A theoretical study of the Si-O bond in disiloxane and related molecules

Raymond J. Abraham and Guy H. Grant

The School of Chemistry, The University of Liverpool, P.O.Box 147, Liverpool L69 3BX, U.K.

SUMMARY

A comparison of semi-empirical (MNDO) and ab initio (GAUSSIAN) calculations for disiloxane and related molecules is given. The STO-3G* basis set well reproduced the observed geometries of disiloxane (<SiOSi observed 144°, calculated 140°), dimethoxy-dimethylsilane (<OSiO obsd tetrahedral, calc 102°), methyl silyl ether (<COSi obsd 121°, calc 118°) and correctly predicted the planar geometry found for cyclo-trisiloxane. In contrast, more complex basis sets (3-21G(*), DZP, TZVP) gave much poorer agreement with the observed geometries.

Comparison of the STO-3G* and the STO-3G basis sets demonstrates the necessity of including d-orbitals on the silicon. However, the semi-empirical MNDO program gave, despite the absence of d-orbitals, a better approximation to the molecular geometry than the complex ab initio basis sets.

Force field parameters have been calculated for k_{SiOSi}, k_{OSiO}, 0.089 and 0.73 mdyneÅ/rad², and the SiOSiO torsion which has a V_1 potential of –0.68 kcal/mol. In addition, the HSiOH torsion is shown to have a three-fold potential of 0.78 kcal/mol. These are profoundly different from the analogous carbon-oxygen force constants, demonstrating that C-O parameters cannot be transferred to the corresponding Si-O systems.

INTRODUCTION

The molecular mechanics method [1] is widely regarded as a useful method for structural determination, and in the case of large molecular systems, where a quantum-mechanical approach may be prohibitive, accurate structural information may be obtained. In order that a molecular mechanics force field accurately reproduces the results from other methods, experimental or ab initio, it is necessary to obtain a reliable and consistent set of force field parameters. One method of achieving this is by application of MO calculations to model compounds [2].

The nature of the bond between silicon and any electronegative atom, especially oxygen, has been the subject of considerable debate [3–8]. Various studies, both experimental and theoretical, have attempted to investigate the importance of d_π-p_π bonding and its effect upon the molecular structure of these molecules, but the picture is still unclear.

Disiloxane is the most frequently discussed molecule of this type, and because it is the simplest molecule containing the SiOSi unit it is of extra importance as a model compound for larger SiO systems such as zeolites and silicates. The SiOSi bond angle in disiloxane is found to be 144.1° [9] and it is this considerable deviation from an sp^3 oxygen, together with the shortening of the SiO bond length which has provoked much of the discussion.

The two most commonly encountered explanations for this distortion in geometry are d_π-p_π bonding [9,10] and coulombic effects [6,7]. The d_π-p_π argument is based upon the fact that two of the silicon d-orbitals (x^2-y^2 and z^2) are of suitable energy to form strong π bonds [11]. These normally large and diffuse orbitals are contracted by the positively charged silicon core, thus facilitating overlap with oxygen p-orbitals. Although the main contribution to this anomalous behaviour is attributed to d_π-p_π overlap it is important to note that minor effects such as the variability of the bridging bond angle and changes in the SiO bond length have been attributed not to d_π-p_π bonding but to coulombic and steric effects [7].

The opposing argument, which has been presented in a number of studies [6–8] can be summarised as follows: All unusual effects found when considering the SiO link (or any bond between silicon and electronegative atom) can be attributed solely to coulombic and steric effects. These studies [6–8] have been made on disiloxane using relatively large, flexible basis sets: in the first [8], optimisation of the whole molecule was attempted using STO-3G and 4-31G (the effect of omitting d-functions was being investigated); the results showed that although 4-31G could reproduce most structural features of the molecule it failed completely to handle the SiOSi angle (the final result gave a bond angle of 180°), but on the other hand STO-3G produced an energy minimum with $<$ SiOSi $\sim$ 124°. Both can be seen to be unsuitable models but the 4-31G geometry was compared to two experimental determinations of the structure which pointed to the molecule being virtually linear: in an attempted microwave determination [12] the experimental spectrum could not be analysed in terms of a non-linear structure, Sauer and Zurawski's final conclusion [8] was that the structure could be a 'quasi-linear double rotor with a low-energy hump for the linear SiOSi chain'. This type of structure has also been reported from a Raman study [13].

