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MOLECULAR MECHANICS (MM2) CALCULATIONS ON SILOXANES*

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ABSTRACT

The MM2 force field has been extended so that calculations may be carried out on siloxanes. The parameters chosen give a good fit to available experimental data.

INTRODUCTION

The MM2 force field was first published in 1977,[2,3] and described molecular mechanics calculations on hydrocarbons.[4] [The original version of the MM2 program, MM2(77), together with an operations manual, is available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47401, USA). A later version which includes the subroutines designed to deal with conjugated systems, including those described in this paper, MM2(85), and an operations manual are available to commercial users from Molecular Design, Ltd, 2132 Farallon Dr., San Leandro, CA 94577, USA, and to academic users from the Quantum Chemistry Program Exchange, Department of Chemistry, University of Indiana, Bloomington, IN 47405, USA.] The calculations were subsequently extended to all of the common functional classes of organic molecules.[5] A recent paper dealt with silanes.[6] Silicon is more often found in an oxidized state than in the silane state, and this paper records the necessary parameters that were developed to permit calculations on molecules of the siloxane type.

Since this work was completed, another research group has published MM2 parameters explicitly for siloxanes. Grigoras and Lane[7,8] used *ab initio* calculations and a slightly modified version of MM2 to develop molecular mechanics parameters for siloxanes and other organosilicon compounds. In this work we utilized, exclusively, published experimental data.

ELECTRONIC AND STRUCTURAL PROPERTIES

In contrast to the silanes, the siloxanes exhibit a number of unusual structural and physical properties which had been ascribed, until recently, to the interactions of the oxygen lone pairs with the higher empty orbitals on silicon.[9]

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One of the more dramatic effects in silicon structural chemistry occurs not in the siloxanes but in silylamines. Trisilylamine is found to be planar with SiNSi bond angles of 120° instead of pyramidal with bond angles close to tetrahedral.[10] In addition, the SiN bond length is found to be 0·06 Å shorter than that predicted by the Schomaker–Stevenson equation.[10] [Discrepancies from the Schomaker–Stevenson equation are often cited as evidence of effects on bond lengths other than differences in electronegativity, which the equation is supposed to take account of: $r_{AB} = r_A + r_B - 0{\cdot}08\,|X_A - X_B|$, where r_{AB} is the expected bond length, r_A and r_B are the covalent radii for the atoms A and B and X_A and X_B are the Pauling electronegativities (see Ref. 11).] Tris(trimethylsilyl)amine has no basic properties, which implies a strong interaction of silicon with the nitrogen lone pair.[12]

The siloxanes themselves also exhibit unusual structural effects. For instance, the average SiO bond length for the siloxanes (1·63 Å) is shorter than that predicted by the Schomaker–Stevenson equation (1·69 Å), i.e. a shortening of 0·06 Å.[11] Also, the SiOSi angles in disiloxane and hexamethyldisiloxane have been determined to be wide, 144° and 149°, respectively, compared with the corresponding hydrocarbons, 112° and 123°, respectively.[13] This is in spite of the reduced steric repulsions expected because the Si—O bond is considerably longer than the C—O bond (1·63 Å and 1·41 Å, respectively).

Another interesting feature of this class of compounds is the unexpectedly low dipole moments. Dimethyl ether has a dipole moment of 1·31 D compared with 0·99 D (calculated) for disilyl ether.[14] Now, some of this difference is undoubtedly due to the wider bond angle, but the bond moment parameter that we derived from experimental dipole moments of simple, low molecular weight siloxanes is smaller than the similarly derived parameter for hydrocarbon ethers (0·40 vs 0·44 D, respectively). This occurs in spite of the longer SiO bond length relative to CC and the larger difference in electronegativity ($X_O - X_{Si} = 1{\cdot}70$ and $X_O - X_C = 1{\cdot}0$, Pauling scale).[11]

Finally, the SiO bond appears to be much stronger than would be expected. Vibrational spectra give force constants from 5·0 to 6·2 mdyne $Å^{-1}$.[15–17] Using the Seibert equation, this corresponds to a bond order of about 1·45. (The Seibert equation is $f = 7{\cdot}2 Z_A Z_B / n_A n_B$, where f is the force-constant for an ideal single bond A—B, Z_A and Z_B are the atomic numbers and n_A and n_B are the principle quantum numbers for atoms A and B.).

