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Electrostatic Potential Maps of Silacyclohexane: The Origin of the "Gauche Effect" on Silicon Compounds

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The incorporation of heteroatom to hydrocarbon molecules changes the conformational preference dramatically. One of the interesting features is a phenomenon known as the "gauche effect".¹ Many molecules containing N, O, S, P, F, or Cl atom show the preference to adopt the gauche conformation.^{1,2} The "gauche effect" in these molecules has been interpreted on the basis of electronic natures such as lone-pairs, electron/nuclear charge distributions, and polar bonds.

The "gauche effect" is also ubiquitous in various silicon compounds.^{3,6} Various butane-like silicon compounds such as ethylmethylsilane ($\text{CH}_3\text{CH}_2\text{SiH}_2\text{CH}_3$),^{3a,b,4,6b} ethylchlorosilane ($\text{CH}_3\text{CH}_2\text{SiH}_2\text{Cl}$),^{6b,c} 1,2-dimethyldisilane ($\text{CH}_3\text{SiH}_2\text{SiH}_2\text{CH}_3$),^{5a,b,6a} and (chloromethyl)methylsilane ($\text{ClCH}_2\text{SiH}_2\text{CH}_3$)^{6c,d} are more stable in the gauche conformation than in the anti conformation. Cyclic 6-membered ring systems also provide valuable information about the "gauche effect". The A value, the free energy difference between the axial and equatorial conformations, is largely attributed to the gauche/anti energy difference of the torsional frame which is composed of the substituent and 3 ring atoms. 1-Methylsilacyclohexane and 1-chlorosilacyclohexane are more stable in the axial conformation than in the equatorial conformation by 0.13 kcal/mol,^{3b} and 0.81 kcal/mol,^{6c} respectively. In contrast to other heteroatoms, the "gauche effect" of silicon compounds has been explained mostly by steric reasons due to the longer Si-C bond length.^{3b,4,6a,b,c}

In connection with the conformational analyses of various monosubstituted silacyclohexanes (SCHs), we have been interested in the structure and electronic nature of SCH. Understanding the exact structural and electronic natures of SCH is important, because SCH serves as the reference molecule in quantifying the A values of various monosubstituted SCHs. Especially, it is our intention to analyze electronic natures including the electrostatic potential (ESP), which is generally accepted to furnish useful information about the

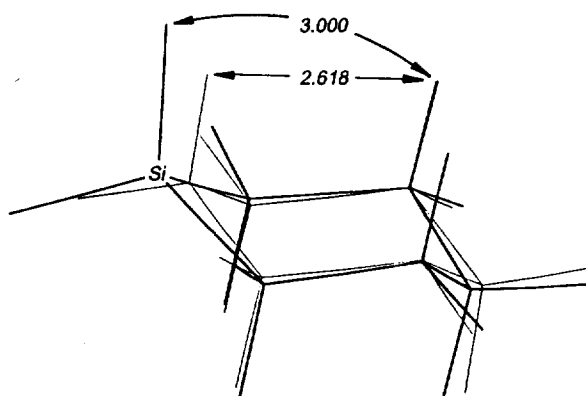


Figure 1. MP2/6-31G* optimized chair conformation of CH (---) and SCH (—); least-square fit using 4 ring carbons (2α -carbons and 2β -carbons in SCH).

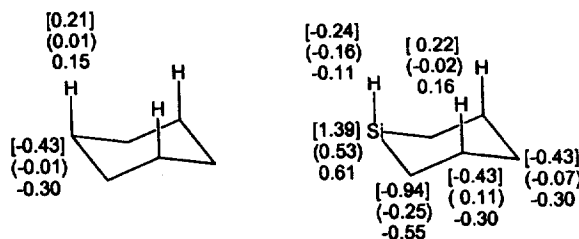


Figure 2. [NP], (CHELPG), and MP charges of ring atoms and axial hydrogens in CH and SCH calculated by MP2/6-31G*.

charge distribution around the molecule.⁷

Ab initio molecular orbital calculations have been performed using the GAUSSIAN-92 series of programs,⁸ on a Cray Y-MP computer. The geometries of cyclohexane (CH) and SCH have been optimized at the MP2/6-31G* level of theory.⁹ Only the chair conformation has been considered by imposing D_{3d} symmetry on CH and C_s symmetry on SCH.

The MP2/6-31G* calculated structures of SCH and CH are compared in Figure 1. An interesting structural modification in SCH is that the axial hydrogen attached to Si moves away from the ring. According to our MP2/6-31G* calculations, the torsional angles of ring carbons in CH are 55.6° . In SCH, the torsional angle of C-Si-C-C is only 45.8° which shows the Si tip of the ring quite flattened. The torsional angle of C₂-C₃-C₄-C₅ in SCH is 65.8° which indicates the puckering degree of γ -carbon greater (See Figure 1). Consequently, the change of ring skeleton forces the geometric parameters including hydrogens to be altered substantially. The distances from the axial hydrogen of Si to the axial hydrogens of β -Cs in SCH are 3.00 Å, while the distances between 1,3-diaxial hydrogens in CH are 2.62 Å. This implies that most axial substituents at Si atom of SCH may relieve unfavorable 1,3-diaxial interactions due to (1) the longer Si-bonds, i.e. Si-C ring bonds and exocyclic Si bonds to substituents, and (2) flattening of Si tip. However, the subtle increase of the distance between 1,3-diaxial hydrogens by 0.4 Å may not be accounted for the "gauche effect" of silicon compounds entirely.