Other theoretical investigations of disiloxane [6,7] have used d-functions but the interpretation of the results has tended to focus on the silicon, although Ernst et al. [7] stated that polarisation functions are needed on the oxygen to reproduce the experimental SiOSi angle. Hehre et al. [14] discuss whether the d-orbitals included in a starred basis set are essentially polarisation functions which compensate for the inadequacy of the sp basis set, or if they can actually be considered to represent explicit inclusion of d-orbitals. They also have shown that, in the case of ammonium oxide, the overlap populations between the oxygen p-orbitals and nitrogen d-orbitals are a reflection of π back donation. The silicon oxygen bond presents a similar situation. In contrast, von Schleyer [15] states that 'the phenomena attributed to d_π-p_π bonding have other causes, in particular negative hyperconjugation with electron donation into σ^*, rather than into d-orbitals'.

In a more recent study Grigoras and Lane [16] have carried out an extensive series of ab initio calculations on disiloxane to determine the effect of polarisation functions at the 3-21G level. They find that two possible values of the silicon exponent (0.3 and 0.9) can be used and have modified the standard 3-21G* [17] basis set to include the optimum value of 0.3. These calculations give the optimised value of the SiOSi angle to be 149.5°, slightly higher than the experimental value [9].

The object of this work is to investigate silicon oxygen containing molecules using ab initio and semi-empirical techniques. Once a reasonable theoretical model for these compounds has been

found it will then be possible to use these model compounds in calculations to determine force constants for use in a molecular mechanics type model of zeolites.

It should, however, be taken into account that when deciding upon the best level of theory to use one must bear in mind that '... the final choice of detailed quantum mechanical model ... must ultimately depend not only on the established levels of performance, but also on practical considerations ... even HF/STO-G3 and HF/3-21G often perform remarkably well in calculating certain properties. In these cases it is not necessary to employ more sophisticated treatments' [14].

The molecules under consideration are disiloxane, methyl silyl ether, silanol, dimethoxy-dimethylsilane, cyclotrisiloxane and hydroxydisiloxane (see Fig. 1). Cyclotrisiloxane is a very interesting case as the experimental geometry of the closely related hexamethyl cyclotrisiloxane [18] is found to be planar and also has a very open SiOSi angle.

RESULTS AND DISCUSSION

Complete optimisations were attempted on four of the molecules under consideration using the MNDO [19] program, as part of the MOPAC [20] package. Also single point and partial optimi-
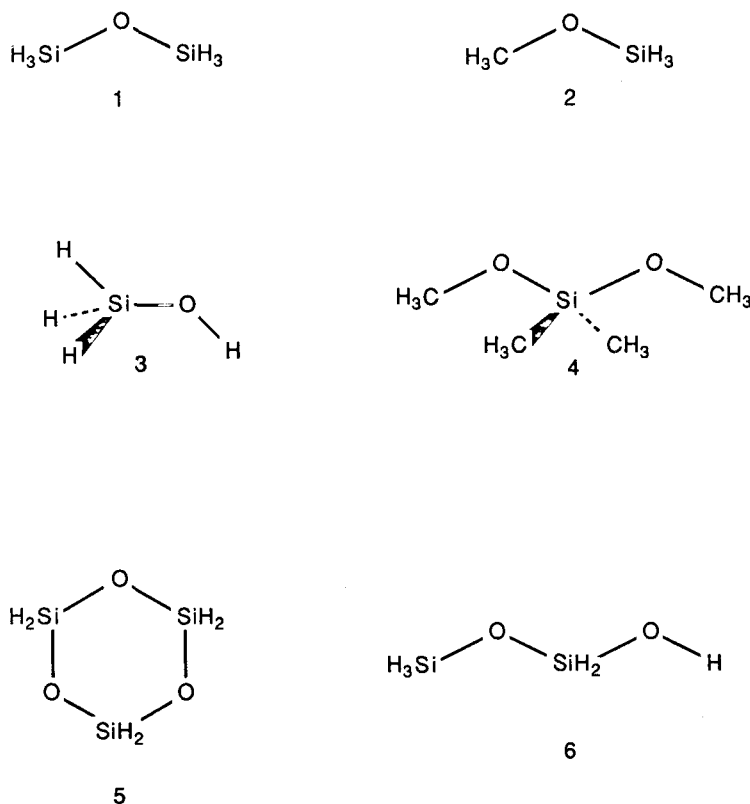

Fig. 1 Molecular structures of disiloxane (1), methyl silyl ether (2), silanol (3), dimethoxy-dimethylsilane (4), cyclotrisiloxane (5) and hydroxydisiloxane (6).

sations were carried out using the various basis sets allowed in the GAUSSIAN76 [21] and GAMESS [22–24] programs.