It had been generally accepted that these effects were due to (p–d) π interactions.[9] Most theoreticians now seem to think that (p–d) π contributions to the observed structural features are minimal at best,[7,18,19] although there continues to be discussion of this point.[20,21] In any case, the final outcome of the debate may not be relevant to molecular mechanics. The results obtained here seem to indicate that structural properties of siloxanes may be calculated from molecular mechanics without direct consideration of electronic properties except as described.

RESULTS AND DISCUSSION

The parameters arrived at for treating the siloxanes are given in Table 1. The calculated and experimental structures which were studied in this work are summarized in Table 2. Unless explicitly stated, all staggered and symmetrical torsional geometries were assumed.

The parameters here differ significantly from and are not directly comparable to the parameters developed by Grigoras and Lane,[7,8] with the exception of the stretching force constants. The differences are easily explained. The bending energy function of Grigoras and Lane[8] utilizes a cubic anharmonic term whose coefficients were optimized for each different angle type. Thus A—Si—B would have a different anharmonicity correction than A—Si—C,

Table 1. Force field parameters for the siloxanes[a,b]

Bond Dipole

Bond	u
O—Si	−0·40

Stretching

Bond	l_0	k_s(MM2)	k_s(exp.)	Ref.
SiO	1·626	5·50	5·1, 5·6, 5·9	15–17
CC[c]	Polarization correction for silicon = 0·015 Å			
SiC[c]	Polarization correction for oxygen = −0·020 Å			

Bending

Angle	Θ_0	k_θ(MM2)	k_θ(Lit.)	Type	Ref.
SiOSi	145·7	0·15	0·10, 0·15, 0·09	All	15–17
OSiO	113·5	0·45	–	All	–
CSiO	108·5	0·10	–	All	–
OSiH	109·5	0·07	–	All	–
SiO(LP)	97·5	0·35	–	All	–
COSi	114·6	0·40	–	All	–

Torsion

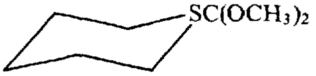
Dihedral angle	V_1	V_2	V_3
CCOSi	0·0	0·0	0·40
HCOSi	0·0	0·0	0·40
COSiC	0·0	0·0	0·23
COSiH	0·0	0·0	0·132
HCOSi	0·0	0·0	0·40
OSiCC	0·0	0·0	0·167
OSiCH	0·0	0·0	0·210
COSiO	0·0	0·0	0·15
(LP)OSiC	0·0	0·0	0·0
HSiO(LP)	0·0	0·0	0·0
CSiO(LP)	0·0	0·0	0·0
CSiOSi	0·0	0·0	0·10
OSiOSi	0·0	0·0	0·10
OSiO(LP)	0·0	0·0	0·0
HSiOSi	0·0	0·0	0·10
HCSiO	0·0	0·0	0·22

[a] Parameters not mentioned are already in the program [MM2(85)]. See Introduction. The full current MM2 parameter set is available from N.L.A. on request. Units: distances, Å; dipole moments, D; bending angles, degrees; stretching constants, mdyn Å^{-1}; bending constants, mdyn Å rad^{-2}; torsional constants, kcal mol^{-1} deg^{-1}.

[b] Oxygen here is atom type 6, and has two lone pairs attached.

[c] A bond length correction added to the indicated bond due to the attachment of the indicated heteroatom; see discussion of polarization effects.

