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Relative energies, stereoelectronic interactions and conformational interconversions in silathiacyclohexanes

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ABSTRACT: Stereoelectronic hyperconjugative interactions and the relative energies of conformers and transition states of 2-, 3-, and 4-silathiacyclohexane were calculated at the B3LYP/6–311+G(d,p) level of theory. The chair conformer of 2-silathiacyclohexane is 15.4 and 15.9 kcal mol^{-1} (1 kcal = 4.184 kJ), respectively, lower in energy than the chair conformers of 3- and 4-silathiacyclohexane. Intrinsic reaction path calculations were used to connect the transition states between the respective chair and twist conformers and different chair–chair conformational interconversion paths were located for 3- and 4-silathiacyclohexane. The energy of the transition state that connects the chair and 2,5-twist conformers of 3-silathiacyclohexane is 5.58 kcal mol^{-1} higher in energy than the chair. The transition state that connects the chair and 2,5-twist conformers of 4-silathiacyclohexane is 4.82 kcal mol^{-1} higher in energy than the chair. The energy differences (ΔE, kcal mol^{-1}) between the chair conformer of 2-silathiacyclohexane and the respective 1,4-twist ($\Delta E = 4.16$), 2,5-twist ($\Delta E = 3.20$) and 3,6-twist ($\Delta E = 3.87$) conformers were calculated. Small relative energy differences were calculated between the chair conformer and the respective 1,4-twist ($\Delta E = 3.95$), 2,5-twist ($\Delta E = 4.07$) and 3,6-twist ($\Delta E = 3.46$) conformers of 3-silathiacyclohexane. The calculated energy differences (ΔE) between the chair conformer and the 1,4-twist and 2,5-twist conformers of 4-silathiacyclohexane were 3.50 and 4.04 kcal mol^{-1}, respectively. The geometric parameters and stereoelectronic hyperconjugative interactions in the silathiacyclohexanes are compared and discussed. Copyright © 2004 John Wiley & Sons, Ltd.

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KEYWORDS: conformational interconversion; intrinsic reaction path calculation; silathiacycloalkane; stereodynamics; structure

INTRODUCTION

The conformational properties, geometric parameters and stereoelectronic hyperconjugative interactions of carbocycles and heterocycles are of considerable interest to a wide range of scientists. The conformational analysis of cyclohexane and substituted cyclohexanes has been extensively studied experimentally and computationally,[1] but much less attention has been paid to the details of the structures (boats, half-chair, twists, sofas) involved in the conformational interconversions of unsubstituted monoheterocyclohexanes and diheterocyclohexanes containing the Group 14 elements Si → Pb.[2] There have been a few experimental and computational conformational studies on cyclic organosilicon compounds including silacyclohexane (**1**, Fig. 1)[2] and experimental and computational studies on thiacyclohexane (tetrahydro-2*H*-thiopyran, thiane, **2**, Fig. 2).[3–5] Although there are no reports concerning the synthesis of or computational studies on unsubstituted silathiacyclohexanes (2-silathiacyclohexane, **3**, Fig. 3; 3-silathiacyclohexane, **4**, Figs 4 and 5; 4-silathiacyclohexane, **5**, Fig. 6), some of their substituted derivatives have been prepared and investigated.[6]

It is generally accepted that the path for the conformational interconversion of cyclohexane is chair → [half-chair]‡ → twist → [boat]‡ → twist → [half-chair]‡ → chair with the free energy of activation being associated with the step of chair → [half-chair/sofa]‡. Although computational and experimental studies are consistent with a similar conformational interconversion path for thiacyclohexane (**2**),[3–5] there is disagreement concerning the relative energies of conformers and the interconversion paths for silacyclohexane (**1**) and 1-methyl-1-silathiacyclohexane. The barrier to the chair–chair interconversion of silathiacyclohexane (**1**, 5.47 kcal mol^{-1}) (1 kcal = 4.184 kJ) is significantly smaller than that for cyclohexane

