Journal of Organometallic Chemistry, 346 (1988) 305–313
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The anomeric effect at silicon

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(Received November 20th, 1987)

Abstract

The anomeric effect at silicon has been studied by ab initio calculations. The geometries and energies of $H_2Si(XH)_2$, X = O, S were optimized with the basis sets 3-21G, 3-21G $^{(*)}$, and 6-31G *. Single point MP3/6-31G *//6-31G * calculations were also carried out. $H_2Si(XCH_3)_2$, X = O, S, were studied with the 3-21G basis set. All compounds are most stable in the *gauche,gauche* conformation, pointing to the operation of an anomeric effect. The total anomeric interactions given by the energies of the equations: $H_2Si(XH)_2 + SiH_4 \rightarrow 2H_3SiXH$ are (MP3/6-31G *): 8.6 and 2.2 kcal/mol for X = O and X = S, respectively. Rotation barriers on going from the (g,g), to the (g,a) and to the (a,a) conformations are (MP3/6-31G *, kcal/mol): 2.5 and 3.8 in $H_2Si(OH)_2$ and 2.1 and 3.2 in $H_2Si(SH)_2$. Thus, the anomeric effect in $H_2Si(OH)_2$ is large, although smaller than in $H_2C(OH)_2$. In $H_2Si(SH)_2$ and $H_2C(SH)_2$ the anomeric effects are comparable, and both relatively small. The anomeric effect is predicted to be important in determining the conformations of compounds with silicon bonded to 2 oxygens such as $R_2Si(OR')_2$, disilaoxiranes, and related molecules.

Introduction

The anomeric effect at carbon has attracted considerable attention both experimentally and theoretically, and the subject has been reviewed extensively [1]. The anomeric effect (on a generalized broad definition of the concept) is observed in molecules of the general type CH_2XY, where typically X and Y are groups such as OR, SR, and halogens [1]. The anomeric interactions manifest themselves in both the energies and the geometries of these molecules [1,2]. Compounds exhibiting the anomeric effect usually adopt a *gauche* conformation (e.g., $CH_2(OCH_3)_2$), and are significantly more stable than the corresponding singly-substituted analogues [1,2]. For example, at the best level of theory currently available the reaction shown in eq.

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1 is calculated to be exothermic by 15.7 kcal/mol, indicating a strong stabilizing interaction between the geminal-dihydroxy substituents [2].

$$\underset{(\mathbf{1})}{CH_2(OH)_2} + CH_4 \rightarrow 2CH_3OH \tag{1}$$

$$\underset{(\mathbf{2})}{CH_2(SH)_2} + CH_4 \rightarrow 2CH_3SH \tag{2}$$

We have recently studied computationally a variety of silicon compounds which have geminal alkoxy- or thio-substituents, such as substituted silicenium ions [3] (e.g., $(RO)_3Si^+$ and $(RS)_3Si^+$) [3,4*,5*], and multiply bonded silicon compounds (e.g., $(RO)_2Si{=}SiR_2$) [6] and disilaoxiranes [7]. For analysis of these molecules we required a basic knowledge of the interactions between geminal electronegative groups (such as OH) bonded to silicon. Various compounds that contain a silicon atom which is bonded at least to two oxygens are known. Many of these compounds are of commercial importance and have therefore attracted considerable interest. Typical examples are cyclic siloxanes, $(R_2SiO)_n$, which are precursors to high molecular weight silicone polymers [8], and silicates. We were therefore surprised to find that very little is known, either experimentally or theoretically, about the anomeric effect at silicon. The only previous study of the anomeric effect at silicon was reported in 1976 by Hargittai and Seip who performed calculations on $H_2Si(OH)_2$, but their calculations used assumed geometries and relatively simple levels of theory [9]. Ab initio calculations for $Si(OH)_4$ were also reported, but the interactions between the oxygen atoms were not discussed and the role of the anomeric effect was not evaluated [10].