Disiloxane

A number of optimisations were carried out using various large basis sets such as double and triple zeta [23,24] with polarisation functions on Si and O. In each case the SiOSi angle was optimised to a value close to 180.00°, a considerable deviation from the experimental value (see Table 1). We therefore discarded these basis sets as being unsuitable to model systems containing the SiOSi moiety.

The inclusion of polarisation functions in the minimal STO-3G basis set leads to a better reproduction of the molecular dipole moment for a number of silicon compounds [25]. In the case of disiloxane, calculations without polarisation functions have been reported [8] using STO-3G but, as mentioned earlier, this basis set does not reproduce the experimental SiOSi bond angle very well (calc 124°; exptl 144.1°). Thus it is of some interest to evaluate the effect of polarisation functions in this basic molecule, and for a series of fixed SiOSi bond angles, optimisation of the SiO bond length and molecular energy was performed with the STO-3G and STO-3G* basis sets. The results are presented in Fig. 2 and show very clearly the considerable difference in the molecular energy versus < SiOSi for the two basis sets, which will of course be directly reflected in the calculated force constants. For this reason we use henceforth the STO-3G* basis set to calculate the molecular force constants.

The force constants were obtained by calculating the single point energy at small increments ($< 1°$ for a bond angle, <0.01 Å for a bond length) on either side of the minimum energy value, and then fitting a suitable parabola to these points; we assume that the bond stretching and bending potentials are parabolic close to the minimum. The calculated values of the force constants are k_{SiO} 1.86 mdyne/Å, and k_{SiOSi} 0.089 mdyneÅ/rad^2. The stretching constant for the SiO bond is found to be small when compared to experimentally derived values which have been calculated

TABLE 1

CALCULATED AND EXPERIMENTAL GEOMETRIES FOR DISILOXANE

	Experimental	Calculated						
		MNDO[a]	STO-3G*[b]	STO-3G*[a]	STO-3G[b]	3-21G(*)[a]	3-21G*[b]	TZVP[b]
r_{SiO}	1.64	1.67	1.58*	1.58	1.66*	1.63	1.64	1.64
r_{SiH_A}[c]	1.48	1.45	1.48	1.43	1.48	1.47	1.48	1.48
r_{SiH_B}[c]	1.48	1.44	1.48	1.43	1.48	1.47	1.48	1.48
< SiOSi	144.10	157.51	140.00*	137.72	124.53*	180.00	160.74*	180.00*
< H_ASiO[c]	109.90	107.61	109.90	108.72	109.90	110.35	109.90	109.90
< H_BSiO[3]	109.90	108.04	109.90	110.45	109.90	110.14	109.90	109.90
μ D	0.24	0.42	0.93	0.20	0.69	0.00	0.17	0.00

[a] All structural parameters optimised.
[b] *Parameters optimised.
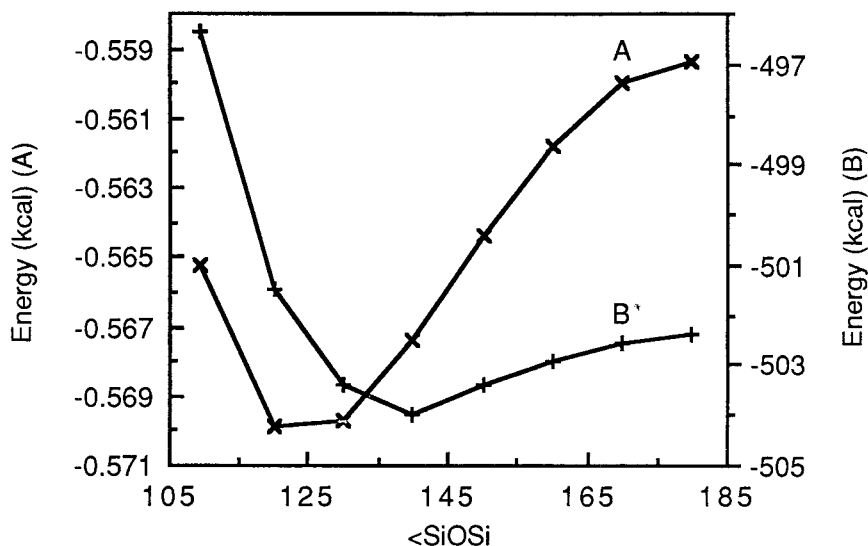[c] H_A in SiOSi plane, H_B out of the plane.

