A Theoretical Study of Conformational Stability in Molecules with Two or Three Si—O Bonds

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The anomeric effect in compounds with C—O bonds [1] has been studied by *ab initio* calculations, *e.g.* on fluoromethanol [2] and methanediol.[3] In the present work we give the results of some *ab initio* calculations on silanediol and silanetriol. This investigation was initiated partly for comparison with previous results on methanediol [3] and partly for supplementing electron diffraction studies on methyl methoxy silanes [$(CH_3)_3SiOCH_3$,[4] $(CH_3)_2Si(OCH_3)_2$,[5] $CH_3Si(OCH_3)_3$,[6] $Si(OCH_3)_4$[7]].

The calculations were carried out with the program MOLECULE [8] which solves the Roothaan-Hall equations for a Gaussian type basis. The functions proposed by Roos and Siegbahn [9] were used for silicon and oxygen, *viz.*

Si: $(10s, 6p, 1d)$ contracted to $(6, 4, 1)$, (d exponent 0.30) O: $(7s, 3p)$ contracted to $(4, 2)$. For hydrogen $(4s)$ contracted to $(2s)$ was used with a scale factor of 1.2 for all the exponents.[10]

The results for the four staggered forms of $H_2Si(OH)_2$ (I—IV) shown in Fig. 1 are given in Table 1. In methanediol only the most stable form (similar to I, Fig. 1) was found to correspond to a minimum in the potential energy surface. The relative energies for silanediol are seen to be in the same order as for methanediol, but the values are considerably smaller. This difference between the silicon and carbon compounds is apparently not related to the use of d-orbitals on silicon; the value obtained
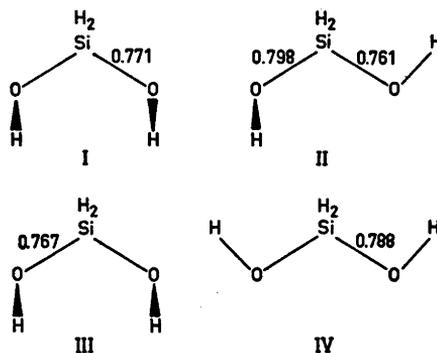

Fig. 1. The four conformations considered for silanediol. The overlap populations obtained for the Si—O bonds are given.

for the relative energy for form III is nearly the same when the d orbitals are not included in the calculations.

The simplest explanation for the smaller relative energies for the silicon compound seems to be that the longer Si—O bond, as compared with the C—O bond, decreases the dipole-dipole interaction between the oxygen lone pairs, and also decreases the contribution of the threefold component to the total potential of internal rotation.

The overlap populations obtained for the Si—O bonds are also given in Fig. 1. Their variations correlate well with the bond length variations found in the analogous conformers of methanediol,[3] except that our results indicate a slightly longer bond length in III than in I.

For silanetriol, calculations were first carried out for models with C_3 symmetry (V, Fig. 2). Table 2 shows the results. The minimum is in the vicinity of $\phi = 60°$. Thus the eclipsed form ($\phi = 60°$) appears to have greater stability than the staggered form ($\phi = 120°$). On the other hand, the electron diffraction data of methyltrimethoxy silane were found

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Table 1. Total and relative energies for conformations I—IV of silanediol.[a] Relative energies for methanediol [3] are given for comparison.

Form	Silanediol Total energy (a.u.)	Rel. energy (kcal/mol)	Methanediol Rel. energy (kcal/mol)
I	−440.73123	0	0
II	−440.73017	0.67	4.4
III	−440.72830	1.85(1.96)[b]	5.5
IV	−440.72625	3.14	11.0

[a] Assumed bond lengths and angles Si—H 1.48 Å, Si—O 1.63 Å, O—H 0.97 Å, H—Si—H 109.5°, O—Si—O 109.5°, Si—O—H 123.0°. [b] Obtained when d-orbitals on silicon were not included in the basis set.
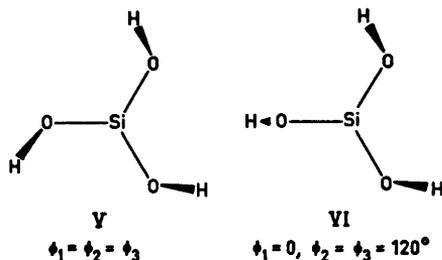
Fig. 2. Symmetric and asymmetric conformations considered for silanetriol.

to be consistent with a C_3 model, the prevailing forms of which having rotation angles between 100 and 155°, essentially a staggered conformation probably with large amplitude torsional motion. However, the structures of $HSi(OH)_3$ and $CH_3Si(OCH_3)_3$ need not necessarily be the same. The non-bonded $O \cdots H$ interactions in $HSi(OH)_3$ are favourable in the eclipsed form, while the oxygen$\cdots$methyl interactions in $CH_3Si(OCH_3)_3$ seem to favour the staggered form. Apart from these non-bonded interactions, the dipole-dipole interactions, the electron delocalization, and the threefold component of the total potential of internal rotation must also be considered (*cf.* Ref. 3). The last term is certainly more favourable in the staggered form, but its relative magnitude is probably small in $HSi(OH)_3$.

Of the possible staggered conformations of $HSi(OH)_3$, form VI of Fig. 2 would be the most likely to display the anomeric effect.[11] As the relevant result shows (Table 2), this form indeed appears to be slightly more stable than the symmetric staggered form, but somewhat less stable than the eclipsed conformation.

These tentative comparisons do not allow far-reaching conclusions. The present results

show the anomeric effect in silanediol but to considerably less extent than in methanediol. On the other hand, our calculations provide no indication of the anomeric effect in silanetriol. In this connection it may be of interest to mention that the length of the $Si - O$ bond in methyl trimethoxy silane $(1.632 \pm 0.004 \text{ Å})$[6] was found to be nearly the same as in trimethyl methoxy silane $(1.639 \pm 0.004 \text{ Å})$.[4] In case of an appreciable anomeric effect more shortening would have been expected in the trimethoxy derivative.

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Table 2. Total and relative energies for silanetriol.[a]

$\phi_1 = \phi_2 = \phi_3$ (°)[b]	Total energy (a.u.)	Rel. energy (kcal/mol)
0	− 515.53998	5.27
30	− 515.54397	2.76
60	− 515.54835	0.0
90	− 515.54771	0.40
120	− 515.54575	1.64 (1.05)[c]
150	− 515.54108	4.58
180	− 515.53725	6.99

[a] Assumed bond lengths and angles $Si - H$ 1.48 Å, $Si - O$ 1.63 Å, $O - H$ 0.97 Å, $H - Si - O$ 109.5°, $Si - O - H$ 123.7°. [b] The *anti* position of the $H - Si - O - H$ chain corresponds to $\phi = 0°$. [c] Obtained for a model with $\phi_1 = 0°$, $\phi_2 = \phi_3 = 120°$ (see Fig. 2).