

Comment on “Relative Energies, Stereoelectronic Interactions, and Conformational Interconversion in Silacycloalkanes”

INGVAR ARNASON, ÁGÚST KVARAN, ANDRAS BODI

Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavík, Iceland

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ABSTRACT: Relative energies for local minima and transition states on the potential energy surface (PES) of silacyclohexane have been calculated at the B3LYP/6-311+G(*d,p*) level of theory. STQN(path), and intrinsic reaction path (IRC) calculations were used to calculate the lowest-energy pathway for the chair-to-chair interconversion. Both methods gave identical results. An earlier description of the PES of silacyclohexane, derived with the MM3 force field, was confirmed. A different path for the ring inversion of silacyclohexane, proposed in a recent work, is shown to be incorrect.

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Key words: conformational interconversion; potential energy surface; conformational globe; silacyclohexane; transition state

Introduction

Five years ago, we published a conformational study on silacyclohexane [1]. The potential (or conformational) energy surface (PES) was mapped using the MM3 force field [2] by varying two opposite dihedral angles of the ring atoms in small steps within the range from 90° to –90°. It was found that the chair-to-chair interconversion proceeds via chair(**1a**) → transition state(**1g[#]**) → twist-C₁(**1c**) → boat(**1e[#]**) → twist-C₂(**1b**) → boat(**1e[#]**) →

twist-C₁(**1c**) → transition state(**1g[#]**) → inverted chair (see Fig. 1). Throughout the text, we will use **1a**, **1b**, **1c**, and so on, for the conformers of silacyclohexane, as used by Freeman et al. [3] in their recent paper, and as shown in Figure 1, as opposed to twist-C₁, twist-C₂, boat, etc., which were used in our previous work [1]. All local minima on the interconversion path were optimized using the Hartree-Fock (HF), Møller-Plesset type 2 (MP2), and density functional theory (DFT) methods and various basis sets. According to our RI-DFT calculations, **1c**, **1e[#]**, and **1b** conformers are 4.89, 5.18, and 3.87 kcal mol⁻¹ higher in energy than the chair conformer, respectively.

Correspondence to: I. Arnason; e-mail: ingvara@raunvis.hi.is

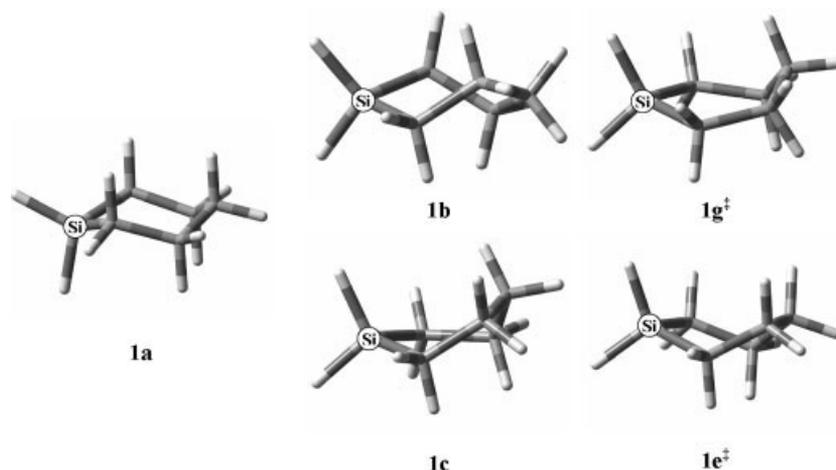


FIGURE 1. Chair (**1a**), twist (**1b**, **1c**), boat (**1e[#]**) and half-chair/sofa (**1g[#]**) conformers of silacyclohexane.

In a recent paper in the *Journal of International Quantum Chemistry*, Freeman et al. [3] report DFT B3LYP/6-311+G(*d,p*) calculations, and find that these relative energies are 4.82, 5.18, and 3.89 kcal mol⁻¹, respectively, in good agreement with our results (ΔE values without ZPE corrections in both cases). The authors then found that intrinsic reaction path (IRC) calculations [4, 5] connected the half-chair transition state **1g[#]** to the chair **1a** and twist **1c**, and argue: "The potential energy diagram for the chair-chair interconversion of silacyclohexane (Fig. 4) is different than the one previously proposed [1], but is consistent with one of the proposed chair-to-chair interconversion mechanisms for cyclohexane." Furthermore, in their concluding remarks the authors write: "The path for the chair-to-chair conformational interconversion of silacyclohexane proceeds via the 2,5-twist [**1c**, our insertion] conformer (intermediate) without going through a boat

conformation." These statements are incorrect, and in this paper we show that our previous description of the chair-to-chair interconversion for silacyclohexane indeed corresponds to the lowest-energy pathway.