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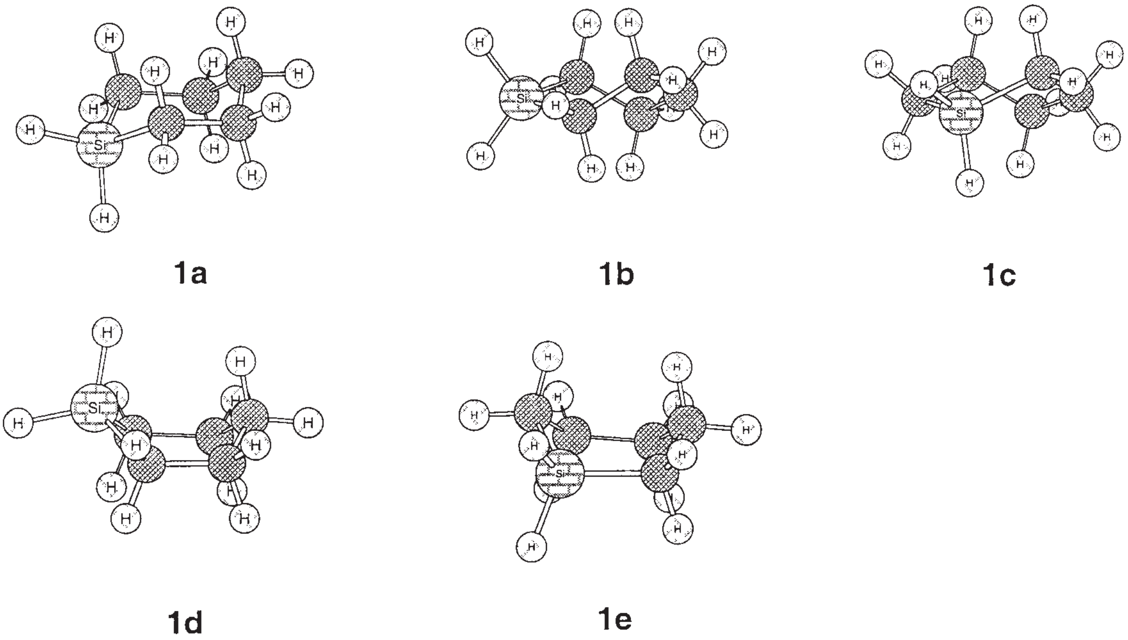


Figure 1. Chair (**1a**), 1,4-twist (**1b**), 2,5-twist (**1c**), 1,4-boat (**1d**) and 2,5-boat (**1e**) conformations of silacyclohexane

(10.2 kcal mol^{-1}) and for thiacyclohexane (**2**, 9.40 kcal mol^{-1}).[2g,h] One of the proposed paths for the chair–chair interconversion of silacyclohexane (**1**) was chair $\rightarrow$ $[sofa]^{\ddagger}$ $\rightarrow$ 2,5-twist $\rightarrow$ $[2,5\text{-boat}]^{\ddagger}$ $\rightarrow$ 1,4-twist $\rightarrow$ $[2,5\text{-boat}]^{\ddagger}$ $\rightarrow$ 2,5-twist $\rightarrow$ $[sofa]^{\ddagger}$ $\rightarrow$ chair[2g] and the other proposed path with the 2,5-twist (**1c**, Fig. 1) as an intermediate is shown in Fig. 7.[2h] Molecular mechanics (MM) calculations[2a,c,h] and ^{1}H NMR studies[2i] at room temperature suggested that the axial conformer of 1-methyl-1-silacyclohexane was favored over the equatorial. A gas-phase electron diffraction (ED) and theoretical study of the conformational preference of 1-methyl-1-silacyclohexane showed the equatorial conformer to be favored in the gas phase and in solution.[2j] B3LYP/6–311+G(d,p) calculated the chair conformer of axial 1-methyl-1-silacyclohexane to be 0.45 kcal mol^{-1} less stable than the chair conformer of equatorial 1-methyl-1-silacyclohexane.[2h] The barrier to the conformational intercon-version of 1,1-dimethyl-1-silacyclohexane, which has been studied by low-temperature NMR methods ($\Delta G^{\ddagger} = 5.4$ kcal mol^{-1}), is close to the values for silacyclohexane (**1a**)[2h] and 1-methyl-1-silacyclohexane (5.55 kcal mol^{-1}).[2k,l]

This computational study of stereoelectronic hyperconjugative interactions and conformational properties of silathiacyclohexanes (**3–5**) was undertaken because they

