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Quantum Chemical Conformational Analysis of Dihydroxysiliconate Ion [$H_3Si(OH)_2^-$]. An Exceptionally Fluxional Pentacoordinate [10-Si-5] System

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Abstract: The global minimum calculated for $H_3Si(OH)_2^-$ has both hydroxyl groups equatorially located in a trigonal bipyramidal (TBP) structure (large basis sets, highly correlated levels of theory). Natural bond orbital (NBO) analysis indicates that hyperconjugative interactions involving the lone pairs of the equatorial hydroxyl groups as donors slightly overcome the otherwise expected tendency for these (electronegative) groups to prefer axial positions in the TBP. A diaxially substituted local minimum structure does exist, and lies only 2.7 kcal/mol in enthalpy (298 K) above the global minimum at the highest level of theory. Another diaxial structure a mere 0.01 kcal/mol additionally higher in enthalpy is calculated to be a transition state for a double-pseudorotation that interconnects two degenerate conformations of a diequatorially-substituted stereoisomer. The conformational potential energy hypersurface may thus be regarded as essentially flat, suggesting that permutation of siliconate ligand positions is facile in dialkoxysiliconates.

1. Introduction

Pentacoordinate monoalkoxysiliconate ions, $ROSiH_4^-$, reduce ketones and aldehydes in the gas phase to produce dialkoxysiliconate ions, $ROSiH_3(OR')^-$.[1-3] The diastereoselectivity of these reactions can be quantitatively determined by comparing the relative yields of RO^- and $R'O^-$ fragment ions produced by collision-induced dissociation (CID) of the reduction product with those obtained from the two independently-produced dialkoxysiliconates possessing the authentic diastereomeric R′O ligands.[1] For example, addition of 3-pentoxide ion, Et_2CHO^-, to *n*-hexylsilane produces a monoalkoxysiliconate ion that reacts with 4-*tert*-butylcyclohexanone to yield a diastereomeric mixture of dialkoxysiliconates possessing *cis*- and *trans*-cyclohexylalkoxy ligands (eq 1, R = *n*-hexyl). Collision-induced dissociation of this ion in a triple quadrupole analyzer produces the cyclohexyl alkoxide and 3-pentoxide fragments in a measured yield ratio, $R_{\mathrm{mix}} = I(C_{10}H_{19}O^-)/I(C_5H_{11}O^-)$, of 1.45. The two dialkoxysiliconate reference ions possessing authentic *cis*- and *trans*-cyclohexylalkoxy ligands can be generated by simply reversing the synthetic order, i.e., by first adding either *cis*- or *trans*-4-*tert*-butylcyclohexyl alkoxide to the neutral silane, followed by reduction of 3-pentanone (eq 2). CID of the cis species gives the two alkoxide ion fragments in a ratio R_{cis} of 7.0, while CID of the trans species gives a ratio R_{trans} of 1.43. The diastereomer yields in the mixture produced by reaction 1 can then be determined from R_{mix}, R_{cis}, and R_{trans} to be 99% trans and 1% cis. These gas-phase stereochemical measurements provide a critical test of current theoretical models for diastereoselectivity in carbonyl addition reactions, since they reveal the intrinsic behavior of the isolated reactants. In the particular example illustrated above, the outcome closely matches the results obtained from reactions of 4-*tert*-butylcyclohexanone in solution with common reducing agents such as $LiAlH_4$ and $NaBH_4$,[4] and the results of molecular orbital calculations for the model gas-phase reductions of cyclohexanone by LiH[5] and by SiH_5^-.[6]

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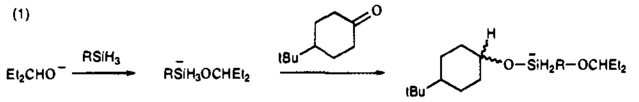

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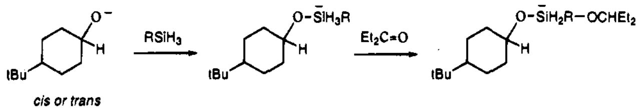

A key requirement of the diastereoselectivity analysis is that the ratio of alkoxide ion fragments produced by CID is insensitive to the order of introduction of the two alkoxy groups in the dialkoxysiliconate ion.[1,2] That is, the same structure or mixture of structures must result from the two complementary alkoxide addition/ketone reduction sequences like eqs 1 and 2 that lead to the dialkoxysiliconate. This behavior could be demonstrated experimentally for several different dialkoxysiliconate ions.[1,2] For instance, addition of cyclohexyl alkoxide ion to *n*-hexylsilane followed by reduction of 3-pentanone produces a dialkoxysiliconate ion that exhibits a CID spectrum which is identical to that obtained from the ion formed by addition of 3-pentoxide ion to *n*-hexylsilane followed by reduction of cyclohexanone (eq 3). Thus, a single common structure or equilibrium mixture of structures is rapidly established by both synthetic sequences.