Results

The relevant conformers of silacyclohexane; **1a**, **1b**, **1c**, **1e[#]**, and **1g[#]** (Fig. 1) have been recalculated at the B3LYP/6-311+G(*d,p*) level using Gaussian 03 [6]. The results are shown in Table I. Two different methods—the synchronous transit-guided quasi-Newton [STQN(Path)] method [7], and IRC calculations—were used to calculate the chair-to-chair interconversion of silacyclohexane at the B3LYP/6-311+G(*d,p*) level. The approach of the two methods is different. The STQN(Path) method works uphill

TABLE I
B3LYP/6-311+G(*d,p*) total energies, zero point energies, and relative energies for conformers and transition states of silacyclohexane.

Conformer	Total energy (hartree)	ZPE (hartree)	ΔE with ZPE correction (kcal mol ⁻¹)	ΔE without ZPE correction (kcal mol ⁻¹)
1a	-487.346949	0.157166	—	—
1g[#]	-487.338242	0.156940	5.32	5.46
1c	-487.339275	0.157111	4.78	4.82
1e[#]	-487.338695	0.157009	5.08	5.18
1b	-487.340758	0.157143	3.87	3.88

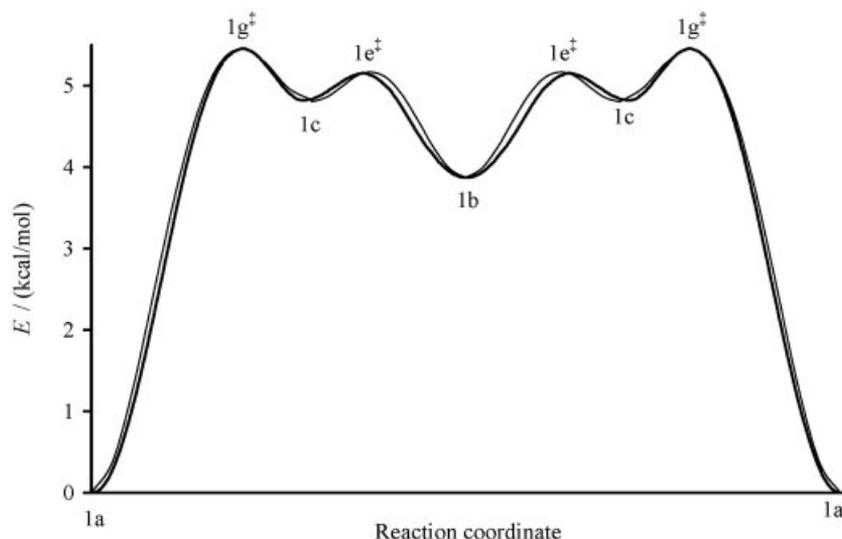


FIGURE 2. Calculated path for the chair-to-chair interconversion of silacyclohexane at the B3LYP/6-311+G(*d,p*) level. Thick line is IRC, thin line is STQN. Reaction coordinates, i.e. arc lengths, are renormalized to span the same range for the two inversion path calculations.

from the minima and finds a transition state that connects two local minima on the PES, producing a minimum energy path connecting the two minima in internal redundant coordinates. Conversely, the IRC method works downhill. It starts at a transition state and searches for the closest local minima on each side, producing a minimum energy path in mass-weighted Cartesian coordinates. The STQN-(Path) method was used to connect conformers **1a** and **1c** (transition state **1g[#]**), as well as conformers **1c** and **1b** (transition state **1e[#]**). Intrinsic reaction path (IRC) calculations were applied on transition state **1g[#]** and a connection of **1a** with **1c** was verified. Furthermore, IRC calculations applied on **1e[#]** connected **1c** with **1b**. Figure 2 shows how both methods result in same energy values for all minima (**1a**, **1c**, and **1b**) and transition states (**1g[#]** and **1e[#]**) and connect a chair with the inverted chair through the same sequence of conformers as we have described previously [1].

In the following discussion, we will show that it is not possible to connect **1a** and its inverted chair via **1g[#]**, **1c**, and **1g[#]** sequence only, contrary to the conclusions of Freeman et al. (see Fig. 4 in Ref. [3], which also has been published elsewhere [8]).

Discussion

One of the references used by Freeman et al. [3] to support their conclusions is an article by Leventis

et al. [9]. It would actually be possible to use the Leventis paper and figures therein to explain why Freeman's group are wrong in their arguments. However, we prefer to use the description of the conformational globe of cyclohexane by Cremer and Szabo [10] for that purpose. In cyclohexane all six carbon atoms are equal in the chair conformer. The chair-to-chair interconversion can start at any carbon and pass through a transition state, which may be sofa-like (envelope) or half-chair (half-twist). It then relaxes forming a twist conformer. In cyclohexane, six twist conformers, and six boat conformers are connected through pseudo-rotation along the equator of the conformational globe (Fig. 3). The chair-to-chair interconversion of cyclohexane, however, can be completed without passing through a boat conformer as is evident from Figure 3. The lowest-energy path then consists of chair \rightarrow half-chair/sofa[#] \rightarrow twist \rightarrow half-chair/sofa[#] \rightarrow inverted chair.