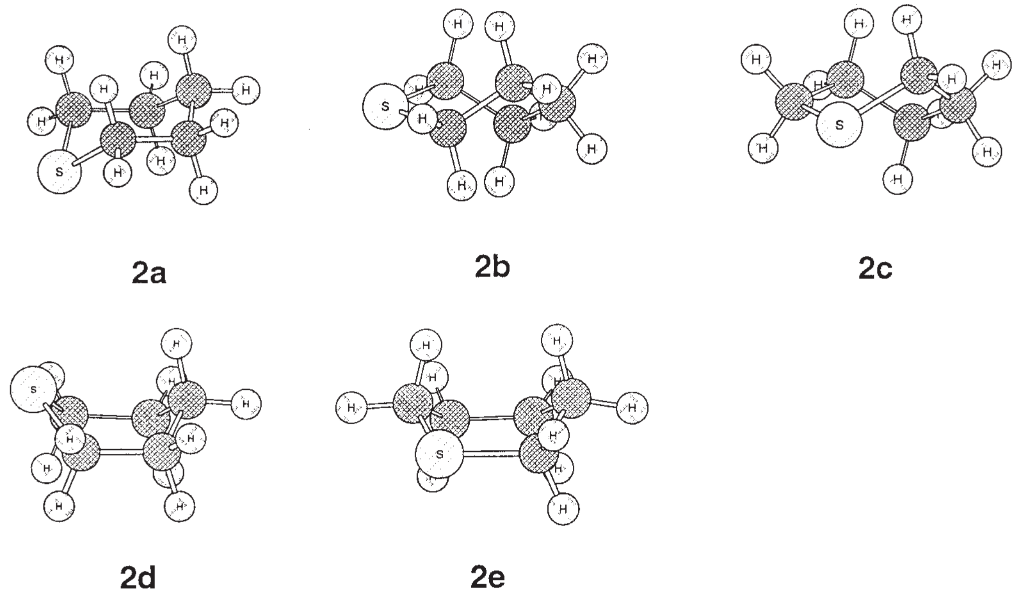
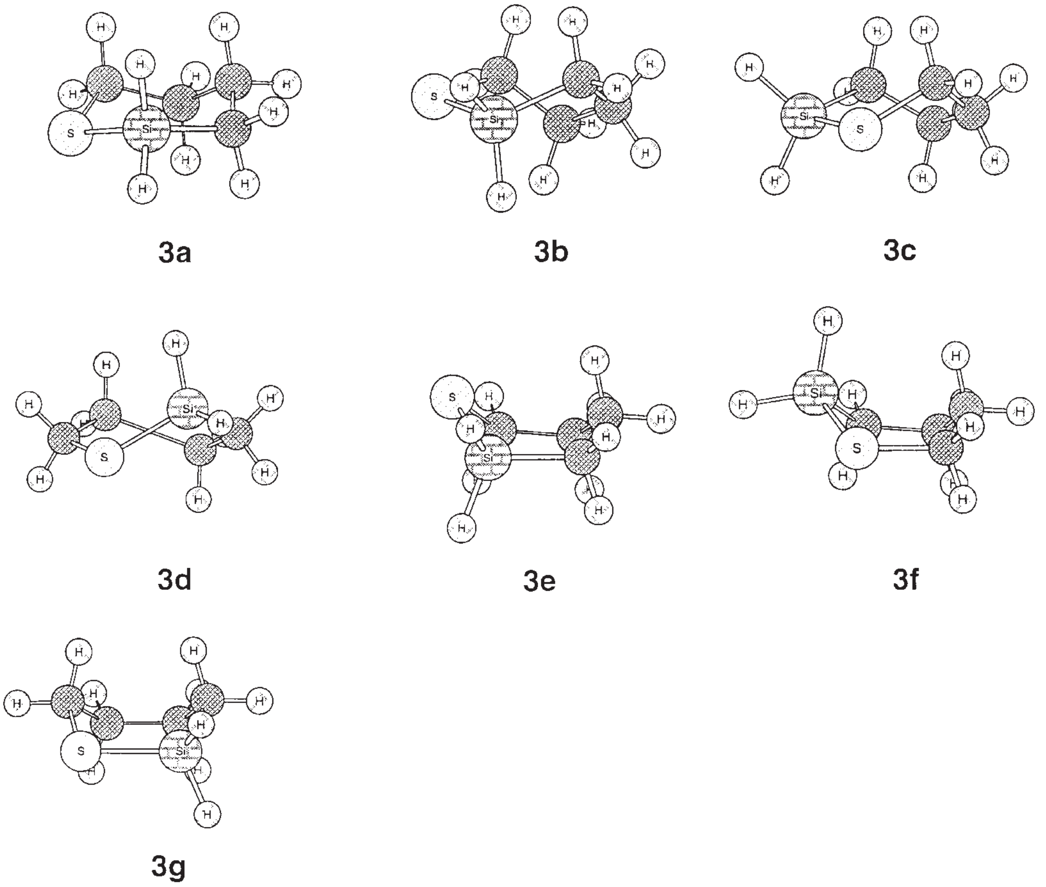