The validity of these stereochemical measurements ultimately depends upon the conformational properties of dialkoxysilicon-

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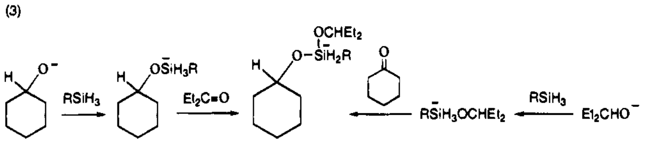
(3)



ate ions. As pentacoordinate silicon [10-Si-5][7] anions, dialkoxysiliconates are expected to prefer trigonal bipyramidal (TBP) structures with three equatorial and two apical ligands. Presumably, the structural interconversions indicated by the experimental results described above take place by low-energy stereopermutative pathways like Berry pseudorotation.[8–10] While it is generally accepted that more electronegative substituents prefer to occupy apical positions in trigonal bipyramids in the absence of steric constraints,[11–13] it has recently been shown[14–16] that favorable hyperconjugative interactions between equatorial substituents can oppose this trend in phosphoranes,[17–20] and their derivative tetrasubstituted phosphoranyl radicals,[14–16,21–26] thereby giving rise to minimum-energy conformations with the hydroxyl ligands occupying equatorial positions. These observations are of particular relevance since [10-P-5] phosphoranes are isoelectronic with [10-Si-5] siliconate ions.

Previous theoretical studies have focused on the structure and conformational dynamics of siliconate anions. Willhite and Spialter[27] considered fictional siliconates derived from SiH_5^- by adjusting one or more of the nuclear charges on hydrogen to values greater than one. Substituted siliconate ions have seen considerable study at both semiempirical[28,29] and ab initio[28–38] levels of theory.

Gordon and co-workers in particular have made many key observations with respect to polyhalogenated siliconate ions.[28,29,34,38] Inter alia, they have established that the nature of individual stationary points for these species can change when correlation effects are included in the calculation of the Hessian matrix;[38] i.e., a transition state structure at the Hartree–Fock (HF) level may become a local minimum at a correlated level, or a local minimum at the HF level may fail to be stationary at correlated levels, etc. In the case of SiH_4F^-, Windus et al. have examined the classical Berry pseudorotation mechanism for permuting the locations of ligands in the TBP and noted a bifurcation in the reaction path for this process.[34] This bifurcation arises because the TBP with the fluorine equatorial is not a local minimum, but instead is itself a transition state. Similar behavior has been noted for PH_4F[39] and for a variety of other substituted phosphoranes and phosphoranyl radicals.[14–16,23] The term "double-pseudorotation" has been coined in the latter work to refer to a stereoisomerization passing through one of these transition states.[14–16] The key difference between a pseudorotation and a double-pseudorotation is that the former interchanges both axial substituents with two equatorial substituents while the latter interchanges a single axial substituent with a single equatorial substituent.

To examine the stereoisomeric lability of dialkoxysiliconates, we have undertaken large basis set ab initio calculations on the analogous model compound $H_3Si(OH)_2^-$ (i.e., the alkyl groups have been replaced with hydrogens). Section 2 describes the theoretical methodology, Section 3 presents the results of the calculations with respect to molecular geometries and relative energies, Section 4 addresses the physical factors controlling the shape of the conformational potential energy surface as well as certain technical details of the calculations, and Section 5 summarizes our conclusions.