Fig. 2. Comparison of bond angle bending potentials for disiloxane using (A) STO-3G and (B) STO-3G* (all energies given relative to −648.0 hartrees in kcal/mol).

using normal coordinate analysis of vibrational spectra of zeolites (3.48 mdyne/Å)[26] and disiloxane (5.1 mdyne/Å)[27]. This is not unexpected as the STO-3G* basis set underestimates the experimental bond lengths [14] and may therefore also underestimate the force constant for the stretching potential. A similar calculation using STO-3G leads to a very much reduced value of 0.57 mdyne/Å, showing the influence of the d-functions on the bond lengths. The calculated value of k_{SiOSi} is very much smaller than those found for organic molecules (typically 0.1–1.0 mdyneÅ/rad^2). This can be clearly seen in Fig. 2 where the potential well is very shallow; the energy difference between the optimised geometry and a linear SiOSi geometry is in the region of 1.5 kcal/mol. This may account, in part, for the difficulty in obtaining a reasonable optimised geometry for disiloxane and if this is representative of the 'real' situation it is possible to see why there has been considerable confusion and ambiguity surrounding the experimental determinations of its structure [9,10,12,13]. This may also explain the very wide range of SiOSi angles found in silicates and zeolites [28].

For the case of disiloxane a full optimisation of the structural parameters has been done and, as can be seen in Table 1, the STO-3G* basis set still gives a reasonable reproduction of the experimental SiOSi angle, although the SiO and SiH bond lengths are shortened by as much as 0.06 Å, a well documented artifact of the basis set in question [14]. In addition we have attempted calculations using the 3-21G* basis set**, the recommended basis set for second-row elements. This basis set is again unable to restrain the SiOSi angle in disiloxane although the bond lengths which are calculated are in much better agreement with experiment (see Table 1). Unfortunately, due to restrictions in computer time, we were unable to utilise this basis set to calculate k_{SiO}. Even the addi-

tion of polarisation functions to oxygen is insufficient to constrain the SiOSi bond angle; the exponent used for silicon is that of Gordon [29].

In parallel with the ab initio calculations semi-empirical calculations using MNDO were also carried out. The structural parameters obtained from a complete optimisation (all bond lengths and angles relaxed) are also presented in Table 1. As MNDO contains no representation for d-orbitals it is not to be expected that it will reproduce the experimental geometry of compounds containing SiO groups. This is found to be the case and MNDO gives a much more open SiOSi angle and longer SiO bond. However, it is of interest to note that despite the acknowledged approximations of MNDO, the calculated structure for disiloxane is much closer to the experimental than those calculated by the complex ab initio basis sets used earlier.

In conclusion, the ab initio calculations carried out on disiloxane show that the STO-3G* basis set gives a reasonable reproduction of the experimental geometry, as opposed to STO-3G which predicts a less open angle. It is also possible to see why the SiOSi angle is so flexible, and why there is such a wide range of experimental values if we consider the barrier to angle bending; from these calculations this is found to be around 1.5 kcal/mol. Analogous STO-3G calculations give a much larger value (9 kcal/mol), again showing that the inclusion of polarisation functions and d-orbitals is necessary to give a correct description of the molecular and electronic structure of SiO bonds.

Dimethoxy-dimethylsilane

Once k_{SiOSi} and k_{SiO} had been obtained the only remaining force constant to be calculated was k_{OSiO}. Dimethoxy-dimethylsilane was taken as a suitable model compound. Although the geometry has been determined experimentally [30], only a partial description of the molecular structure is given. We assume the conformation of the methoxy groups is anti (i.e., COSiO is trans), and it is then possible to carry out an optimisation of the parameter under consideration (i.e., <OSiO). As previously the OSiO angle was optimised using the STO-3G* basis, together with r_{SiO}: the optimised values (Table 2) again show a distortion from tetrahedral geometry. In silicas and zeolites the OSiO angles will be virtually constrained to take a tetrahedral value (each silicon surrounded by four oxygens) but there is no similar constraint placed upon the geometry at the oxygen atoms.

The single point calculations for the force constant determination were carried out as mentioned previously. The final value calculated for the angle bending constant k_{OSiO} is 0.73 mdyneÅ/rad^2.

In order to further test MNDO for SiO-containing molecules and also to provide a comparison with STO-3G* a complete geometry optimisation (all geometric parameters relaxed) was carried out using MNDO. The final geometry is given in Table 2 together with the experimental geometry, and the STO-3G* geometry.