Figure 2. Chair (**2a**), 1,4-twist (**2b**), 2,5-twist (**2c**), 1,4-boat (**2d**) and 2,5-boat (**2e**) conformations of thiacyclohexane

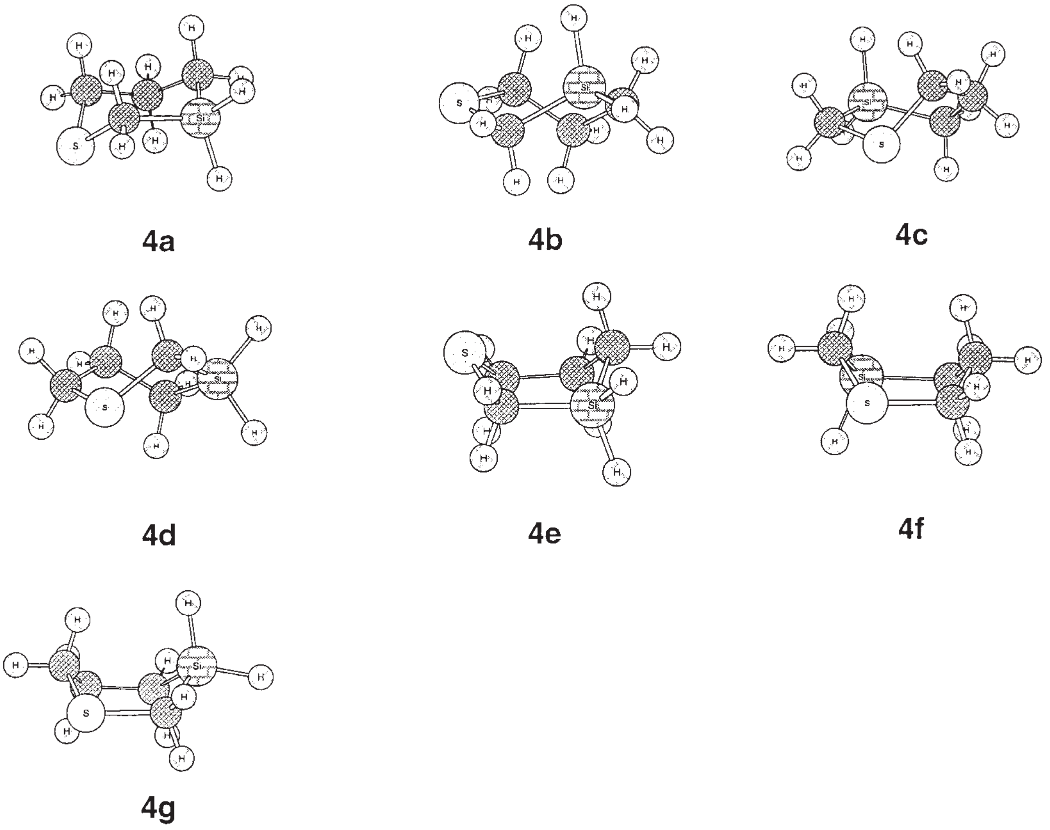


3a **3b** **3c**

3d **3e** **3f**

3g

Figure 3. Chair (**3a**), twist (**3b**–**d**) and boat (**3e**–**g**) conformations of 2-silathiacyclohexane