2. Theoretical Methods

Geometry optimizations were carried out using restricted Hartree–Fock (RHF) and second-order perturbation (MP2) theories. Dunning's augmented correlation-consistent polarized valence-double-ζ basis set[40,41] (aug-cc-pVDZ) was employed for these optimizations (118 contracted basis functions). Stationary points were characterized by analytic frequency calculations at the MP2 level. Reaction paths for individual transition states were assigned by following the intrinsic reaction coordinate (IRC).[42–45]

Single-point calculations were carried out at the MP2 level using Dunning's augmented correlation-consistent polarized valence-triple-ζ basis set[40,41] (aug-cc-pVTZ, 257 contracted basis functions). In addition, coupled cluster calculations including all single, double, and perturbative triple excitations (CCSD(T)) were carried out using the aug-cc-pVDZ basis set to gauge the effects of more completely accounting for electron correlation. Finally, to more completely assess convergence with respect to basis set size, RHF calculations were carried out using the s and p functions from Dunning's augmented correlation-consistent polarized valence-quadruple-ζ basis set[40,41] (aug-cc-pVQZ) and the polarization functions from the aug-cc-pVTZ basis set; we refer to this as basis set "Q" (350 contracted basis functions). We define our best composite electronic energy as

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$$E_{\rm comp} = \text{MP2/aug-cc-pVTZ//MP2/aug-cc/pVDZ} + [\text{CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ} - \text{MP2/aug-cc-pVDZ}] + [\text{HF/Q//MP2/aug-cc-pVDZ} - \text{HF/aug-cc-pVTZ//MP2/aug-cc-pVDZ}] \quad (4)$$

Thermal vibrational enthalpy corrections were obtained from the MP2/aug-cc-pVDZ frequency calculations (unscaled) by standard statistical mechanical formulas.[46,47] Hydroxyl torsional motions were characterized by extremely small force constants, so vibrational entropy corrections were deemed unreliable and are not reported.

Natural bond orbital (NBO) analysis[48,49] was carried out for the RHF/aug-cc-pVTZ wave functions. Energies of hyperconjugative stabilization were calculated from second-order perturbation theory using the NBO Fock matrix.[48,49]

All calculations were carried out with the Gaussian92 program suite,[50] which includes NBO Version 3.1.[51]

3. Results

Structural representations including all Si−X bond lengths may be found in Figure 1 and energies are collected in Table 1; additional energetic and geometric details are provided as supporting information.

Six distinct local minima exist for $H_3Si(OH)_2^-$. Structures **1** and **2** have both hydroxyl groups equatorial. In each case the hydroxyl groups eclipse axial Si−H bonds—in the lower energy **2** the same bond is eclipsed by both hydroxyl groups, while in **1** each axial bond is eclipsed by a single hydroxyl group. Structures **3**, **4**, and **5**, all of which are higher in energy than either **1** or **2**, each have one hydroxyl group axial and the other equatorial. In the lower energy structures **3** and **4**, one hydroxyl group makes a non-ideal hydrogen bond to the other. By contrast, **5** is destabilized by about 2 kcal/mol relative to the other two since its hydroxyl groups are oriented so that their oxygen lone pairs are abutting. Structure **6** has both hydroxyl groups in axial positions. All of the minima possess some degree of symmetry except for **3**.

Three additional stationary symmetric structures, $\mathbf{7}^\ddagger$, $\mathbf{8}^\ddagger$, and $\mathbf{9}^\#$, are also illustrated. Structures $\mathbf{7}^\ddagger$ and $\mathbf{8}^\ddagger$ are transition state (TS) structures; their Hessian matrices are characterized by one negative eigenvalue corresponding to imaginary frequencies of 352.8*i* and 208.9*i*, respectively. The Hessian matrix for **9#** shows two negative force constants; i.e., the structure is a "hilltop" on the potential energy surface and is not chemically relevant. It does, however, lie surprisingly low in energy, and merits discussion (vide infra).

Structure $\mathbf{7}^\ddagger$ has the classical square pyramidal structure associated with a Berry pseudorotational TS. The apical hydroxyl in $\mathbf{7}^\ddagger$ remains in an equatorial position in both the initial and final trigonal bipyramids that are interconverted by the pseudorotation. One pair of anti basal substituents then corresponds to the two other ligands that were equatorial in the initial TBP and are becoming axial, while the other pair corresponds to the ligands that were axial in the inital TBP and are becoming equatorial. Inspection of the IRC associated with $\mathbf{7}^\ddagger$ indicates that it is a TS structure on a pathway connecting stereoisomers **1** and **4**. Although other pseudorotation transition state structures almost certainly exist for interconverting other stereoisomers, we have not performed a thorough search of the potential energy hypersurface in order to locate all of them. The energies of these other TS structures are expected to be within 3 kcal/mol or so of $\mathbf{7}^\ddagger$, based on an exhaustive analysis in a similar system, $H_2P(OH)_2$.[15]