MNDO again gives a reasonable description of the structure of dimethoxy-dimethylsilane, but with some discrepancies. One is the considerable shortening of the SiC bond. A minor anomaly is the increased CH bond length but experience has shown this to be a systematic discrepancy within the program rather than it being a feature of this molecule. Slightly more important is the contraction of the CO bond which would appear to be an extreme reaction to the opening up of the SiOC bond angle, which is distorted considerably from a typical sp^3 angle, even more so than is found in methyl silyl ether [31] (see later).

TABLE 2
CALCULATED AND EXPERIMENTAL GEOMETRIES FOR DIMETHOXY-DIMETHYLSILANE

	Experimental	Calculated	
		MNDO[a]	STO-3G*[b]
r_{SiO}	1.64	1.66	1.59*
r_{SiC}	1.87	1.81	1.87*
$r_{CH}(MeO)$	1.09	1.12	1.09
$r_{CH}(Me)$	1.09	1.10	1.09
r_{CO}	1.42	1.36	1.42
<OSiO	109.47	100.38	102.38*
<COSi	128.30	134.73	137.42*
dihedral HCOSi	180.00	180.00	180.00

[a] All structural parameters optimised.
[b] *Parameters optimised.

If we consider the main bond angles within dimethoxy-dimethylsilane we see that MNDO reproduces, qualitatively at least, the major distortion which takes place at the oxygen of the methoxy groups. The situation is a little more ambiguous for <OSiO as there is no uniquely determined value for this molecule; an underlying assumption in the analysis of the experimental results was that the silicon was sp^3 with tetrahedrally arranged substituents. The 'best' comparison which can be made is with the optimised geometry using STO-3G*. If this can be considered a reasonable comparison then MNDO again qualitatively predicts the extent of the distortion.

Methyl silyl ether

A series of partial geometry optimisations were carried out on this molecule using a range of basis sets, from the minimal STO-3G and STO-3G* to the considerably more flexible 3-21G(*) and triple zeta, and also a complete optimisation using MNDO.

In addition to these calculations an optimisation of the SiO and CO bond lengths together with <SiOC was attempted using STO-3G and STO-3G*. The results are compared with the experimental geometry in Table 3.

Again the STO-3G* basis set gives much better agreement with the experimental geometry of methyl silyl ether than STO-3G. The STO-3G basis set fails to reproduce the distortion from tetrahedral oxygen due to the silicon substituent and, in fact, the calculated SiOC angle of 113.57° is closer to that of dimethyl ether (<COC 111.0°) where there can be no interaction between the d- and p-orbitals. Also worthy of note is the fact that the value of <SiOC obtained using the 3-21G(*) basis set is much larger than the experimental value and this, together with the previous calculations on disiloxane, would suggest that one must be extremely careful as regards the value taken for the Si d-orbital exponents.

The results from the MNDO optimisation show considerable distortion of the molecular geometry with the SiH bond length being shortened by 0.1 Å; there is also a small degree of contraction of the CO bond and an increase in the COSi angle. This increase of an angle involving Si and O is similar to that found in disiloxane and dimethylsilane (<SiOSi and <SiOC, respectively).

TABLE 3
CALCULATED AND EXPERIMENTAL PARAMETERS FOR METHYL SILYL ETHER

	Experimental	Calculated				
		MNDO[a]	STO-3G*[b]	STO-3G[b]	3-21G*[b]	TZV/TZVP[b,c]
r_{SiO}	1.64	1.66	1.65*	1.67*	1.64	1.64
r_{SiH}	1.48	1.38	1.48	1.48	1.48	1.48
r_{CO}	1.42	1.37	1.43*	1.45*	1.42	1.42
r_{CH}	1.09	1.12	1.09	1.09	1.09	1.09
<COSi	121.00	133.26	117.84*	113.57*	132.72*	126.75*
<H_ASiO[d]	109.47	109.47	109.47	109.47	109.47	109.47
<H_BSiO[d]	109.47	112.11	109.47	109.47	109.47	109.47
<H_CCO	109.47	106.99	109.47	109.47	109.47	109.47
<H_DCO	109.47	109.23	109.47	109.47	109.47	109.47
μ D	1.15	1.0	0.97	1.11	1.47	1.30

[a] All structural parameters optimised.
[b] *Parameters optimised.
[c] TZV on Si; TZVP on C, O, H. When polarisation functions were added to Si, convergence problems occurred.
[d] H_A and H_C in COSi plane, H_B and H_D out-of-plane.