Table 2. The siloxanes[a]

Compound	Structural feature	Experimental	MM2
Disiloxane, SiH_3OSiH_3	SiO	1·634(2)(ED)^{22}	1·627
	SiH	1·486(10)	1·489
	SiOSi	144·1(9)	145·0
	HSiO	109·9(13)	110·3
	SiH	109·1(13)	108·7
	Dipole	—	0·993
Hexamethyldisiloxane, $Me_3SiOSiMe_3$	SiO	1·626(2)(XR)^{23}	1·628
	SiC	1·851(4)	1·860
	OSiC	108·9(2)	108·6
	CSiC	110·1(2)	110·3
	SiOSi	148·8(2)	147·5
	Dipole	0·78	0·63
Hexamethylcyclotrisiloxane, $(Me_2SiO)_3$	SiO	1·635(ED)^{24}	1·641
	SiC	1·845	1·844
	SiOSi	131·6(4)	131·3
	OSiO	107·8(7)	107·0
	Symm.	—	C_{3v}
Octamethylcyclotetrasiloxane, $(Me_2SiO)_4$	SiO	1·622(3)(ED)^{24}	1·631
	SiC	1·844(3)	1·846
	SiOSi	144·8(12)	145·2
	OSiO	110·0(18)	110·5
	CSiC	111·2(18)	110·4
	Symm.	—	S_4
Cyclotetrasiloxane, $(SiH_2O)_4$	SiO	1·628(4)(ED)^{25}	1·629
	SiH	1·48	1·49
	OSiO	112·0	111·8
	SiOSi	148·6	143·7
	Symm.	S_4	S_4
Methoxysilane, CH_3OSiH_3	SiO	1·640(ED)^{26}	1·631
	CO	1·418	1·418
	COSi	120·6	120·9
	HSiH	110·1	108·6
	Barrier(SiO)	1·10^{27}	1·11
	Dipole	1·165^{14}	1·145
Methoxytrimethylsilane, $MeOSiMe_3$	SiO	1·639(4)(ED)^{28}	1·632
	CO	1·423(4)	1·417
	SiC	1·864(4)	1·861
	SiOC	122·5(6)	122·1
	OSiC	108·6(2)	109·1
	SiCH	110·5	—
	Barrier(SiO)	1·02^{29}	1·01
	Barrier(SiC)	2·14^{29}	2·01
	Dipole	1·18^{30}	1·15
1,1-Dimethoxy-1-silacyclohexane	SiO	1·632(2)(ED)^{30}	1·635
	CC	1·527(3)	1·539
	CSi	1·866(2)	1·856
	CO	1·408(2)	1·417
	CSiC	107·4(2)	103·2
	COSi	122·3(2)	121·6
	OSiO	123·0(4)	113·9

[a] Units: bond lengths, Å; bond angles, degrees; conformational barriers ('barrier'), kcal mol^{-1}; dipole moments, D. ED = electron diffraction; XR = x-ray.

and there is such an additional parameter for each bending degree of freedom. The MM2 program used in this work utilizes a sextic term and has a fixed coefficient for all angle types, and comes into play only when bending is very severe, which it is not in any compounds discussed here. This means that neither the k_B nor the θ_0 values are directly comparable to Grigoras and Lane's parameters. In order to reduce the total number of parameters needed for the siloxanes, Grigoras and Lane[8] also chose not to utilize torsional potentials at all for simple siloxanes. This meant that the van der Waals (non-bonded) potentials had to be adjusted to reproduce satisfactorily the preferred conformations and torsional energies. Van der Waals radii were increased by 20% and the hardness factors were reduced by a smaller amount. However, utilizing these van der Waals parameters required that bonded interactions be separated mathematically from non-bonded (torsional) interactions during minimization, otherwise the geometries became too distorted. This strategy could prove useful in structural studies involving non-cyclic, relatively unstrained structures such as the acyclic siloxanes, where one would expect the torsional – bending interactions in the normal energy minimization to be small and where development of all of the torsional terms required would be an especially heavy burden.

The bending parameters in general tend to be smaller than the related parameters involving ether fragments. However, this is consistent with a number of experimental observations made about disiloxane, for example, the Si—O—Si bond angle is easily deformed: it possesses a low barrier to linearization (0·30 kcal mol^{-1}),[31] a low dipole moment and is easily polarized.[32] Experimentally, it has also observed that a number of the cyclic siloxanes are 'flexible'[24] (perhaps more properly described as having large-amplitude bending vibrations), which would also suggest that small bending force constants are appropriate.