The nonbonded interactions between neutral atoms usually contribute small energy differences with respect to electro-

static interactions between partially charged species. We have examined the excess charges of ring atoms and axial hydrogens from various population schemes, *i.e.* Mulliken population (MP),¹⁰ CHELPG,¹¹ and natural population (NP) analysis.¹² Results are summarized in Figure 2. According to MP charges, the hydrogen attached to Si atom has an excess negative charge (hydride type characteristics), while the hydrogen attached to C atom bears a slight positive charge. Previously, we¹³ and others¹⁴ have confirmed that most atoms, except metallic elements, attached to Si atom withdraw electrons to be more negatively charged due to the strong electropositive nature of Si atom. Thus, the different nature and magnitude of the polarization in between C and Si bonds yield a distinct discrepancy of the charge distribution around molecules. One of typical examples can also be found in the charge distributions of CH and SCH. The layout of excess charges obtained from both MP and NP analyses shows that attractive electrostatic interactions between the axial hydrogen attached Si and the axial hydrogens of β -carbons are indeed present in SCH. On the other hand, the repulsive electrostatic interactions between axial hydrogens are observed in CH. Although the opposite trend may not be expected in electronwithdrawing substituents, the magnitude of attractive electrostatic interactions can be augmented in SCH. The electronwithdrawing groups withhold more electrons to have larger negative charges when they are bound to Si atom.¹³

As one may noticed in Figure 2, excess charges obtained from CHELPG method supply notably different values compared to the ones from other methods. We believe that this large disagreement is originated from the factor that CHELPG charge partitioning scheme is based on ESP, not the molecular orbital which both MP and NP schemes utilize. Many scientists in molecular modeling society consider that CHELPG charges supply better results than other schemes do. Therefore, it is quite surprising that CHELPG scheme provides charge values which are serious disagreement with chemical intuition. In addition, previously, we have noticed that CHELPG scheme sometimes assigns a small positive charge to an atom which develops significantly negative ESPs at the back pocket.¹⁵ Since this problem may be a common shortcoming in atomic centered charges, we feel that much more realistic views of charge distributions around the molecule can be disclosed by examining ESP maps.

Accordingly, we have investigated ESP maps of various molecular planes from MP2/6-31G* calculations in order to comprehend electrostatic interactions between axial hydrogens. Figure 3 illustrates ESPs in (1) the plane containing 3 axial hydrogens, and (2) 1 Å above the plane of the axial hydrogens. Since the distances between axial hydrogens are approximately the sum of two van der Waals radii, the inner circle is highly positive due to the dominant contributions from nuclear charges. The outer region usually reflects more precise electronic natures. Going from CH to SCH, the back-side negative pocket becomes smaller at the axial hydrogens attached to β -carbons, and gets greater to the hydrogen attached to Si. We can observe a clear difference in the plane 1 Å above axial hydrogens. In SCH, the ESP shows two separate regions; negative above the Si atom and positive above β carbons. This layout clearly supports attractive electrostatic interactions in SCH. The ESP as well as the charge distribution around the molecule varies significantly due to

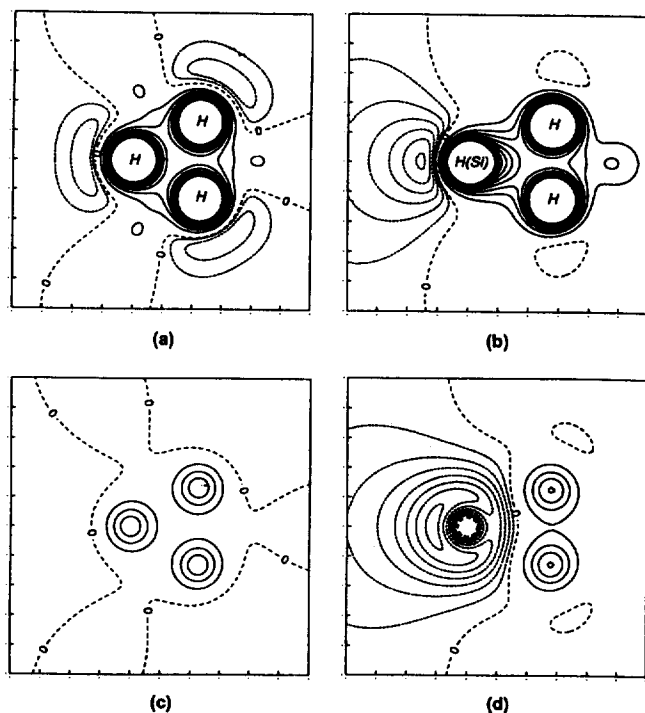


Figure 3. MP2/6-31G* derived ESP maps of CH and SCH. In the plane including 3-axial hydrogens ((a) for CH, (b) for SCH; isopotential lines of 40, 30, 20, 10, 0, -1, -2, -3, -4, -5, and -6 kcal/mol). In a plane 1 Å above the 3-axial hydrogens ((c) for CH, (d) for SCH; isopotential lines from 8 to -8 kcal/mol with an interval of 1 kcal/mol).

the different group in an axial position. However, we are interested in only the difference rather than the absolute charge values. It is a general trend that the charge of the axial substituent at Si atom in SCH is more negative compared with the one in CH. Therefore, our explanation appears to be retained in various substituents including electronwithdrawing groups.

In summary, our investigation on the structural and electronic nature in SCH strongly implies that *the origin of the "gauche effect" in silicon compounds comes from both the favorable nonbonded interactions and the attractive electrostatic interactions.* Further studies including the conformational preference of various monosubstituted SCHs are in progress, and will provide more insight into the nature and origins of the "gauche effect" on silicon compounds.

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