The STO-3G* geometry has been used to calculate a bending constant for COSi; this value is found to be 0.38 mdyneÅ/rad² and is of a similar order of magnitude to many other stretching constants [32].

The calculations on methyl silyl ether again show that STO-3G* performs well for SiO compounds, and compares favourably with larger basis sets.

Cyclotrisiloxane

Although cyclotrisiloxane is the silicon analogue of 2,4,6-trioxan it has been found experimentally, as stated earlier, to have a quite different structure; electron diffraction studies on hexamethyl cyclotrisiloxane [18] show the ring to be planar.

As hexamethyl cyclotrisiloxane is too large to be handled by the programs we have available it was decided to carry out this investigation using cyclotrisiloxane, i.e. no methyl groups. For a cyclic compound with a threefold axis perpendicular to the molecular plane it is necesary to define only one dihedral in order to describe the ring conformation. Using this rationale, ab initio optimisations were carried out using the STO-3G basis set, computer time constraints making this choice necessary, for a range of values of the ring dihedral angle; from the planar ring (0°) through to 60°. For the planar conformation the experimental value of 108.4° of the OSiO angle was assumed and the SiOSi angle calculated accordingly. For the non-planar conformations these angles were optimised for each value of the ring dihedral angle. On obtaining the optimised geometry, single point calculations were then carried out for each conformation using STO-3G* and MNDO to show the variation of energy with respect to changing the ring dihedral. The results are presented in Table 4.

The STO-3G optimisation of the planar conformation gives <SiOSi to be approximately 3°

TABLE 4
PARTIAL GEOMETRY OPTIMISATION RESULTS FOR CYCLOTRISILOXANE

Ring dihedral	< SiOSi	< OSiO	Energy		
			STO-3G*[a]	STO-3G[a]	MNDO[b]
0[c]	131.60	107.80	–	–	–
0	128.76	111.24	–322.81	2.37	0.00
10	128.37	111.14	–323.41	2.25	0.29
20	127.15	110.85	–323.02	1.95	1.27
30	125.08	110.30	–322.99	1.69	3.12
40	122.15	109.37	–321.38	2.10	6.22
50	118.32	107.86	–319.30	4.70	11.42
60	113.70	105.35	–311.32	12.34	20.49

[a] Energies relative to –1082.0 hartrees, in kcal/mol.
[b] Heat of formation, relative to –254.83 kcal/mol.
[c] Experimental geometry, derived from hexamethyl cyclotrisiloxane [30].

smaller than that found experimentally. This result is consistent with our previous calculations which show that STO-3G underestimates any angle involving SiO (cf. disiloxane and methyl silyl ether), but in this case the result is considerably better than would be expected. Another interesting feature is the lack of distortion of the OSiO angle over the range of dihedrals: going from the planar form to the chair form there is relatively little change, with the optimised value deviating only slightly from a tetrahedral value. On the other hand there is a much larger change in < SiOSi which shows a gradual decrease until the ring dihedral takes a value of 40°, and then decreases considerably until, at a ring dihedral of 60°, it has a value close to that found for <COC in dimethyl ether [33].

If we consider the energies in Table 4, for the STO-3G* basis set the minimum energy conformer is that with a ring dihedral of 10°, rather than the planar form found experimentally. However, the optimised geometry for the planar form is only 0.6 kcal/mol higher in energy than the 10° form; a similar effect is also seen for higher values of the ring dihedral with the 20° form being only ~ 0.4 kcal/mol higher in energy than the minimum, and even the 40° form is only 2 kcal/mol less stable. These very small energy differences would imply rapid interconversion between these forms and for standard conditions there would be a considerable population in each. For ring dihedrals > 40° there appears to be a much greater energy difference, and this increase continues dramatically, showing the 60° form to be > 10 kcal/mol less stable. A roughly similar picture is found for STO-3G at the same geometries although there is a shift in the minimum to around 20°, but the planar form is only ~ 0.4 kcal/mol higher in energy. Surprisingly, the calculations carried out using MNDO show the 'best' picture, with respect to the experimental results, with the minimum being found at the planar geometry; small energy differences are found between the conformations 0–40°, and then there is a large increase. In line with our previous comparisons the energy differences at the higher dihedrals are exaggerated by MNDO, with respect to STO-3G*.

Thus both the computational and experimental methods point to the structure of cyclotrisiloxane being planar. This may be due to the effect of d_π-p_π bonding with the ring forming a kind of

pseudo-aromatic system (if each oxygen donates 2 electrons then the $4n+2$ rule is obeyed) or at least a series of localised π systems which constrain the ring to be planar.

