Si in SiH_3OSiH_3 (144°) is very similar both to the bridging angles observed in other siloxanes and to the average bridging angle (148°) in the silica polymorphs coesite, low quartz, low cristobalite and low tridymite. However, the angles in the SiO_2 polymorphs display a fairly large range (135–180°) of values. Despite the even larger range of $\angle$Si—O—Si ($\sim$125 to 180°) recorded for the silicates (Fig. 5) and vitreous silica (Mozzi & Warren, 1969), the mean angle for the populations (144°) is identical with the bridging angle in SiH_3OSiH_3.

This may be understood by examining the energy curve for SiH_3OSiH_3 (Fig. 2). The curve shows a parabolic portion near the minimum of 150°, a steep portion at narrower angles, and a flat portion from 160 to 180°. Thus the $\angle$Si—O—Si may be easily increased from its gas-phase value in order to accommodate the bonding and packing requirements and the varying sizes of the M cations in a crystal structure without destabilizing the resulting configuration excessively. Although a crystal structure will not form unless most of the bonding and geometrical requirements are satisfied, it is doubtful whether all the requirements need be exactly satisfied in a complex structure like a silicate. On the other hand, such adjustment stresses should be inadequate to overcome the intrinsic instability of $\angle$Si—O—Si below $\sim$125°. Thus the SiH_3OSiH_3 total-energy curve qualitatively explains the wide range of Si—O—Si angles recorded for silicates, the average bridging angle of 144° and the exclusion of angles below $\sim$125°.

To model the effect of d(Si—O) on the equilibrium $\angle$Si—O—Si, we have completed calculations with d(Si—O) values of 1·58, 1·61, 1·63, 1·66 and 1·70 Å for SiH_3OSiH_3 in the singly eclipsed conformation and d(Si—O) values of 1·61 and 1·66 Å in the doubly eclipsed conformation. Energy curves are shown in Fig. 4 for 1·58, 1·63 and 1·70 Å singly eclipsed. Clearly the minimum-energy angle decreases as d(Si—O) is increased with the minimum becoming sharper and better defined. Interpolated equilibrium angles and the resulting Si—Si distances are given in Table 3; note the essential constancy of Si—Si distance. It has been observed that d(Si—O) and $-\sec \angle$Si—O—Si are linearly correlated in silicates with a partial correlation coefficient $R = 0.63$ (Gibbs et al., 1972). A plot of the negative secant of the calculated equilibrium angle vs
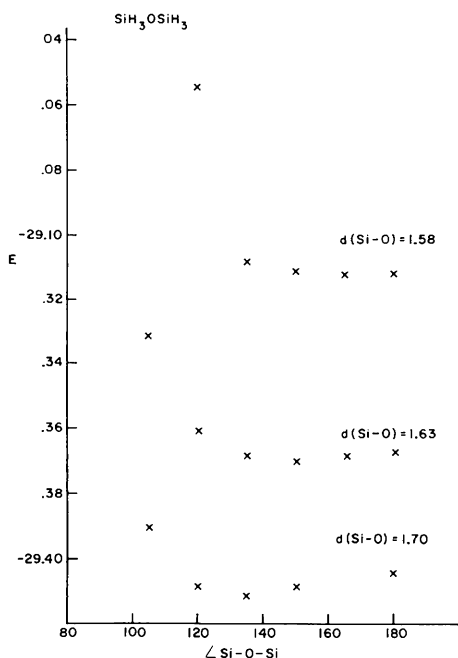

Fig. 4. Calculated total energy vs $\angle$Si—O—Si for SiH_3OSiH_3, singly eclipsed and d(Si—O) = 1·58, 1·63 and 1·70 Å.
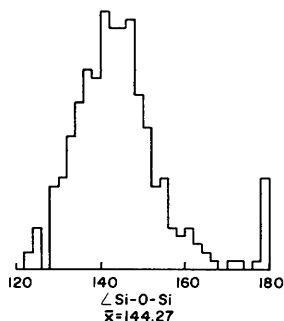
Fig. 5. Histogram of $\angle$Si—O—Si observed in silicates (obtained from a literature search through 1976).

d(Si—O) is given in Fig. 6. We also include a line corresponding to d(Si—Si) = 3·10 Å, which is twice the 'one-angle' nonbonded radius of Si derived by Glidewell (1975). Finally, we plot the mean Si—O bond length for each tetrahedron in the silica polymorphs vs the average $-\sec\angle$Si—O—Si value of the four Si—O—Si angles involving the tetrahedron and the regression line through these experimental points (Meagher, Tossell & Gibbs, 1977).