In this paper we report the first detailed information on the anomeric effect at silicon [11*,12] for both oxygen and sulfur substituents. The results and the analysis of them are relevant to a variety of organosilicon molecules with silicon bonded to two or more oxygen or sulfur atoms.

Results and discussion

Ab initio molecular orbital calculations [13*] were carried out for the prototype molecules $H_2Si(OH)_2$ (**3**) and $H_2Si(SH)_2$ (**4**) and their methylated derivatives $H_2Si(OCH_3)_2$ (**5**) and $H_2Si(SCH_3)_2$ (**6**). The geometries of **3** and **4** were fully optimized by use of gradient techniques [13] and three basis sets: (a) the split valence 3-21G basis set [14]; (b) 3-21G $^{(\star)}$, which includes a set of *d*-functions on third-row atoms only (i.e., Si and S) [15], and (c) 6-31G *, a fully polarized basis set which includes *d*-functions on all non-hydrogen atoms [16]. More reliable energy comparisons were obtained by including corrections for electron correlation. Thus, single-point MP2/6-31G * and MP3/6-31G * calculations [17] at the 6-31G * optimized geometries (denoted by MP2/6-31G *//6-31G * and MP3/6-31G *//6-31G *, respectively) were also carried out. The optimized geometries at the 3-21G, 3-21G $^{(\star)}$ and 6-31G * level for **3** and **4** are shown in Fig. 1, and the

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* This and other references marked with asterisks indicate notes occurring in the list of references.

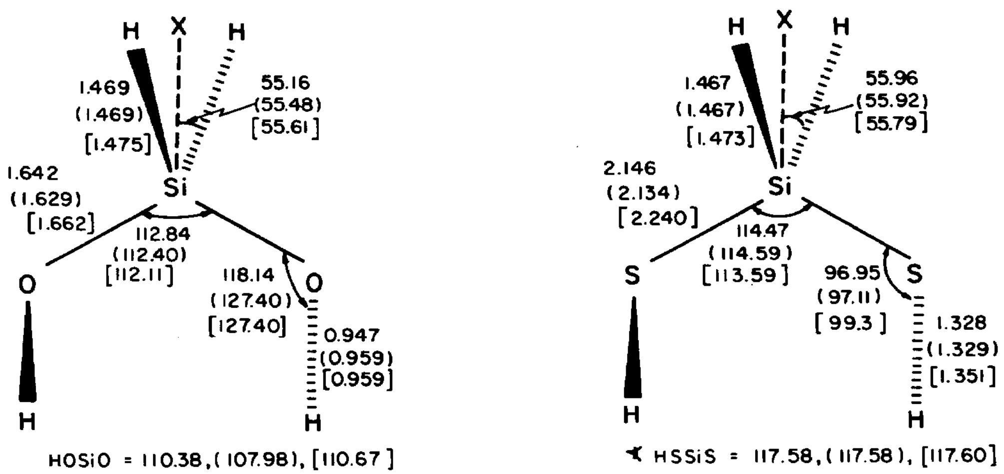


Fig. 1. Calculated geometries of $H_2Si(OH)_2$ and $H_2Si(SH)_2$ at 6-31G * (no brackets), 3-21G $^{(*)}$ (round brackets) and 3-21G (square brackets). X is a notional atom on the bisector of the HSiH angle.

corresponding total energies are listed in Table 1 (which also gives the 3-21G//3-21G total energies for **5** and **6**).

$H_2C(OH)_2$ (**1**)	$H_2Si(OH)_2$ (**3**)	$H_2Si(OCH_3)_2$ (**5**)
$H_2C(SH)_2$ (**2**)	$H_2Si(SH)_2$ (**4**)	$H_2Si(SCH_3)_2$ (**6**)

The lowest energy conformations of both **3** and **4** is *gauche* [18*]. This is the case (at 3-21G) also for the corresponding methyl ether **5** and methyl thioether **6**, as well as for the carbon analogues **1** and **2** [1,2]. This conformational preference is a strong indication of the operation of an anomeric effect [1,2] at silicon (see below).