It is interesting to note at this point, that the function derived from these energies, especially those from MNDO, approximates to $1 - \cos\varphi$ (where φ is ring dihedral): a similar cosine dependence has been used to describe the variation of the π resonance integral β with respect to the change in dihedral angle [34]. For ring dihedrals between $0°$ and $40°$ there would still be a substantial degree of π overlap between the silicon d-orbitals and the oxygen lone pairs. When the molecule is in a conformation where π overlap is difficult to achieve then less stable forms are generated. The optimised geometries also show this effect to some extent, with $<$ SiOSi approaching a more tetrahedral, sp^3 value, at the $60°$ ring dihedral there being little possibility for π overlap, and hence d_π-p_π donation to the silicon.

In a recent series of calculations carried out on silanols Reed et al. [35] have found that there is evidence to suggest that the back donation of charge from an oxygen to a silicon takes the form of transfer of nonbonding electrons into σ^* (Si-H) orbitals. Although the cyclotrisiloxane molecule would appear to have the correct configuration for an anomeric effect to be present (two electronegative atoms at silicon), the preferred conformation of the ring, i.e. almost planar, is such that this would be disfavoured.

The Mulliken population analysis calculated using the STO-3G* wavefunction for cyclotrisiloxane indicates that there is some degree of interaction between the silicon d-orbitals and the oxygen p-orbitals: the total overlap population (between one silicon and one oxygen) is greater than 0.1 electrons and this would suggest that this interaction plays some part in determining the structure (the overall d-orbital population for each silicon is in the region of 0.5 electrons).

The only other explanation which can be put forward to explain the distortion of cyclotrisiloxane from typical sp^3 behaviour is that which has been used to explain the very large SiOSi bond angle in disiloxane [7], i.e. there is considerable coulombic repulsion between the β atoms because of the very large charges which have developed. This explanation is based upon charges derived from the Mulliken population analysis which has been criticised for calculating partial atomic charges which would appear to be unrealistically large [36]. It is not surprising that the electrostatic interaction would seem to give a reasonable explanation. If we take, for example, the charges generated from the STO-3G* and MNDO wavefunctions for cyclotrisiloxane and compare them to these calculated using CHARGE2 [25] we get the following: STO-3G*: Si 0.68e, O –0.43e; MNDO:Si 1.06, O –0.77; CHARGE2:Si 0.3, O –0.2. Although this argument could be used to explain the distorted bond angles, depending upon whether one accepts the size of the charges, or not, it gives no indication as to why the compound should be planar.

In conclusion, ab initio and semi-empirical calculations have shown that the most favourable conformation of cyclotrisiloxane is one where the ring is approaching planar, or a shallow chair (as opposed to the chair conformation found for the analogous trioxan) and the most consistent way of accounting for this behaviour would appear to be d_π-p_π bonding.

Silanol and hydroxydisiloxane

The final stage in the development of the molecular mechanics force field for silicates is the calculation of various torsional constants, together with force constants describing vibrations, etc. with respect to terminal hydrogen atoms. The model compounds used in this case were silanol,

which provides k_{OH}, k_{SiOH} and the torsional potential for HSiOH; and hydroxydisiloxane which contains an SiOSiO dihedral angle.

As our previous calculations have shown that the STO-3G* basis set gives reliable and economical results for SiO containing compounds it was decided to investigate these molecules solely at this theoretical level. In both cases it was appropriate to take as a starting point a set of standard structural parameters and then use partial optimisation where necessary: the parameters which have been assumed are as follows; < HSiO 109.9°, < SiOSi 144.0°, < OSiO 109.47°, r_{SiH} 1.48, and r_{SiO} 1.64.

In the case of silanol the OH bond lengths and < SiOH were optimised to give values of 0.985 Å and 109.45°, respectively. The corresponding force constants are 5.09 mdyne/Å and 0.32 mdyneÅ/rad². Using this geometry we calculated the rotational potential for the HSiOH torsion, which has a threefold barrier of 0.78 kcal/mol with the minimum at the staggered conformation.

When considering the structure of the hydroxydisiloxane molecule it was considered convenient to utilise the optimised structural parameters which were calculated for silanol. In order to minimise any steric effects due to the hydroxyl hydrogen we assumed a trans conformation with respect to the main chain throughout.