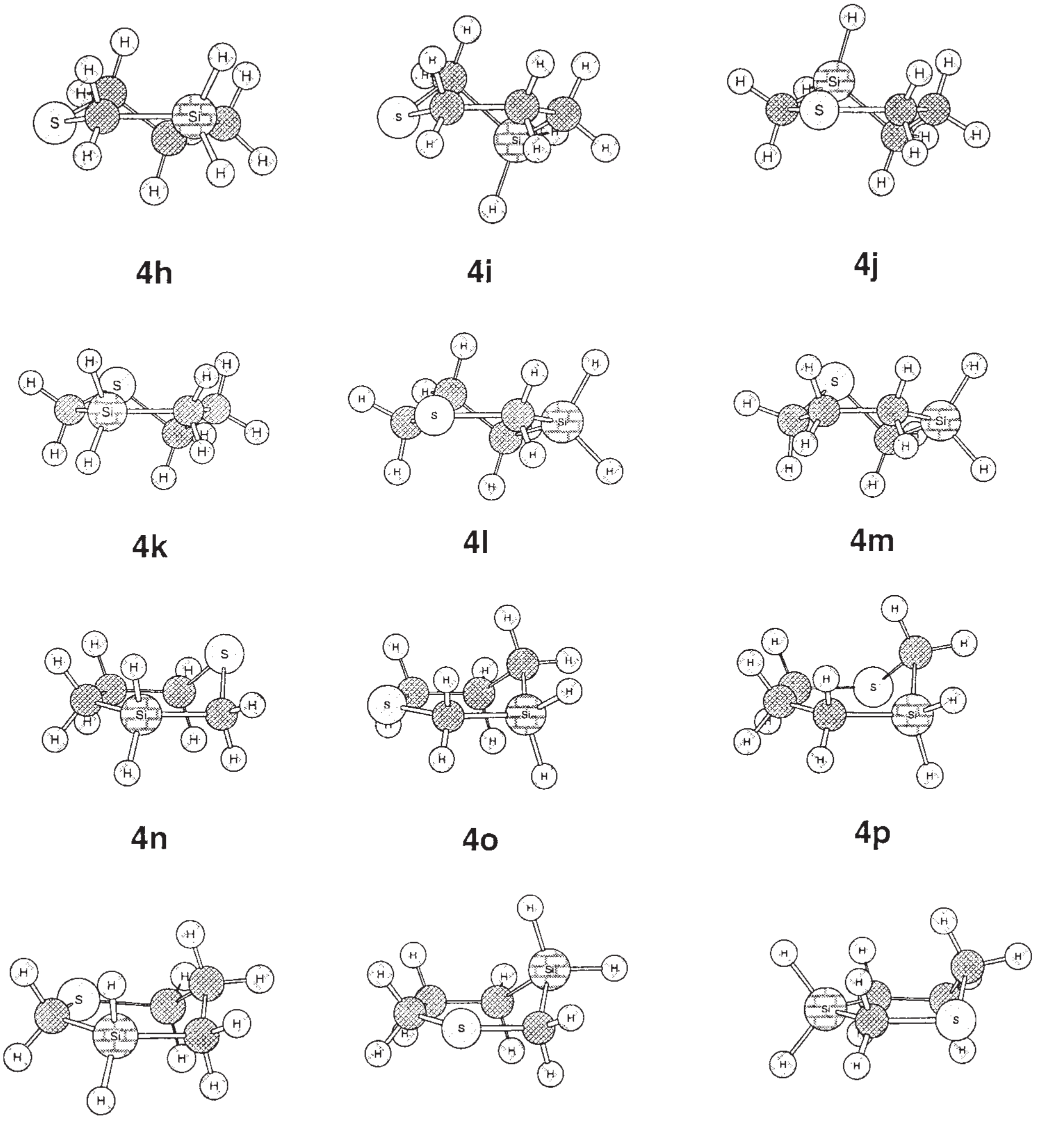


4a **4b** **4c**

4d **4e** **4f**

4g

Figure 4. Chair (**4a**), twist (**4b**–**d**) and boat (**4e**–**g**) conformations of 3-silathiacyclohexane