In line with the molecular orbital interpretation of the anomeric effect at carbon [1], we attribute the anomeric effect at silicon to the interactions of the lone pairs of

Table 1

Absolute energies (in Hartrees) for $H_2Si(OH)_2$ and $H_2Si(SH)_2$ in the (*g*,*g*)-conformation **12**, at various levels of calculation [a]

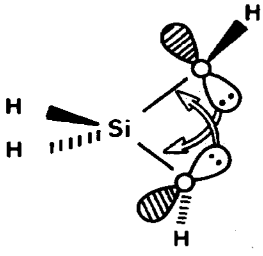
Method	$H_2Si(OH)_2$	$H_2Si(SH)_2$
3-21G//3-21G	−438.69108	−1080.86778
3-21G$^{(*)}$//3-21G$^{(*)}$	−438.81548	−1081.19324
6-31G *//6-31G *	−441.04713	−1086.31746
MP2/6-31G *//6-31G *	−441.48540	−1086.63280
MP3/6-31G *//6-31G *	−441.49792	−1086.67339

[a] The 3-21G//3-21G total energies for (*g*,*g*)-$H_2Si(OCH_3)_2$ and of (*g*,*g*)-$H_2Si(SCH_3)_2$ are −438.69108 and −1080.86778 Hartrees, respectively.

the heteroatoms (O or S) with the geminal-Si-X (X = O, S) σ^* orbitals, as shown schematically in **7**. According to this model the *gauche,gauche* conformation (g,g) is expected to be the most stable, because in this stereochemical arrangement the σ^* (Si–X) orbital is properly aligned to interact with the $2p$ lone-pair on the heteratom. On the other hand, in the *gauche,anti* conformation (g,a) one of the $2p$ lone-pairs interacts with σ^* (Si–H) (see **8**). As the interaction of $2p$ with σ^* (Si–H) is weaker than with σ^* (Si–X) (see below) conformation **8** is less stable than **7**. In the *anti,anti* conformation (a,a) the $2p$ lone-pairs on the two heteroatoms are out of conjugation with the adjacent (Si–X) bonds, as shown in **9**, and the interactions between the geminal groups are significantly reduced.

The stronger interaction of $2p$ with σ^* (Si–X) than with σ^* (Si–H) can be understood in terms of qualitative Perturbation Molecular Orbital (PMO) theory [19]. According to this theory the second-order energy stabilization resulting from the interaction of two orbitals i and j is proportional to $S_{ij}^2/\Delta\epsilon_{ij}$, where S_{ij} is the overlap matrix element and $\Delta\epsilon_{ij}$ is the energy difference between the interacting orbitals [19]. Qualitatively it is expected that σ^* (Si–X) will be lower in energy than σ^* (Si–H) and that the $2p$-σ^* (Si–X) overlap will be larger than the $2p$-σ^* (Si–H) overlap owing to the greater polarization towards silicon of σ^* (Si–X) than of σ^* (Si–H). Thus according to this model, both the numerator (S_{ij}^2) and the denominator $(\Delta\epsilon_{ij})$ of the above PMO expression favor the $2p$-σ^* (Si–X) interaction, making it more stabilizing than the $2p$-σ^* (Si–H) interaction. A recent quantitative Natural Bond Orbital (NBO) energetic analysis of this problem by Reed and Schleyer [12] showed that the overlap factor (S_{ij}^2) contributes much more than the energy factor $(\Delta\epsilon_{ij})$ to the difference in hyperconjugative stabilization between these two situations (see Von R. Schleyer's papers [12] in particular ref. 12a for a more detailed discussion). Note that in **9** the sp^2 lone-pairs on X are properly aligned to interact with the adjacent σ^* (Si–X) orbitals. However, as the sp^2 lone-pairs are lower in energy and have also smaller overlap with σ^*(Si–X) than the $2p$ lone-pairs, conformation **9** is less stable than **7** or **8** (i.e. both $\Delta\epsilon_{ij}$ and S_{ij} are larger in **9** than in **7**).