Clearly, the experimental and calculated trends are in the same direction, although they differ in slope by a factor of about two. The points from the CNDO/2 calculations lie at lower values of $-\sec\angle$Si—O—Si, consistent with the observation that the calculated angles are slightly but consistently larger than the experimental ones. Since the secant is a rapidly varying function, Fig. 6 tends to accentuate the discrepancy between calculation and experiment. In terms of slope, the CNDO/2 points and the line with d(Si—Si) = 3·10 Å are similar. The line for constant d(Si—Si) is definitely curved, while there is a suggestion of curvature in the CNDO/2 points. However, since the curvature is small, the experimental data for a small range of d(Si—O) may be approximately fitted by a straight line.

The difference between the slope from the CNDO/2 calculations and that obtained for the silica polymorphs may arise from a number of sources. First, as we have seen, the CNDO/2 calculated angles are sometimes appreciably in error for gas-phase molecules. Second, the SiH$_3$OSiH$_3$ molecule is only a simple model system for silicates and differs from them in many respects. In the silica polymorphs the 'nonbonding' anions are, of course, all bridging oxygens, rather than hydrogens. The calculated $\angle$Si—O—Si would certainly be different for Si(OH)$_3$OSi(OH)$_3$ and the trend of angle vs d(Si—O) might be quantitatively different. Perhaps more importantly, in the silica polymorphs each silicate group is bridge-bonded to four others and adjustment stresses resulting from these polyhedral linkages (Baur, 1971) and O—O nonbonded repulsions may modify the angles (Ribbe, Phillips & Gibbs, 1974). Indeed, the surprising thing is the existence of such a simple trend for the silica polymorphs and the qualitative agreement of experiment and calculation. For more general classes of silicate minerals, with different degrees of polymerization of the silicate tetrahedra and

Table 4. *Calculated and experimental* $\angle$Si—Y—Si (°) *and* d(Si—Si) (Å) *in gas-phase molecules and solids*

Compound	$\angle$Si—Y—Si			d(Si—Si)		
	Calculated	Experimental (g)	(s)	Calculated	Experimental (g)	(s)
SiH$_3$OSiH$_3$	151	144	144 (SiO$_2$)	3·16	3·10	3·10
SiH$_3$NHSiH$_3$	130	128	118 (α-Si$_3$N$_4$)^a	3·12	3·10	2·98
SiH$_3$SSiH$_3$	109	98	109^b, 115^c	3·50	3·21	3·50

(a) Marchand, Laurent, Lang & Lebihan (1969). (b) SiS$_2$, high-pressure polymorph with BPO$_4$ structure (Prewitt & Young, 1965). (c) Si$_2$S$_7^{6-}$ ion in Ag$_{10}$Si$_3$S$_{11}$ (Mandt & Krebs, 1976).
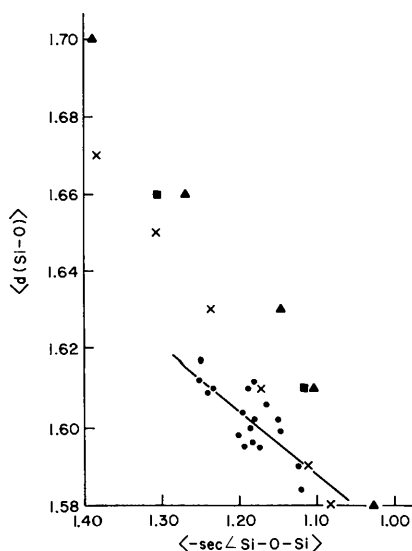
Fig. 6. $\langle$(Si—O)$\rangle$ vs $\langle-\sec\angle$Si—O—Si$\rangle$; ▲, ■, points from CNDO/2 calculations for singly and doubly eclipsed geometries respectively; ×, points from assumption d(Si—Si) = constant = 3·10 Å; ●, experimental data for SiO$_2$ polymorphs; ———, regression line to experimental data points.
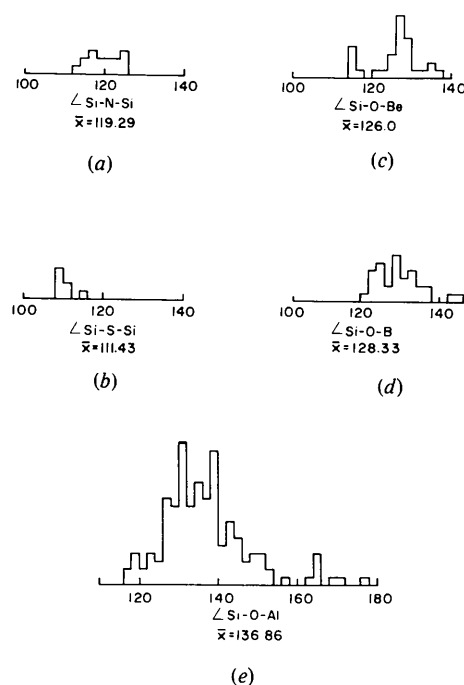
Fig. 7. Histograms of observed $\angle$Si—Y—T: (a) Si—N—Si, (b) Si—S—Si, (c) Si—O—Be, (d) Si—O—B, (e) Si—O—Al (obtained from literature searches through 1976).