This molecule has recently been the subject of another theoretical study [37] where it was used to provide a rotational potential for the SiOSiO group (using a modified 3-21G* [16] basis set). We have also applied this approach using the standard STO-3G* basis set to provide values for the torsion within our molecular mechanics model. It should be noted that the force field developed by Grigoras and Lane [16] differs from that developed here in that their force field contains no explicit representation of torsional interactions; these are accommodated within the enlarged van der Waals interactions.

The potential which was obtained for rigid rotation about the central Si-O bond (0–180°) contained only one barrier to rotation, (with the maximum occurring at 180°). The magnitude of this barrier is of the order of 1 kcal/mol. This result initially seemed surprising but is in very close agreement with that of Grigoras and Lane [37]. The form of the torsional potential which we are using is as follows:

$$E_{tor} = \Sigma V_i/2.(1 + cos i\omega)$$

where ω is the dihedral angle and V_i the torsional barrier. Fitting this equation to the ab initio energies for hydroxydisiloxane gives $V_1 = -1.044$, $V_2 = 0.03$ and $V_3 = 0.03$ kcal/mol. Subtracting the threefold contribution due to the two HSiOSi torsions, using the HOSiH potential from silanol, results in a curve which differs from the previous curve only in its threefold contribution: this in fact compensates almost exactly for the energy difference resulting from the removal of the HSiOSi torsions. For this reason it was decided to use a V_1 potential of -1.04 kcal/mol (the other contributions being essentially zero) to represent rotation of an O-SiR$_2$-O-Si fragment.

The explanation put forward by Grigoras and Lane [37] for the nature of this potential is based upon the favourable electrostatic interaction between Si(1) and O(4) in the given dihedral; it must be remembered, however, that this explanation is based upon charge distributions calculated using the Mulliken population analysis (see Table 5) together with a dielectric constant of 5.0. When the charge distribution is calculated using EHT methods, Grigoras and Lane [37] found that a different dielectric constant (8.7) is necessary to reproduce their earlier results. This is an example of the inconsistency between partial charges calculated using different MO methods, and in this case,

TABLE 5
PARTIAL ATOMIC CHARGES FOR HYDROXYDISILOXANE

	3-21G*[a]	CHARGE2[b]
Si (H$_3$)	0.69	0.35
H	−0.08	−0.08
O	−0.92	−0.20
Si (H$_2$)	1.10	0.26
H	−0.10	−0.05
O (H)	−0.88	−0.39
H	0.46	0.33

[a] Charges taken from Ref. 37.
[b] Charges calculated using CHARGE2 [25].

when considering gas-phase ab initio conformations, a dielectric constant of 1.0 is appropriate. We have used CHARGE2 [25] to ascertain the contribution of the electrostatic interactions and, using a dielectric constant of 1.0, only ~1/3 of the barrier is due to electrostatic interactions; the residual energy difference may be due to a more favourable orbital overlap in the eclipsed situation which may aid possible π stabilisation. The final value for the V$_1$ potential, i.e. after subtracting the electrostatic and van der Waals energies is −0.68 kcal/mol.

Again it has been shown that the STO-3G* basis set performs well, when compared to the more flexible 3-21G*, for SiO compounds and may be considered as a suitable theoretical level for further calculations in this area.

CONCLUSIONS

From this study a number of conclusions may be drawn. The most striking is that the STO-3G* basis set would appear to be a suitable standard basis set for molecules containing SiO linkages. In the case of disiloxane both minimal and higher level split-valence basis sets have been shown to be inadequate when attempting to reproduce experimental features such as the SiOSi bond angle.

The calculations also show that the SiOSi and OSiO bond angles are very flexible; the barrier to linearisation in disiloxane is ~1.5 kcal/mol. This is in accordance with experimental data available for bond angles in zeolitic materials, where the SiOSi bond angles typically range from 130° to 180°, with the average falling at around 145° [28]. On the basis of our calculations this can be understood on energetic grounds.

The MNDO calculations show that although this method contains no representation of d-orbitals it reproduces the opening of the SiOSi(C) angles. However, this opening of the angle appears to be overestimated and this, together with the distortion of certain bond lengths suggests that MNDO wavefunctions may not be reliable or accurate enough for force constant calculations.

In conclusion, it would appear that STO-3G* is a reasonable basis set upon which to base a model of zeolite compounds, and the differences which are found between this and STO-3G suggest that the inclusion of d-orbitals is necessary to reproduce certain structural features of SiO compounds. However, in the case of SiO bond lengths, STO-3G* performs poorly, and perhaps the more flexible 3-21G* basis set would be a better choice in this case.

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