

Eclipsed conformers of oligosilane derivatives by intramolecular hypercoordination

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Abstract

The eclipsed conformers of $\text{ClSiH}_2\text{SiH}_2\text{SiH}_2\text{OH}$ (**1**) and $\text{DL-ClSiH}_2(\text{OH})\text{SiHSiH}(\text{OH})\text{SiH}_2\text{Cl}$ (**2**) are the most stable due to the attractive 1,4-hypercoordination by the n_{O} and σ_{SiCl}^* orbital interaction. The eclipsed rotamer of $\text{ClSiH}_2(\text{OH})_2\text{SiSi}(\text{OH})(\text{SiH}_2\text{Cl})_2$ (**3**) is the exclusive conformer stabilized by the threefold 1,4-hypercoordination.

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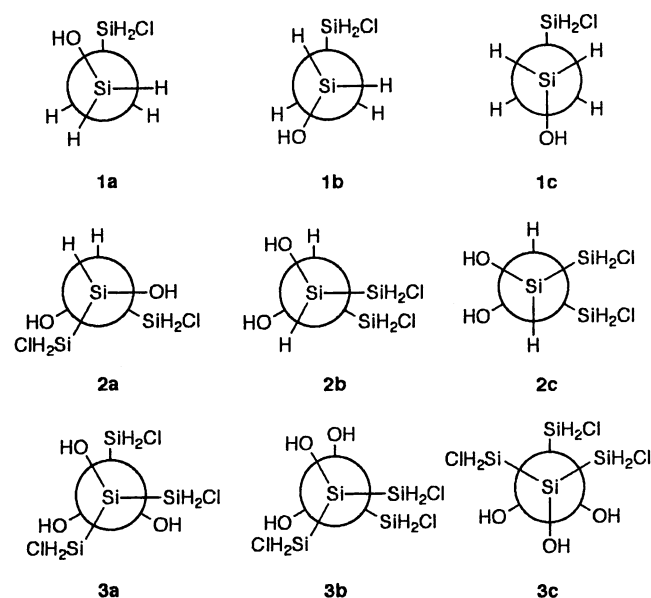
1. Introduction

Oligosilanes have invoked much interest in their unique physical properties [1], which are greatly affected by the conformation of silicon chains. Many model molecules with fixed conformations were designed and synthesized to investigate conformational effects on their properties [2]. Ring structures have been used so far to fix the conformations. Here, we design relatively or exclusively stable eclipsed conformers of open-chain oligosilane derivatives with anticlinal Si–Si–Si conformations.

In most of open-chain molecules, staggered conformers are local minima on the potential energy surface, while eclipsed conformers are the transition structures of the rotation about the single bond. Eclipsed conformers were, however, observed for some carbon-chain molecules [3]. Hypercoordination was shown to control the stabilities of the conformers [4]. Here, we apply the hypercoordination to the design of relatively and exclusively stable eclipsed conformers of oligosilane derivatives.

2. Results and discussion

We calculated $\text{ClSiH}_2\text{SiH}_2\text{SiH}_2\text{OH}$ (**1**) at the MP2/6-31G* level [5]. The eclipsed conformer **1a** (Fig. 1) is a local energy minimum (Fig. 2), which is more stable by $1.6 \text{ kcal mol}^{-1}$ than the anti conformer **1c**. The energy barrier to the anti conformer is low (2.1 kcal/mol). Almost eclipsed conformers (the dihedral angle $\text{SiSiSiO} \cong 20^\circ$) were located at the HF/6-31G* and B3LYP/6-31G* levels.



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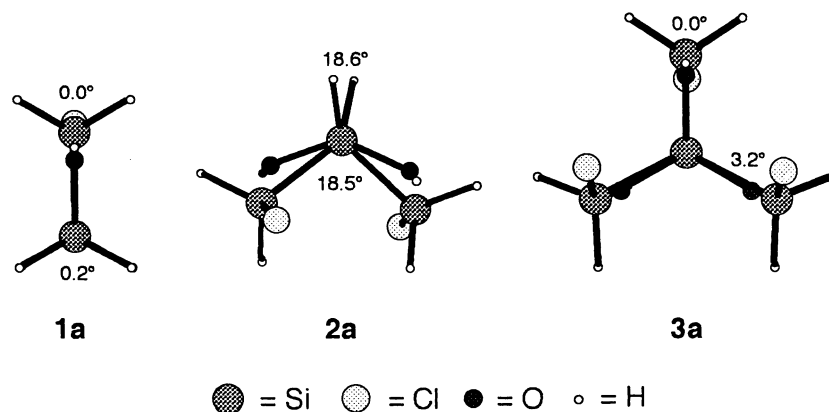


Fig. 1. Relatively or exclusively stable eclipsed conformers. Dihedral angles of X–Si–Si–Y (X, Y = H, OH, SiClH₂) in **1a**, **2a** and **3a** at MP2/6-31G* level.