The torsional parameters are also relatively small and barriers are well reproduced using only V_3 terms. This parallels the observed trend that increasing central bond lengths reduces torsional barriers and allows the use of smaller torsional constants.

Polarization corrections to the SiC bond length

Examination of the SiC bond lengths in Table 2 indicates the shortness of the bonds relative to the same bonds in the simple silanes.[6] This is another example of the polarization effect discussed earlier.[6,33] The C—C bond in an ether is also shortened (by about 0·008 Å [33]) by this effect. In the siloxanes, we found that a correction of about −0·020 Å needed to be added to the natural bond length (l_0) of an Si—C bond if an oxygen atom were attached to the silicon end of the bond (no information is available on attachments to the carbon end). For multiple substitutions on silicon, the usual treatment applies.[33]

Individual compounds in Table 2

Hexamethylcyclotrisiloxane

The workers who investigated this structure concluded that the molecule is very flat and flexible, and for this reason, only the conformationally independent structural features were assigned.[24] In our calculations we assumed the probable conformation (C_{3v}) and worked from there. This siloxane was reasonably well fitted. Even the polarization-corrected bond length for the dioxygen-substituted SiC bond (geminally substituted on silicon) is close to the experimental value.

Octamethylcyclotetrasiloxane and cyclotetrasiloxane

Again, these structures were reported to be very close to being planar and flexible, so that only the conformationally independent features are given.[24,25] Note that in these two compounds (in contrast to that above) the SiOSi angle is able to open up to its acyclic value. The methylated cyclotetrasiloxane and the parent cyclotetrasiloxane have very similar structures.

Methoxysilane

This compound is interesting because of its relationship to disiloxane; one of the silicons of disiloxane is replaced with a carbon, which results in a much smaller angle at oxygen and, in fact, the COSi angle in methoxysilane and the SiOSi angle in disiloxane differ by about half as much as the difference between the corresponding angles in disiloxane and dimethyl ether.

The calculated SiO bond length too short by about 0·009 Å and the HSiH angle is too small by about 1·5°. The barriers to rotation about the Si—O bonds are fitted fairly well. There is also good agreement between the calculated and experimental structures for the related methoxytrimethylsilane.

1,1-Dimethoxy-1-silacyclohexane

The results here are not as good as the qualified successes with most of the other compounds in Table 2 if we take the experimental quantities at face value. The calculated C—C bond length would be too long even when the polarization correction for a silicon attached to a C—C bond is taken to be zero.

It is clear what is happening here. If we take the analogy of an amino group, which is an electron donor under most circumstances, and compare this with a nitro group, we find that the latter is a strong electron-withdrawing group. Alternatively, attaching the oxygens to the nitrogen makes the nitrogen much more electronegative. The same effect is observed here. The silicon of a silane (attached to carbons or hydrogens) is a strong electropositive group. However, attaching two oxygen atoms to the silicon converts it into a more electronegative group (the electronegativity shortening of a C—C bond by an SiO_2 group should apparently be about zero). The altered electronic character of the silicon atom may also explain why the CSiC angle is much more open here (107·4°) than that in silacyclohexane itself (104·8°).[6,33]

However, it is not clear that we should take the experimental numbers at face value. In this molecule there are a substantial number of bonds which are similar, but different, in length and that are not experimentally resolved. Hence the model chosen fits the data to within the standard deviations suggested, but the model in fact may be much poorer than indicated by those standard deviations. If some bonds are too long and some are too short, the same electron diffraction pattern could well be obtained.

It is not clear why the calculated OSiO angle should be so inaccurate (113·9° vs the experimental value of 123·0°). It is true that in assigning the 'natural' or equilibrium value for this bond angle we had no acyclic structures to guide us. On the other hand, the octamethylcyclotetrasiloxane has features in common with the acyclics because of its large size and flexibility (note that the SiOSi angle in octamethylcyclotetrasiloxane is close to the acyclic value of 145°). Overall, we mimic the structural features of this class well, considering that it represents something of a special case.

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