4h **4i** **4j**

4k **4l** **4m**

4n **4o** **4p**

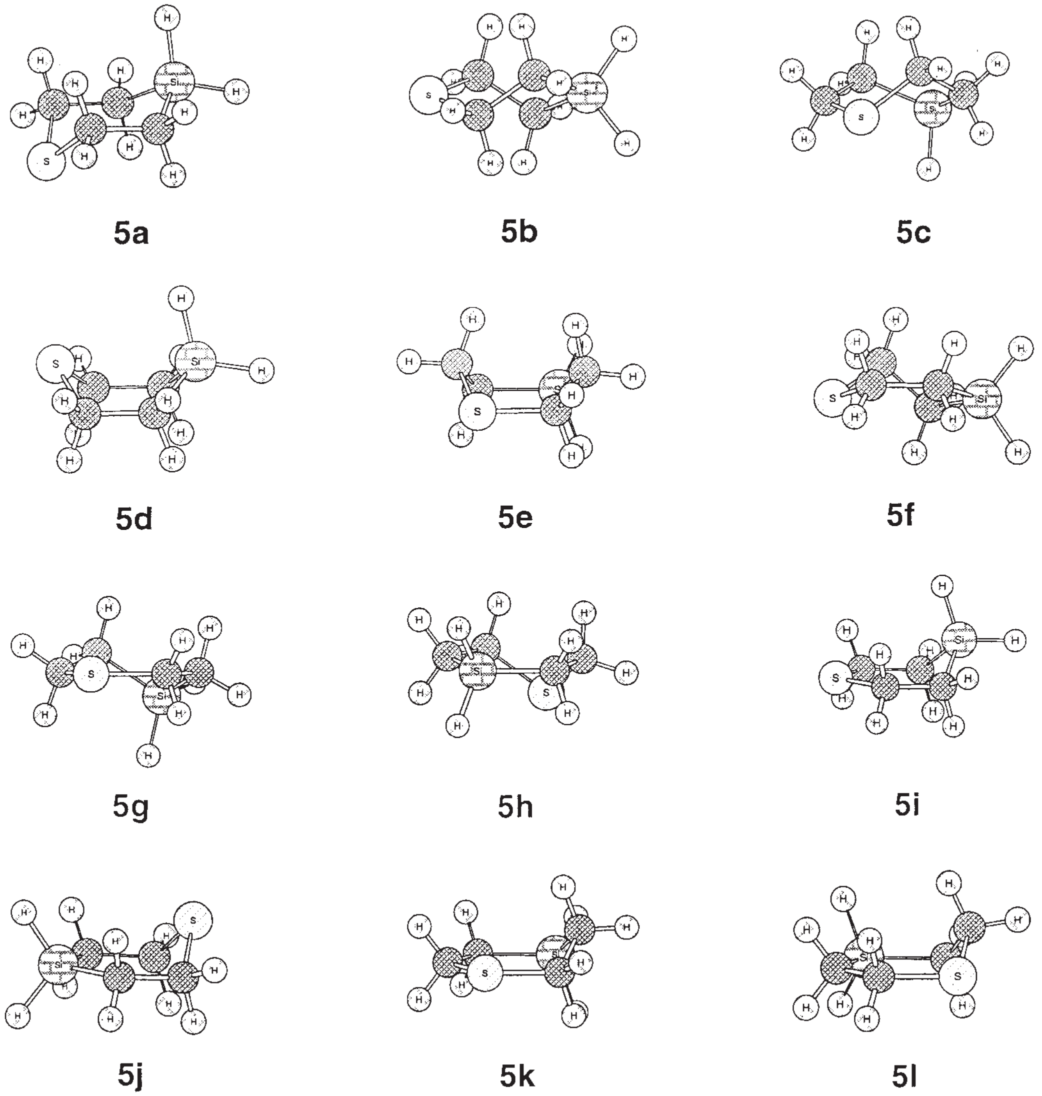
4q **4r** **4s**

Figure 5. Half-chair (**4h**–**m**) and sofa (**4n**–**s**) conformations of 3-silathiacyclohexane

represent an interesting class of heteroatom derivatives of cyclohexane. Silathiacyclohexanes are different from other types of previously studied diheterocyclohexanes in that they contain two heteroatoms of different nature, one with lone pair electrons and the other showing a strong inductive electron-donating effect but simultaneously possessing vacant d-orbitals. These factors could lead to conformational properties and stereoelectronic hyperconjugative interactions in silathiacyclohexanes which may be different than those observed in previously investigated diheterocyclohexanes[7–13] (F. Freeman, V. de Venecia Carino and T. Q. Tu, unpublished data).