with different nontetrahedral M cations, the distance vs angle correlation may be poorly developed (Baur, 1977). On the other hand, we have established that the SiH_3OSiH_3 model system gives a semiquantitatively correct picture of equilibrium $\angle Si-O-Si$ and its dependence on $d(Si-O)$, matching the experimental data for the silica polymorphs which lack nontetrahedral cations.

We also find that the CNDO/2 gas-phase molecule results describe the difference between $\angle Si-O-Si$ and $\angle Si-S-Si$ reasonably well. In Table 4 we give calculated and experimental angles and $d(Si-Si)$ in selected solids and gas-phase molecules for $Si-O-Si$, $Si-NH-Si$ and $Si-S-Si$ linkages. Note that the average angles in the gas and solid phases are fairly similar.

Unlike the total energy vs angle curves calculated for SiH_3OSiH_3, the curves for SiH_3NHSiH_3 and SiH_3SSiH_3 are sharper and better developed, indicating that the range of $\angle Si-N-Si$ and $\angle Si-S-Si$ in silicon nitrides and sulfides should be less than that observed for $\angle Si-O-Si$ in silicates. Frequency distributions of angles observed in these solids conform with this assertion as evinced by Fig. 7(a) and (b) which show $\angle Si-N-Si$ and $\angle Si-S-Si$ to range from 110 to 130° and 105 to 115° respectively. Also note that the average $\angle Si-N-Si$ and $\angle Si-S-Si$ of 119 and 112° are in reasonable agreement with the calculated minimum-energy angles of 130 and 109° respectively.

The $Si-O-T'$ minimum-energy angle is also found to be reduced when we replace one of the Si atoms in disilyl ether by B or Be. Table 2 compares these minimum energy angles with average values recorded for a large number of B-, Al- and Be-bearing silicates. It has been previously observed (Brown & Gibbs, 1970) that tetrahedra containing Mg, Al, Be, B tend to have smaller average $T-O-T'$ angles than those between Si-containing tetrahedra. This result has been difficult to verify for certain Al–Si systems because Al and Si are similar in size, because they possess about the same number of electrons and because these cations are often disordered in a structure. On the other hand, in the case of Be- and B-bearing silicates, the tetrahedral cations are rarely disordered and $Si-O-Si$, $Si-O-Be$ and $Si-O-B$ linkages are thus distinct.

A frequency distribution of the angles recorded for beryllium silicates (Fig. 7c) shows $\angle Si-O-Be$ to range between 115 and 140°. Despite the fair agreement between the mean angle (125°) for this distribution and the minimum-energy value calculated for $(SiH_3-OBeH_3)^{2-}$, the molecule is an unrealistic model for $Si-O-Be$ linkages in a silicate because the bridging oxygen in the model system is underbonded in the Pauling (1929) sense. That is, it receives a bond strength sum, p_O, of only 1·5 e.s.u., while in most silicates bridging oxygen atoms tend to receive a p_O value fairly close to 2·0 e.s.u. We may (over) compensate for this by protonating the bridging oxygen to obtain the cluster $(SiH_3-$

$OHBeH_3)^{1-}$ with a p_O value of 2·5 e.s.u. For this latter cluster, the calculated minimum energy $\angle Si-O-Be$ decreases to 114°, about the same as the narrowest angle recorded to date in Be-bearing silicates where p_O ~2·0 (Zachariasen, 1972). This is in accord with the general observation that an increase in coordination number for the bridging oxygen tends to result in a decrease in the bridging angle.