These PMO arguments lead to the conclusion that if the anomeric effect is important then the expected order of stabililty should be **7** > **8** > **9**; this is indeed the stability order that we calculate (see Table 2 and discussion below), pointing to the operation of an anomeric effect in **3**, **4**, **5** and **6**.



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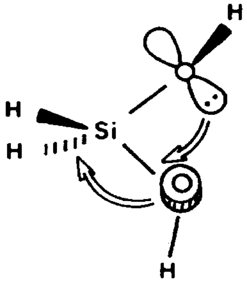

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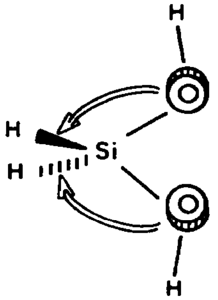
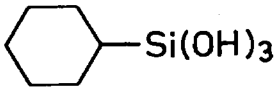


(9)

Detailed experimental data for **3**–**6**, or similar molecules that can be compared directly with the calculations are unfortunately not available. The crystal structures of several organosilanediols [20] and of two organosilanetriols [21] have been determined experimentally. However, in these compounds there are strong intermolecular hydrogen bonds which affect the geometry [20,21] and prevent direct comparison with our calculations. In cyclohexylsilanetriol (**10**), the disorder of the hydrogen-bond network even prevents determination of the conformation around the HOSiO bonds [21(a)]. The possible operation of the anomeric effect was not mentioned in reports of these studies [20,21]. The most relevant experimental data come from an electron diffraction study of the molecular structure of $CH_3Si(OCH_3)_3$ by Hargittai et al. [22]. These authors found that the data are consistent with a molecule of C_3 symmetry, the predominant forms of which have rotational angles between 100° and 155° around the Si–O bonds (the *anti*-conformation of the C–Si–O–C chain corresponds to 0°). Unfortunately, the uncertainty in the determination of the rotational angle is large, and it is not possible to conclude whether or not an anomeric effect is operating in this molecule (the anomeric effect is not discussed in ref. 22).



(10)

In addition to the conformational preferences, further intimate structural details are also available from the calculations. As in the carbon analogues [1a], the Si–O and the Si–S bonds are somewhat shorter in **3** and **4** than in H_3SiOH (1.647 Å, 6-31G *) and H_3SiSH (2.15 Å, 6-31G *) [23], respectively. It is noteworthy that the Si–X bond lengths are shortened significantly when *d*-functions are added to the basis set (Fig. 1). This phenomenon is well documented for silicon and other third-row elements [23–25]. Experience shows that 6-31G * calculations provide a very good description of the geometries of molecules such as **3**–**6** [10,23–25]. For example, Hargittai et al. have reported that in $CH_3Si(OCH_3)_3$, r(Si–O) 1.632 ± 0.004 Å [22], in good agreement with the calculated 6-31G * value for **3** of 1.642 Å. As the present calculations neglect electron correlation we estimate that the experimental Si–O and Si–S bond lengths in **3** and **4** are actually slightly longer (by ca. 0.01 Å) than the calculated 6-31G * values [24,25].

The magnitude of the anomeric effect can be estimated by using two methods, each referring to a different aspect of this phenomenon [1]. The first method measures the total interaction between the geminal substituents. The second method relates to the conformational preference of the *gauche* structure. We evaluate first the total interactions between the two geminal substituents in **3** and **4**, by means of equations 3 and 4, respectively. The calculated energies are given in Table 2.

$$H_2Si(OH)_2 + SiH_4 \rightarrow 2H_3SiOH \qquad (3)$$

$$H_2Si(SH)_2 + SiH_4 \rightarrow 2H_3SiSH \qquad (4)$$

Table 2

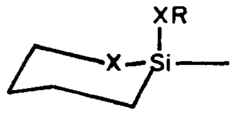
Total interaction energies (eq. 3 and 4) and relative energies of conformers of $H_2Si(OH)_2$ and $H_2Si(SH)_2$ [a]