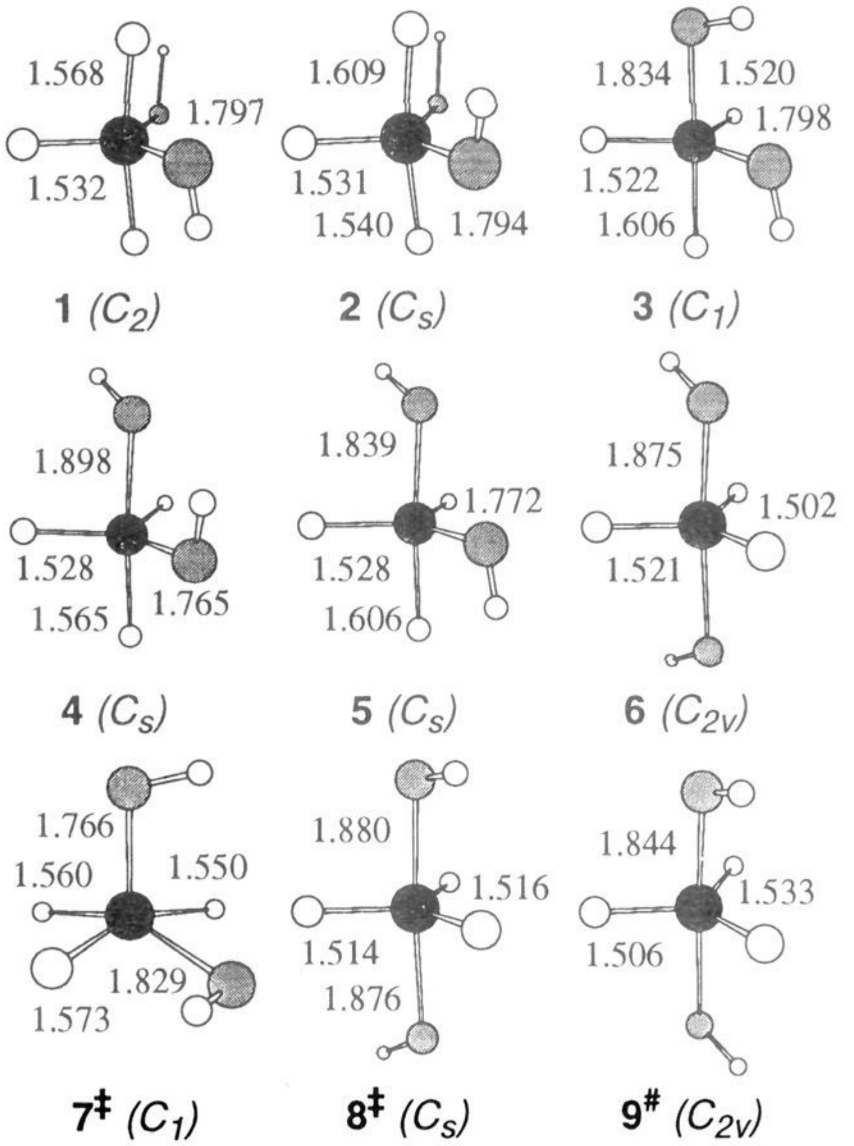

Figure 1. $H_3Si(OH)_2^-$ stationary points. Si−X bond lengths are given in angstroms for MP2/aug-cc-pVDZ optimized structures.