QUANTUM MECHANICAL METHODS

Equilibrium geometries, conformational paths and transition states (first-order saddle points) are indispensable in the study of conformational analysis. Mapping out the potential energy surface (PES) involves optimizing conformations and finding the transition states that connect them.[14–18] The geometry-optimized structures and the energy calculations were carried out at the B3LYP/6–311+G(d,p) level of theory with the Spartan'02 Macintosh,[16,19] Spartan'02 Unix[16,19] and Gaussian 98[20,21] computational programs. Intrinsic reaction path (IRC) calculations were done using the procedure of Schlegel and Gonzalez.[14,22] The B3LYP method[23] makes use of a three-parameter functional that is a hybrid of exact (Hartree–Fock) exchange terms and gradient-corrected exchange and correlation terms, similar to those first suggested by Becke.[24] Density functional theory provides electron correlation which is often important in conformational studies.[25] The use of *d*-functions for polarization is important and basis sets with diffuse functions are important for anions and for molecules with lone pair



5a **5b** **5c**

5d **5e** **5f**

5g **5h** **5i**

5j **5k** **5l**

Figure 6. Chair (**5a**), twist (**5b**, **c**) boat (**5d**, **e**), half-chair (**5f**–**h**) and sofa (**5i**–**l**) conformations of 4-silathiacyclohexane

electrons. The 6–311+G(d,p) basis set takes into account the relatively diffuse nature of lone pairs and the more spread out electron density of anions relative to neutral atoms.[21a,26] It is the practice to use the MP2/6–31G(d) level of theory for charge distribution analysis calculations.[21a]

All structures were characterized as minima (zero imaginary frequency) or transition structures (first-order saddle points, one imaginary frequency). Vibrational frequencies were computed on the geometry-optimized structures at 298.15 K and 1 atm pressure. The zero point vibrational energies (ZPE) were scaled by 0.9804 in the relative thermodynamic parameters calculations.[12a,27] The atomic charges, additional geometric parameters and thermochemical data for conformers of the silathiacyclohexanes are given in the Supplementary Information (SI), available in Wiley Interscience. Total energies are given in hartrees [1 hartree = 1 atomic unit (au) = 627.5095 kcal mol^{-1}] and the other energies are in kcal mol^{-1}. The dipole moments are given in debye (D) and the entropies are given in entropy units (eu).

RESULTS AND DISCUSSION

Structural parameters, if critically evaluated, are very reliable probes for predicting, diagnosing and understanding stereoelectronic hyperconjugative interactions. The weakening (elongation) of the axial C—H bond has been observed experimentally and computationally for the chair, twist and boat conformers of cyclohexane, silacyclohexane (**1**, Fig. 1),[2h] thiacyclohexane (**2**, Fig. 2)[4,5] and other heterocyclohexanes.[7–13,28,29] The longer C—Hax bond (versus C—Heq) in cyclohexane and in silacyclohexane (**1**) ($\sigma_{\text{C—Hax}} \rightarrow \sigma^*_{\text{C—Hax}}$) and the longer Si—Hax bond (versus Si—Heq) in silacyclohexane (**1**) is the result of stereoelectronic hyperconjugative interactions ($\sigma_{\text{C—Hax}} \rightarrow \sigma^*_{\text{Si—Hax}}$). In the chair conformer (**2a**)