The minimum-energy angle (127°) for $(SiH_3-OBH_3)^{1-}$ is in close agreement with the average Si–O–B angle (128°) observed for the borosilicates and the range is from 120 to 140° (Fig. 7d). The calculated minimum-energy angle (150°) for $(SiH_3OAlH_3)^{1-}$ is about 10° greater than the average $Si-O-Al$ angle found for Al-bearing silicates (137°) while the majority of values recorded for $\angle Si-O-Al$ range between 115 and 170° (Fig. 7e). The calculated value is essentially the same as that for SiH_3OSiH_3, even though observed $\angle Si-O-Al$ are narrower than $\angle Si-O-Si$.

In Fig. 8 we plot on a common scale the energy vs bridging angle curves for the clusters studied. It is apparent from a comparison of Figs. 5, 7 and 8 that those bridging bonds with steeper slopes for their energy vs angle curves show narrower distributions of experimental angles. Thus, the molecular-model calculations give information on both the average bridging angles in solids and upon the range of variation to be expected.

V. Chemical effects determining the minimum energy bridging angle

Although any decomposition of the total energy of a molecule into components is necessarily arbitrary, we have found in the past that the analysis of the energy
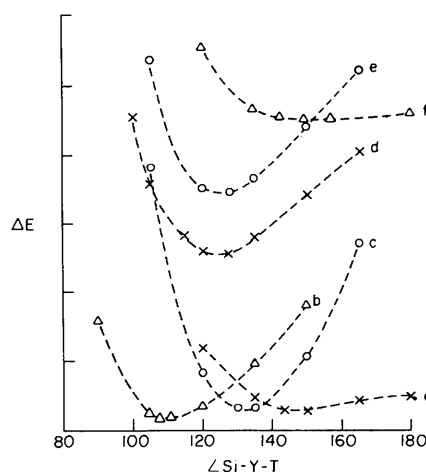

Fig. 8. Calculated total energy vs $\angle Si-Y-T$ for: (a) SiH_3OSiH_3. (b) SiH_3SSiH_3, (c) SiH_3NHSiH_3, (d) $SiH_3OBeH_3^{2-}$, (e) $SiH_3OBH_3^{1-}$ and (f) $SiH_3OAlH_3^{1-}$. Energy divisions on vertical scale are equal to 0·01 hartrees = 6·3 kcal mol^{-1}.

into one and two-center terms utilized by Gordon (1969) provides considerable insight into bonding forces. In many cases the total-energy trend is found to be closely related to changes in certain two-center energy terms. The two-center energy terms incorporate both ionic and covalent contributions to the total energy (unlike bond-overlap populations which are associated only with covalency) and can give a rough measure of the strength of a bond. Plots of the Si—Si and the Si—O two-center energies as a function of $\angle$Si—O—Si are given in Fig. 9 for SiH_3OSiH_3 with d(Si—O) = 1·63 Å. Trends in Si—Si and Si—O energy are similar for all the other d(Si—O) values. Although the Si—Si interaction is repulsive, it has a minimum at a d(Si—Si) value of about 2·6 Å. In Si_2 on the other hand, the E_{Si-Si}, term is negative and has its minimum at about 2·1 Å. Thus, the Si—Si interaction appears to depend strongly on the chemical state of the Si. However, in SiH_3OSiH_3 the minimum in total energy does not occur at d(Si—Si) = 2·6 Å. Since E_{Si-O} becomes progressively more negative as $\angle$Si—O—Si widens, the minimum total energy actually occurs at about d(Si—Si) = 3·15 Å. The equilibrium values of d(Si—Si) are closely equal to 3·15 Å for all bond lengths between 1·58 and 1·70 Å because the slopes of E_{Si-O} vs $\angle$Si—O—Si and E_{Si-Si} vs $\angle$Si—O—Si are virtually identical for the various d(Si—O). Since the nature of the competition betweeen the Si—O and Si—Si interactions does not change, the minimum energy d(Si—Si) remains constant and $\angle$Si—O—Si thus decreases as d(Si—O) increases.