Structure $\mathbf{8}^\ddagger$, on the other hand, looks at first glance as though it should be a local minimum: it has a typical trigonal bipyramidal structure with both hydroxyl groups placed axial. Indeed, this placement might be regarded as optimal given standard arguments about the apicophilicity of more electronegative substituents (in monohydroxysiliconate ion Gordon[52] has calculated the apicophilicity of OH to be 1.0 kcal/mol at the MP4/6-31++G**//MP2/6-31++G** level). Analysis of the IRC corresponding to $\mathbf{8}^\ddagger$, however, indicates that it is a TS structure on a double-pseudorotation pathway connecting two "copies" of **1**. The double-pseudorotation exchanges one axial hydrogen for an equatorial hydrogen, so that (in the absence of atom-labeling) the initial and final structures are indistinguishable. The double-pseudorotation is so named because *if* the TS structure $\mathbf{8}^\ddagger$ were to be a minimum, the total stereoconversion (i.e., progressing from the first copy of **1** to the second) would correspond to two consecutive pseudorotations. Were this situation to prevail, one would expect to find square pyramidal TS structures similar to $\mathbf{7}^\ddagger$ along the pathway from **1** to **8**. Such structures are indeed found along the IRC, but since the saddle point on the reaction coordinate is located at $\mathbf{8}^\ddagger$, they cannot be stationary. Structure **i** is a non-stationary example taken from

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Table 1. Relative Energies (kcal/mol) for $H_3Si(OH)_2^-$ Stationary Points at Various Levels of Theory[a]

level[b]	**1**	**2**[c]	**3**	**4**	**5**	**6**	**7**‡	**8**‡	**9**#
HF/aug-cc-pVDZ	0.0	0.0	−0.1	−0.8	1.8	0.3	6.6	1.0	1.9
MP2/aug-cc-pVDZ	0.1	0.0	0.9	0.2	2.9	0.0	7.4	0.6	1.3
CCSD/aug-cc-pVDZ//MP2	0.1	0.0	0.5	−0.2	2.5	0.1	6.9	0.7	1.4
CCSD(T)/aug-cc-pVDZ//MP2	0.1	0.0	0.6	0.0	2.7	0.2	7.0	0.8	1.5
HF/aug-cc-pVTZ//MP2	0.1	0.0	0.3	−0.2	1.9	2.1	6.4	2.7	3.6
HF/Q//MP2	0.1	0.0	0.4	−0.1	1.9	2.4	6.4	3.1	4.0
MP2/aug-cc-pVTZ//MP2	0.1	0.0	1.4	1.0	3.1	2.4	7.4	3.0	3.7
E_{comp}[d]	0.1	0.0	1.3	0.9	2.9	3.0	7.0	3.6	4.3
ZPVE	0.0	0.0	−0.5	−0.6	−0.6	−0.9	−0.9	−1.1	−1.3
ZPVE + $H_{298} - H_0$	0.0	0.0	−0.3	−0.2	−0.3	−0.3	−1.1	−0.9	−1.5
composite H_{298}[e]	0.2	0.0	1.0	0.7	2.5	2.7	5.9	2.7	2.8

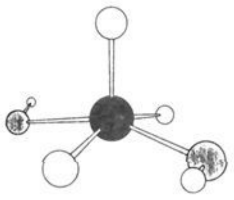
[a] Numbers that do not appear to properly sum result from rounding of unreported decimal places. [b] MP2/aug-cc-pVDZ geometries are indicated by "//MP2". [c] Absolute energies (au) for this column are −441.629 35; −442.192 23; −442.219 91; −442.237 80; −441.687 68; −441.703 32; −442.372 67; −442.432 42; 0.052 38; 0.057 17; −442.361 07. [d] Equation 4. [e] E_{comp} + ZPVE + $H_{298} - H_0$.

Table 2. Hyperconjugative Stabilization Energies (kcal/mol) from NBO Analysis[a]

structure	$n_{O(eq)} \rightarrow \sigma^*_{Si-H(eq)}$	$n_{O(eq)} \rightarrow \sigma^*_{Si-O(eq)}$	$n_{O(eq)} \rightarrow \sigma^*_{Si-H(ax)}$	$n_{O(eq)} \rightarrow \sigma^*_{Si-O(ax)}$	$n_{O(ax)} \rightarrow \sigma^*_{Si-H(eq)}$	$n_{O(ax)} \rightarrow \sigma^*_{Si-H(eq)}$	$n_{O(ax)} \rightarrow \sigma^*_{Si-H(ax)}$	$n_{O(ax)} \rightarrow \sigma^*_{Si-O(ax)}$
2	17.9	14.6	4.8					
4	19.1		2.7	0.0	4.0	4.4	2.7	
6					16.8			7.8

[a] Anlysis from HF/aug-cc-pVTZ calculations.