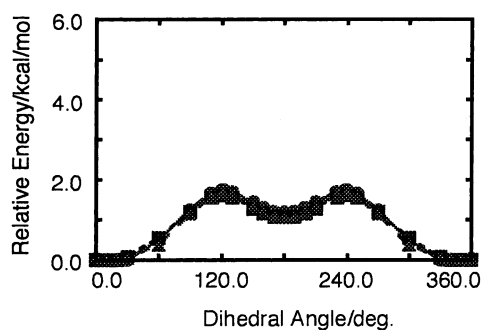


Fig. 2. The dependence of the relative energy of ClSiH₂SiH₂SiH₂OH (**1**) on the dihedral angle SiSiSiO, calculated at the HF/6-31G* (●), the B3LYP/6-31G* (■), and the MP2/6-31G* levels (▲).

At these levels, the completely eclipsed conformer is not a local energy minimum, but has no appreciable energy difference from the local minimum. The bond model analysis [6,7] confirmed the significance of the attractive 1,4-hypercoordination. According to the calculated interbond energy (IBE) [7], the n_{O} and σ_{SiCl} bond interaction stabilizes the almost eclipsed conformer (–1.93 kcal/mol). The stabilizing delocalization from the n_{O} orbital to the σ_{SiCl}^* orbital (–2.36 kcal/mol) overcomes the repulsion (0.42 kcal/mol) between the corre-

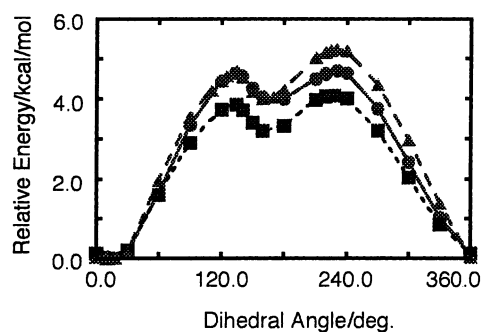


Fig. 3. The dependence of the relative energy of ClSiH₂(OH)SiHSiH(OH)SiH₂Cl (**2**) on the dihedral angle SiSiSiO, calculated at the HF/6-31G* (●), the B3LYP/6-31G* (■), and the MP2/6-31G* levels (▲).

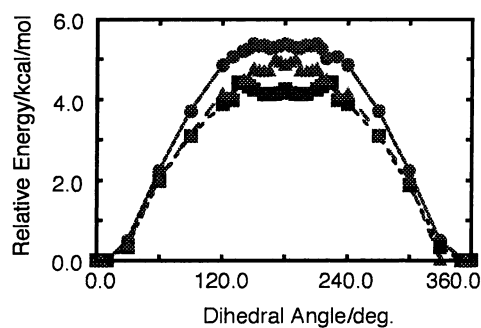


Fig. 4. The dependence of the relative energy of ClSiH₂(OH)₂SiSi(OH)(SiH₂Cl)₂ (**3**) on the dihedral angle SiSiSiO, calculated at the HF/6-31G* (●), the B3LYP/6-31G* (■), and the MP2/6-31G* levels (▲).

sponding occupied n_{O} and σ_{SiCl} orbitals. The significant $n_{\text{O}}-\sigma_{\text{SiCl}}^*$ attraction suggested that the increase in the number of the 1,4-hypercoordinations should more stabilize the eclipsed conformers.

We calculated the potential curves of DL-ClSiH₂(OH)SiHSiH(OH)SiH₂Cl (**2**) with the twofold hypercoordination. The almost eclipsed conformer **2a** (the dihedral angle SiSiSiO $\cong 20^\circ$, Fig. 1) was located as an energy minimum and has no appreciable energy difference from the completely eclipsed conformer (Fig. 3). The stability (3.1–4.0 kcal/mol) relative to the staggered (the dihedral angle SiSiSiO $\cong 170^\circ$) or synclinal conformer **2c** increased as was expected. The rotational barriers through another eclipsed conformer **2b** as the transition structure are 3.8–4.7 kcal/mol from **2a** to **2c** and 0.7 kcal/mol from **2c** to **2a**.

Now, we can expect that the eclipsed conformer **3a** of ClSiH₂(OH)₂SiSi(OH)(SiH₂Cl)₂ (**3**) with the threefold hypercoordination is relatively more stabilized or possible to be the exclusively conformer. We calculated the potential curve of **3** (Fig. 4). The most stable conformer is almost eclipsed (the dihedral SiSiSiO angle = 0–5°: Fig. 1). The anti conformer is not an effective local

energy minimum. The potential well for the conformer with the SiSiSiO dihedral angle of 160° as a local energy minimum is too shallow to be observed by experiments. The eclipsed conformer **3a** is an exclusive conformer.

3. Conclusion

The manifold 1,4-hypercoordination was demonstrated to be strong enough to control the conformations of oligosilane derivatives. The relatively stable eclipsed conformer **2a** and the exclusively stable one **3a** have anticlinal Si–Si–Si–Si structures. The eclipsed conformers enable us to investigate chemical and physical properties of silanes resulting from the unique conformations.

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