For SiH_3SSiH_3 we find the plots of E_{Si-S} and E_{Si-Si} to be similar to the analogous plots for SiH_3OSiH_3. However, in each case the slope of the plots as a function of angle is slightly smaller. The balance of
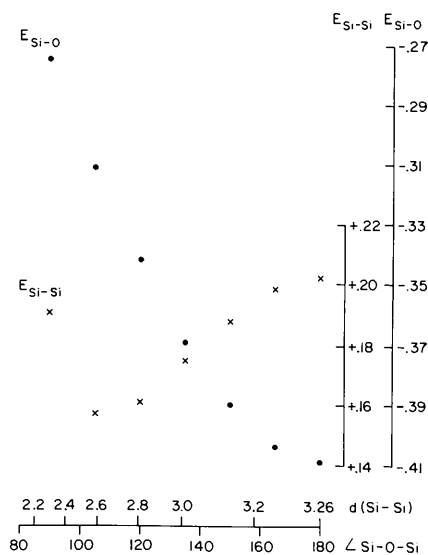
Si—S and Si—Si forces leads to a longer d(Si—Si) of 3·50 Å. Nonetheless, because of the larger Si—S distance, this Si—Si distance corresponds to an $\angle$Si—S—Si of only 109°. Thus the smaller bridging angle in SiH_3SSiH_3 (compared with SiH_3OSiH_3) is a result of the similarity of Si—Si interactions in the two molecules and the larger Si—S bond distance.

In SiH_3NHSiH_3 we find E_{Si-Si} to have its minimum at a substantially longer d(Si—Si) of 3·10 Å. Since E_{Si-N} changes rather slowly as a function of $\angle$Si—N—Si, the equilibrium Si—Si distance is about 3·12 Å and the $\angle$Si—N—Si consequently 130°. Thus, although the Si—Si equilibrium distances in SiH_3OSiH_3 and SiH_3NHSiH_3 are very similar, they result not from a constant nonbonded repulsion between the Si atoms but from a competition of Si—Si and Si—Y interactions which is different in the two molecules.

VI. Assessment of theories proposed to explain bonding in silicates

Our results indicate that simple MO calculations neglecting $Si(3d)$ orbitals are adequate to explain experimental data that had previously been explained on the basis of $3d$-orbital participation. This is consistent with earlier approximate MO calculations (Gibbs et al., 1972; Tossell & Gibbs, 1976) showing identical calculated trends with and without $3d$ orbitals. Thus, by Occam's razor (i.e. the assertion that the number of different concepts brought into the theory should be kept small), it would seem prudent to discard the $d-p$ π bonding interpretation of these phenomena. We admit the possibility that $3d$-orbital participation in the bonding in these compounds may affect some of their properties, but we do not consider it to be of chemical significance for describing ground-state geometries.

Recently, Baur (1971, 1977) concluded that the variation in d(Si—O) is independent of $\angle$Si—O—Si in silicates in which $p_O = 2·0$ and that the geometry of a silicate group cannot be understood by considering only those forces internal to the group. Although the relation of d(Si—O) to $\angle$Si—O—Si will be explored in more detail elsewhere (Meagher, Tossell & Gibbs, 1978), we note for the silica polymorphs in which $p_O = 2·0$ that a weighted linear-regression analysis of accurately refined data shows the correlation between d(Si—O) vs —sec $\angle$Si—O—Si to be highly significant with a correlation coefficient $r = 0·91$. Meagher & Gibbs (1976) completed a weighted linear regression on the d(Si—O) and $\angle$Si—O—Si data for the five silica polymorphs studied by Baur (1971, Table 7); the data for the four pyrosilicates were excluded because their bond-length data were considered to belong to a population distinct from that of the silica polymorphs. The analysis permitted them to reject the null hypothesis (at the

Fig. 9. Si—O and Si—Si two-center energies vs $\angle$Si—O—Si for SiH_3-$OSiH_3$, d(Si—O) = 1·63 Å.

0.001 level) that there is no relation between d(Si—O) and $\angle$Si—O—Si.

A correlation of d(Si—O) with $\angle$Si—O—Si has even been found for the pyrosilicates ($r = -0.72$) by Baur (1971), where variations in oxygen coordination number and the identity of the nontetrahedral cations might be expected to obscure the correlation. However, he considered the correlation to be independent of Cruickshank's (1961) π-bonding theory and to be a secondary consequence of his empirical extended electrostatic valence rule. Ribbe, Gibbs & Hamil (1977) have shown that d(Si—O) is highly correlated with $-$sec $\angle$Si—O—Si for a population consisting of five ring silicates and four cyclosiloxanes. In addition, similar correlations have been obtained for the feldspars (Brown, Gibbs & Ribbe, 1969), selected silicates (Brown & Gibbs, 1970), the zeolites (Gibbs, Meagher, Smith & Pluth, 1977) and cordierite (Cohen, Ross & Gibbs, 1977).