this IRC—the anti basal O−Si−O and H−Si−H angles are both about 153°. Consistent with the usual preference for more electronegative substituents to prefer basal positions in a square pyramid over apical ones,[13] **i** is about 5 kcal/mol lower in energy than **7**‡. We have not searched for an analog of **8**‡ that interconverts two copies of **2**. Since the double-pseudorotation TS structure would in principle closely resemble **6** (i.e., parallel alignment of hydroxyl groups) it seems likely that the one-step double-pseudorotation pathway does not exist. Instead, **6** intervenes. However, the range of energy spanned by **6**, **8**‡, and **9**$^{\#}$ is only 0.1 kcal/mol! Given that these structures differ only as hydroxyl group rotamers, this suggests that the well in which local minimum **6** lies is not especially deep.



i

4. Discussion

For **1**−**5**, the O−H bonds of the equatorial hydroxyl groups always eclipse axial bonds in the TBP. The hyperconjugative origin of this effect (i.e., oxygen lone pair delocalization into appropriately oriented unfilled orbitals) has been discussed for phosphorus TBPs.[14-16,19,23] One manifestation of this hyperconjugation is the significant lengthening of Si−X bonds that are eclipsed by a hydroxyl group. For instance, in **2** the axial Si−H bond that is eclipsed by both OH groups is 0.07 Å longer than the one that is not eclipsed. As might be expected, the axial Si−H bonds in **1**, both of which are eclipsed by a single hydroxyl group, are longer by about half the amount found for the doubly-eclipsed bond in **2**. Similar trends are revealed in a comparison of **3**, **4**, and **5**. When the axial Si−O bond is eclipsed by the equatorial hydroxyl group in **4**, it lengthens by 0.06 Å compared to **5**, where it is not eclipsed. In contrast, when the equatorial Si−O bond is eclipsed by the axial hydroxyl group in **3**, it lengthens by only 0.03 Å compared to **5**, where it is not eclipsed. This would appear to indicate that hyperconjugation is less efficient in the latter case than in the former; this is quite reasonable insofar as overlap is reduced in the latter case because the axial Si−O bonds are longer than the equatorial bonds. Finally, when considering equatorial Si−H antibonding orbitals as acceptors in hyperconjugative interactions, it is not obvious what bond length should be chosen as a reference. It is apparent, however, that the equatorial Si−H bonds are shortest in **6**, longer in **3**, **4**, and **5**, and longest in **1** and **2**. Again, this suggests that equatorial hydroxyl groups serve as more efficient donors in a hyperconjugative sense than they do when they are axial.

Quantitative confirmation of the above geometric analysis may be obtained from natural bond orbital (NBO) analysis.[48,49] Table 2 lists the energetic stabilizations from all possible $n_O \rightarrow \sigma^*_{Si-X}$ hyperconjugative delocalizations for stereoisomers **2**, **4**, and **6**. In diequatorially substituted **2**, the two $n_O \rightarrow \sigma^*_{Si-O(eq)}$ delocalizations are about as energetically stabilizing as the two $n_O \rightarrow \sigma^*_{Si-H(eq)}$ delocalizations. This is in part because of the similar energies of the two kinds of σ^* orbitals. Both of these interactions are considerably more stabilizing than $n_O \rightarrow \sigma^*_{Si-H(ax)}$ delocalization. A similar trend with respect to the accepting ability of axial vs equatorial Si−H antibonding orbitals is observed in **4**. Moreover, the stabilization arising from delocalization of lone pair density on the axial oxygen is much less than that calculated for the equatorial oxygen. Axial oxygen lone pair delocalization is also minimal for **6**, where 12 possible hyperconjugative interactions involving equatorial Si−H antibonding orbitals (4 lone pairs, 3 acceptor orbitals) sum to only 16.8 kcal/mol. Axial/axial interactions are always small as well.

Somewhat surprisingly, no stabilization is predicted from delocalization of equatorial oxygen lone pair density into the axial Si−O antibond in **4**; this does not appear to be consistent with the geometrical analysis presented above. Moreover, the absolute magnitudes of the stabilizations listed in Table 2 obviously are not in quantitative agreement with the small range of energy separating the three isomers in question. However, it must be remembered that while NBO analysis is a well-defined method for analyzing hyperconjugative interactions, by its reliance on an orbital localization scheme it is also necessarily arbitrary in its partitioning of the electron density. Many other interactions, some very large in magnitude, contribute to the overall molecular energies. As a result, we consider the NBO analysis to be complementary to geometric analysis, but still qualitative in nature, at least for dihydroxysiliconate. Thus, the NBO analysis provides support for the rationalization that the global minimum in $H_3Si(OH)_2^-$ is diequatorially substituted because hyperconjugative effects outweigh the intrinsic apicophilicity of the hydroxyl group.