In cyclohexane the Gibbs free energy of activation for the step "chair \rightarrow half-chair/sofa[#] \rightarrow twist" is generally accepted to be 10.1–10.5 kcal mol⁻¹. In silacyclohexane the activation energy is about one-half this value [1, 11].

The reason for the lower activation barrier is that the chair-to-chair interconversion starts at the Si atom because it is much easier to flap the Si to the plane of C₂, C₃, C₅, and C₆ forming a half-chair/sofa transition state than it is to do so with any of the five carbon atoms [1]. Let the carbon marked C₁

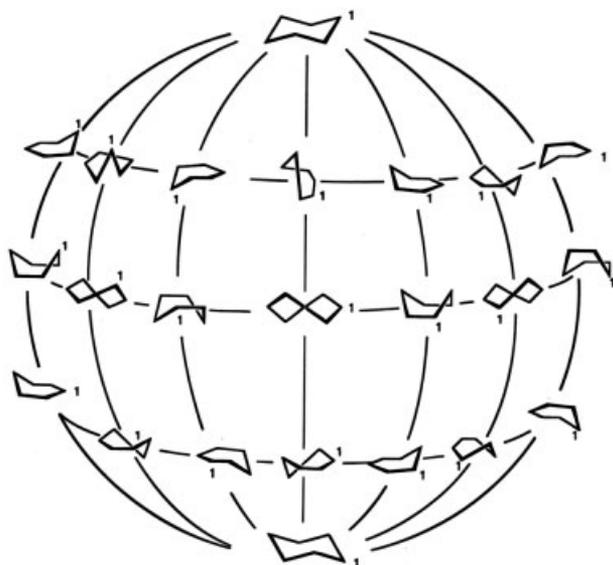


FIGURE 3. Conformational globe of cyclohexane. Distinct ring forms are shown in steps of 30° along the equator, the Tropic of Cancer, and the Tropic of Capricorn. For reasons of clarity only the front side of the globe is shown. Atom C₁ is always indicated. Reproduced with permission from ref. 10.

in Figure 3 correspond to the Si atom in silacyclohexane, and let us begin with the chair at the north pole. It is evident that flapping down the Si atom results in the twist form far to the right (east) on the equator. In this case, it is not possible to reach the south pole (inverted chair) along the lowest-energy pathway unless pseudo-rotation along the equator first takes place. A connection from the south pole to the twist far to the east (and vice versa) would mean that C₄ is flapped to the plane of C₂, C₃, C₅, and C₆ forming a half-chair/sofa transition state, but in that case the activation energy is about the one of cyclohexane (twice as high). Apparently, this fact was overlooked by Freeman et al. The only possibility to use the low activation energy involving silicon being the flapped atom for a second time is first to perform pseudo-rotation from east to west, involving twist-boat-twist-boat-twist corresponding to the path $1c \rightarrow 1e^{\#} \rightarrow 1b \rightarrow 1e^{\#} \rightarrow 1c$ in Figure 2.

Figure 3 shows only the front side of the globe. The remaining conformations are on the back side. Because the chair conformer of silacyclohexane has C_s symmetry, which is lost during the interconver-

sion, a second enantiomeric lowest-energy pathway for chair-to-chair interconversion is on the back side of the globe. This corresponds exactly to our previous description of the PES of silacyclohexane [1].

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References

1. Arnason, I.; Thorarinnsson, G. K.; Matern, E. Z. *Anorg Allg Chem* 2000, 626, 853.
2. Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J Am Chem Soc* 1989, 111, 8551.
3. Freeman, F.; Fang, C.; Shainyan, B. A. *Int J Quantum Chem* 2004, 100, 720.
4. Gonzalez, C.; Schlegel, H. B. *J Chem Phys* 1989, 90, 2154.
5. Gonzalez, C.; Schlegel, H. B. *J Phys Chem* 1990, 94, 5523.
6. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03*; Gaussian: Wallingford, CT, 2004.
7. Ayala, P. Y.; Schlegel, H. B. *J Chem Phys* 1997, 107, 375.
8. Freeman, F.; Cha, C.; Fang, C.; Huang, A. C.; Hwang, J. H.; Louie, P.; Shainyan, B. A. *J Phys Org Chem* 2005, 18, 35.
9. Leventis, N.; Hanna, S. B.; Sotiriou-Leventis, C. *J Chem Educ* 1997, 74, 813.
10. Cremer, D.; Szabo, J. In *Conformational Behavior of Six-Membered Rings*; Juaristi, E., Ed.; VCH: New York, 1995; p 59.
11. Arnason, I.; Kvaran, A.; Jonsdottir, S.; Gudnason, P. I.; Oberhammer, H. *J Org Chem* 2002, 67, 3827.