These experimental observations are consistent with our calculations, which show a clear dependence of $-$sec $\angle$Si—O—Si on d(Si—O) although less extreme than that observed experimentally. Thus, although effects arising outside the SiX_3YSiX_3 cluster can modify $\angle$Si—Y—Si, the main chemical effects on the angle seem to be internal to the cluster.

In the same way, effects internal to the SiX_3OTX_3 cluster cause the $\angle$Si—O—T to be reduced when B or Be is substituted for Si. The reduction in $\angle$Si—O—T equilibrium angle is therefore not simply a result of increased coordination number for the bridging oxygen (Baur, 1971), although our (SiH$_3$OHBeH$_3$)$^{1-}$ calculations do show that increased coordination number results in an additional reduction in $\angle$Si—O—T.

It has recently been proposed that $\angle T$—Y—T' equilibrium angles can be understood in terms of 'one-angle' nonbonded radii, intermediate in size between covalent and van der Waals radii (Glidewell, 1975, 1977; O'Keeffe & Hyde, 1976). We indeed find that the calculated equilibrium Si—Si distance in SiH$_3$OSiH$_3$ does remain constant at about 3.15 Å as the Si—O distance is changed. However, the concept of a nonbonded radius seems to us to imply that the Si—Si repulsion should increase dramatically when the Si atoms approach to the sum of their nonbonded radii. However, our energy analysis is not in accord with this expectation. Rather than finding the Si—Si interactions becoming sharply repulsive around 3.1 Å, as the nonbonded-radius argument suggests, we find a minimum in the Si—Si two-center energy around 2.6 Å. The (near) constancy of d(Si—Si) in the oxides is therefore not a result of Si—Si repulsions alone, but arises from the competition of Si—O and Si—Si interactions, as described in § V. Consistent with this is the dependence of d(Si—Si) on the ligand. In silicon nitrides d(Si—Si) is in the range 2.9–3.1 Å while in the sulfide it is 3.2–3.5 Å. The difference in equilibrium Si—Si

distance is a result of a difference in the dependence of Si—Si and Si—Y two-center energies upon angle. It is also important to note that although the most probable value of d(Si—Si) in silicates is about 3.10 Å, shorter distances are not really uncommon. For example, in vitreous silica Si—Si distances of 2.92 Å are half as probable as those of 3.10 Å (Mozzi & Warren, 1969, Fig. 5). This suggests a dependence of total energy on d(Si—Si) considerably less extreme than that of a nonbonded repulsion.

Thus, we are not convinced that the replacement of the d—p π-bonding theory by the nonbonded-radius concept is a theoretical advance in the description of these materials, although in practice it can estimate closest-approach distances for T atoms. Since quantum-mechanical methods can now be usefully applied to such problems, the qualitative concepts used for description should be consistent with the quantum-mechanical results. Thus, although the nonbonded-radius concept gives accurate T—T distances for oxides, we are of the opinion that the T—T interaction does not correspond to that of a steeply repulsive potential. Further studies, with more accurate quantum-mechanical methods, will be needed to confirm this interpretation.

VII. Conclusions

The CNDO/2 method gives reasonably good predictions of bridging bond angles in gas-phase molecules of formula TX_3YTX_3. In particular, it distinguishes well between angles at bridging O, NH and S and accurately describes the effect of replacing Si by Be or B. However, for Si—O—Al linkages the observed angles are smaller than those calculated. This is probably a result of a poor choice for the β_{Al}^o parameter. Using the Santry & Segal (1967) value rather than our extrapolated value gives a calculated minimum-energy angle of about 125° for (SiH$_3$OAlH$_3$)$^{1-}$. Clearly, the question of parameter choice needs further study.

Calculated minimum-energy $\angle$Si—Y—Si are also consistent with observed angles and trends in solids. The calculated dependence of $\angle$Si—O—Si on d(Si—O) is also similar, although not identical, to that observed in the silica polymorphs. Angular trends can be reasonably interpreted in terms of a competition of Si—Si and Si—Y interactions. Our results are inconsistent with both the d—p π-bonding theory and the concept of a steeply repulsive nonbonded interaction between the T atoms.

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