Method	Δε (eq. 3)	Relative energy			Δε (eq. 3)	Relative energy		
		12 (g,g)	13 (a,g)	14 (a,a)		12 (g,g)	13 (a,g)	14 (a,a)
	$H_2Si(OH)_2$				*$H_2Si(SH)_2$*			
3-21G//3-21G	10.6	0.0	3.3	7.8	0.3	0.0	2.3	5.6
3-21G$^{(*)}$//3-21G$^{(*)}$	8.2	0.0	2.3	5.9	1.0	0.0	1.9	4.9
6-31G*//6-31G*	7.2	0.0	2.1	5.3	0.7	0.0	1.8	4.6
MP2/6-31G*//6-31G*	8.5	0.0	2.6	6.5	2.6	0.0	2.2	5.6
MP3/6-31G*//6-31G*	8.6	0.0	2.5	6.3	2.2	0.0	2.1	5.3
	$H_2C(OH)_2$				*$H_2C(SH)_2$*			
6-31G*//6-31G*	15.0 [b]	0.0 [d]	4.4 [d]	10.1 [d]	0.6 [c]	0.0 [d]	1.9 [d]	5.2 [d]
MP2/6-31G*//6-31G*	16.6 [b]	0.0	4.9	11.2	2.3 [c]	0.0	2.4	6.3
MP3/6-31G*//6-31G*	15.8 [b]	0.0	4.8	10.8	1.4 [c]	0.0	2.3	6.0

[a] All energies in kcal/mol. [b] For eq. 1. [c] For eq. 2. [d] For conformations of $CH_2(OH)_2$ and $CH_2(SH)_2$ analogous to **12–14**.

At the MP3/6-31G*//6-31G* level eq. 3 and 4 are exothermic by 8.6 and 2.2 kcal/mol, respectively (Table 2). These energies reveal a significant stabilization of the disubstituted silicon compounds relative to the corresponding monosubstituted derivatives, the effect being much larger for two oxygens than for two sulfurs. In a subsequent paper we will show how the differences in the magnitude of the anomeric effect at silicon between oxygen and sulfur affect the energies of dissociation of $(HO)_3SiH$ and $(HS)_3SiH$ to the corresponding silicenium ions [3,4*]. In the corresponding carbon series the anomeric stabilization is also larger for oxygen than for sulfur [1,2]. However, there are important differences in the behavior of the carbon and the silicon systems. With oxygen as the substituent, the geminal interactions at carbon are much larger than at silicon. On the other hand, the anomeric effect of sulfur is relatively small, and is of almost the same magnitude when bonded either to silicon or to carbon.

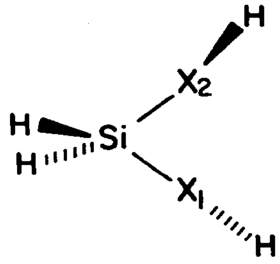
The rotation barriers around the Si–XH bonds in **3** (X = O) and **4** (X = S) reveal the magnitude of the structural (torsional) manifestations of the anomeric effect. This information is relevant to the conformational analysis of analogous organosilicon compounds such as $R_2Si(XR')_2$ (R′ = alkyl, aryl; X = O, S; R = H, alkyl) and cyclic systems such as **11**, for which axial and equatorial conformers are possible.



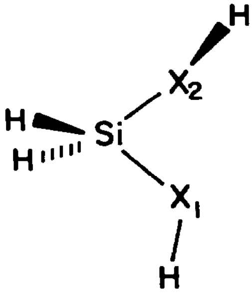
(11)

Rotation of one of the XH groups in **3** and **4** (using the "rigid rotor" model [26*]) from the (*g*,*g*)-conformation **12** (which is the most stable) to the (*a*,*g*)-conformation **13** ($HX_1SiX_2 = 180°$; $HX_2SiX_1 = 110.4°$ in **3** and 117.6° in **4**) requires at the MP3/6-31G * level 2.5 and 2.1 kcal/mol, respectively (Table 2). Rotation in **13** of the second XH group to an *anti*-orientation, i.e., to the (*a*,*a*)-conformation **14**, requires 3.8 and 3.2 kcal/mol (MP3/6-31G *) for **3** and **4**, respectively. Thus, rotation of the second XH group out of conjugation requires slightly more energy than the rotation of the first group.