Assignment of the global minimum requires convergence of the relative electronic energies and thermal vibrational effects (the former generally being the more challenging). Differential changes in the relative energies of the isomers as a function of theoretical level may also provide some insight into chemical aspects of the electronic structure. The data provided in Table 1 merit some discussion in this regard.

We begin by comparing the relative energies calculated at the HF/aug-cc-pVTZ//MP2/aug-cc-pVDZ level to those calculated at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level (rows 5 and 7 of Table 1). Accounting for the effects of electron correlation at the MP2 level raises the *relative* energies of the axial/equatorial isomers **3**−**5** and the square pyramidal **7**‡ by about 1.2 kcal/mol but does not differeniate significantly between diaxial and diequatorial isomers. Similar results are obtained when HF and MP2 energies are compared for the smaller aug-cc-pVDZ basis set (rows 1 and 2 of Table 1). Rationalizing correlation effects can be challenging since such effects are not necessarily local. However, in this instance it seems reasonable to note that in trigonal bipyramids the orbital subsystem devoted to the central atom and the equatorial ligands has minimal overlap with the orbital subsystem devoted to the central atom and the axial ligands. Thus, when the two electron-rich oxygen atoms are not found in the same orbital subsystem (i.e., the substitution is axial/equatorial), there is less correlation energy. A similar argument applies to square pyramidal **7**‡, where one oxygen is apical and the other basal.

We next consider the effects of electron correlation beyond the MP2 level by comparing CCSD/aug-cc-pVDZ calculations to MP2/aug-cc-pVDZ calculations (rows 2 and 3 of Table 1). At the CCSD level, the differentiation between substitution patterns noted above is diminished. In particular, the axial/equatorial minima and **7**‡ are all stabilized by about 0.4 kcal/mol relative to the diaxial and diequatorial structures by including single and double substitutions to infinite order. However, further including triple excitations perturbatively at the CCSD(T) level (row 4 of Table 1) removes about half of this relative stabilization. As a result, it appears that the relative correlation energies are probably converged to well within 0.5 kcal/mol.

We now examine convergence with respect to basis set size. Comparing relative energies calculated at the HF/Q//MP2/aug-cc-pVDZ level to those calculated at the HF/aug-cc-pVTZ//MP2/aug-cc-pVDZ level, we find convergence to within 0.1 kcal/mol for all structures except those having a diaxial hydroxyl substitution pattern. These latter isomers increase in relative energy by 0.3 to 0.4 kcal/mol. It seems reasonable to rationalize this trend by noting that of all of the substitution patterns, the diaxial one spreads electron density over the most space. Thus, increasing the basis set size has more of an effect on other substitution patterns (i.e., they are better stabilized by comparison) than on the diaxial. Since saturating the basis set is more important for correlated calculations than for HF calculations,[53] the relative energies of **6**, **8**‡, and **9**$^\#$ might be expected to rise by an additional 0.2 to 0.4 kcal/mol were we to calculate relative energies at the MP2/Q level instead of correcting for this effect at the HF level, but for all other stereoisomers, we consider their relative energies to be fully converged with respect to basis set size.

Finally, we consider the thermal vibrational corrections required to calculate relative enthalpies at 298 K. Although Table 1 presents results from MP2/aug-cc-pVDZ calculations, they differ by no more than 0.2 kcal/mol from HF/aug-cc-pVDZ data. Weak axial Si−O bonds contribute less zero-point vibrational energy (ZPVE) so, relative to **1** and **2**, monoaxial stereoisomers **3**−**5** are stabilized by 0.5 to 0.6 kcal/mol, and diaxial stereoisomer **6** is stabilized by 0.9 kcal/mol. Structures **7**‡, **8**‡, and **9**$^\#$ are similarly stabilized by axial hydroxyl substitution, but in addition have fewer normal modes contributing to ZPVE. Thermal corrections to 298 K diminish the magnitude of these differential stabilizations for the local minima. Pople et al.[54] have pointed out that improved agreement between calculated and observed fundamental frequencies may be obtained by scaling the calculated frequencies using constants that are dependent on theoretical level, basis set, and the nature of the normal mode. Insufficient data exist for the derivation of scaling factors that might be applied to this system; however, insofar as theoretical scaling factors are inevitably near 0.9 for levels of theory similar to those applied here, it appears likely that application of such a factor would reduce the relative stabilization of the axially substituted isomers discussed above by about 10%. Although the vibrational contributions are probably well converged with respect to theoretical level, a conservative estimate of the error associated with the harmonic oscillator/rigid rotor approximation[46] used in the frequency calculations might be 0.5 kcal/mol in relative energy.