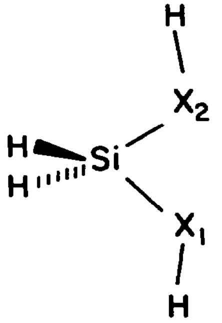
The conformational preferences of $H_2Si(OH)_2$ and $H_2Si(SH)_2$ are similar; for both the (*g*,*g*)-conformation is favoured by ca. 2–3 kcal/mol. Comparison with the carbon analogues shows that the rotation barriers, and thus the conformational preferences, are larger for $H_2C(OH)_2$ than for $H_2Si(OH)_2$, but are similar in $H_2C(SH)_2$ and $H_2Si(SH)_2$. Thus, at the MP3/6-31G * level, rotation of one XH group to an *anti*-conformation (i.e., as in **13**) requires 4.8 kcal/mol in $CH_2(OH)_2$ (2.5 kcal/mol for $H_2Si(OH)_2$) and 2.3 kcal/mol in $CH_2(SH)_2$ (2.1 kcal/mol for $H_2Si(SH)_2$). The rotation of the second XH group to an *anti*-position (i.e., as in **14**) requires 6.0 (3.8) and 3.7 (3.2) kcal/mol for $H_2C(OH)_2$ ($H_2Si(OH)_2$) and $H_2C(SH)_2$ ($H_2Si(SH)_2$), respectively. The trends which are observed when comparing the rotation barriers in the carbon and the silicon compounds parallel the conclusions from equations 1–4 regarding the magnitude of the total anomeric interactions in these compounds. Thus both the total thermodynamic stabilization and the conformational anomeric effect are larger for $H_2C(OH)_2$ than for $H_2Si(OH)_2$, and both effects are relatively small and comparable in magnitude for $H_2Si(SH)_2$ and $H_2C(SH)_2$.



(12)(g,g)



(13)(a,g)



(14)(a,a)

In conclusion, we find a significant stabilizing geminal-anomeric effect at silicon, especially when silicon is bonded to two oxygens. The resulting total thermodynamic stabilization is smaller (by approximately half) than for the analogous carbon systems. The anomeric effect is much smaller for sulfur substituents for both silicon and for carbon. The differences between the carbon and the silicon molecules can be understood, as shown recently by Reed and Von R. Schleyer [12] primarily in terms of the higher electropositivity of silicon. Electronegativity differences are probably also the major factor responsible for the differences between $H_2Si(OH)_2$ and $H_2Si(SH)_2$ (or $H_2C(OH)_2$ vs. $H_2C(SH)_2$), but the longer bonds to sulfur, which reduce the overlap between the geminal orbitals, may also contribute.

The anomeric effect at silicon, although smaller than at carbon, is large enough to influence or even to determine the prefered conformations of appropriate organosilicon compounds such as R_2SiXY where X and Y are OR, SR, halogens [3], disilaoxiranes [7], and cyclic organosilicon molecules such as **11**. We are extending our study to other SiH_2XY systems in which X and Y span the entire second and third-row substituents (i.e., Li to F and Na to Cl).

We hope that this report will stimulate a variety of experimental studies, structural, thermodynamic and kinetic [1], which will establish the importance of the anomeric effect in organosilicon chemistry.

Acknowledgements

We thank Professor P. von R. Schleyer for helpful comments and for preprints of his related work (ref. 12), Dr. M. Karni for some of the calculations, and the United States-Israel Binational Science Foundation (BSF) for financial support for this study.

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