Given the above analysis, we confidently assign the global minimum structure to be diequatorially substituted; however, the energy separation between **1** and **2** is probably below the remaining error in the calculations. Stereoisomers with one hydroxyl group axial in the TBP lie 0.7 to 2.5 kcal/mol higher in energy, and **6**, the only stereoisomer with both hydroxyl groups axial, lies 2.7 kcal/mol higher in energy. One may contrast this with the results of Windus et al.[38] for $H_3SiF_2^-$: at the MP4/6-31++G**//MP2/6-31G** level, the diaxial isomer is lowest in energy, the monoequatorial isomer is 8.9 kcal/mol higher in energy, and the diequatorial isomer is 12.8 kcal/mol above diaxial. The significantly smaller energetic cost to move the second fluorine ligand to an equatorial position compared to the first has also been noted in phosphoranes[17,19,55] and phosphoranyl radicals,[24] and is ascribed to improved hyperconjugative interactions when both fluorine atoms are in equatorial positions. This stabilization is insufficient, however, to compete with the apicophilicity of fluorine, which Windus et al. calculate to be 7.2 kcal/mol at the same level of theory.[38] We emphasize, then, that the reversal in the usual[11] ordering of isomer energies occurs for $H_3Si(OH)_2^-$ not solely because of hyperconjugative interactions but also because of the reduced apicophilicity of the hydroxyl group. It should be noted, however, that the usual stereoelectronic effects that induce electronegative substituents to prefer axial positions are still operative in $H_3Si(OH)_2^-$, i.e., the highest occupied molecular orbital (HOMO) is indeed the nonbonding combination of the axial 3-center orbital system that is localized almost entirely on the axial atoms. This causes the HOMO energy to be about 1 eV lower for **6** than for **2** (all of the anions are bound).

Finally, the small range of relative energies for all stereoisomers together with the low barriers calculated for various interconversions suggests that stereopermutation (i.e., ligand scrambling) should be particularly facile for $H_3Si(OH)_2^-$. Switching from hydroxy to alkoxy groups is not expected to change the conformational potential energy surface dramatically

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in this regard, although alkoxy groups possessing exceptionally large alkyl groups may be subject to steric effects. It thus seems clear that CID spectra observed for dialkoxysiliconate ions should not be expected to be sensitive to the order of introduction of the two alkoxy ligands, as discussed in Section 1. We note in closing that solvation effects on dialkoxy-substituted siliconates in condensed phases should also favor diequatorial substitution because of the greater concentration of negative charge (i.e., the oxygen atoms) over a small region of space for substitution patterns other than diaxial.

5. Conclusions

The conformational potential energy surface for the dihydroxysiliconate ion is remarkably flat. Six minima lie within 2.7 kcal/mol of one another. Although hydroxyl is a weakly apicophilic group in H_4SiOH^-, the global minimum of $H_3Si(OH)_2^-$ has both hydroxyl groups equatorial because the apicophilicity of the hydroxyl group is overcome by improved hyperconjugative interactions available to diequatorially substituted stereoisomers. Local minima are interconverted via both pseudorotations and double-pseudorotations. These processes have barriers of less than 6 kcal/mol associated with them at 298 K, suggesting that $H_3Si(OH)_2^-$ may be considered to be essentially without structure as regards ligand location. The implication for dialkoxysiliconate ions, the CID mass spectra of which have been observed, is that those spectra are independent of the order of introduction of the alkoxide ligands.

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Supporting Information Available: Gaussian 92 archive information with MP2/aug-cc-pVDZ geometries for all isomers (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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