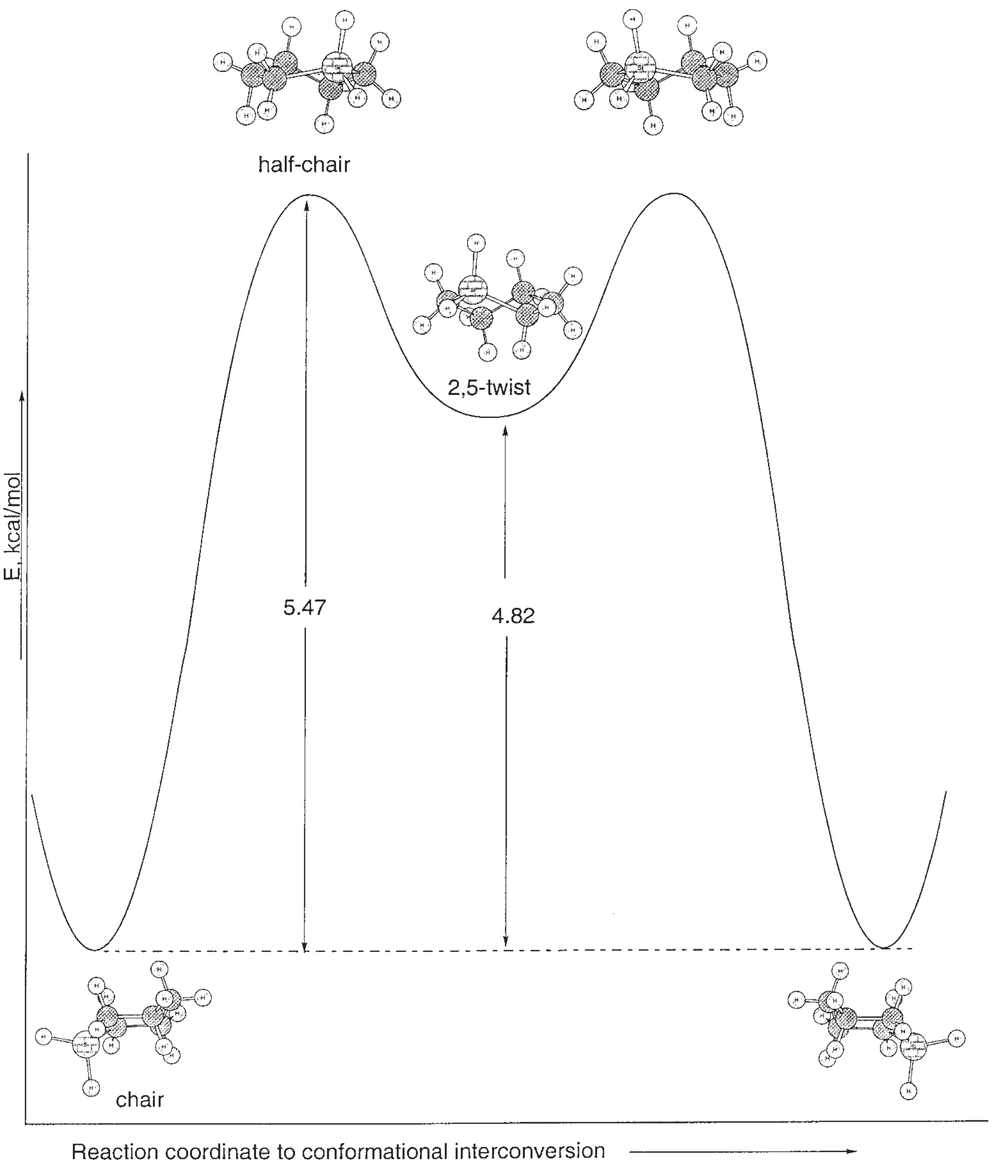


Figure 7. B3LYP/6–311+G(d,p) potential energy diagram for the chair–chair interconversion of silacyclohexane (**1**)

of thiacyclohexane the C2—Hax bond is longer ($\Delta r = 0.002$ Å) than the C2—Heq bond ($\sigma_{\text{C3—Hax}} \rightarrow \sigma^*_{\text{C2—Hax}}$, $\sigma_{\text{C6—S}} \rightarrow \sigma^*_{\text{C2—Heq}}$, $n_{\text{S}} \rightarrow \sigma^*_{\text{C2—Hax}}$).[4,5,11a] The small difference in the C—H bond lengths at C2 in **2a** is consistent with the poor ability of sulfur to participate as a donor in $n_{\text{S}} \rightarrow \sigma^*_{\text{C—Hax}}$ hyperconjugation. The C3—Hax bond in **2a** is shorter ($\Delta r = 0.003$ Å) than the C3—Heq bond [homoanomeric effect $\text{n}_{(\text{S})\text{ax}} \rightarrow \beta\text{—}\sigma^*_{\text{C3—Heq}}$, $\sigma_{\text{S—C2}} \rightarrow \sigma^*_{\text{C3—Heq}} > \sigma_{\text{C2—Hax}} \rightarrow \sigma^*_{\text{C3—Hax}}$ and $\sigma_{\text{C4—Hax}} \rightarrow \sigma^*_{\text{C3—Hax}}$]. The C4—Hax bond in **2a** is longer ($\Delta r = 0.003$ Å) than the C4—Heq bond ($\sigma_{\text{C—Hax}} \rightarrow \sigma^*_{\text{C—Hax}}$), but the C5—Hax bond is shorter ($\Delta r = 0.003$ Å) than the C5—Heq bond ($\sigma_{\text{C—Hax}} \rightarrow \sigma^*_{\text{C—Hax}}$).

The Si—C bond has proven to be a sensitive indicator of the electronic properties of remaining substituents on silicon.[30] Hyperconjugation,[30d,e] negative hyperconjugation (anomeric effect),[30f–i] electronegativity,[30j–l] and participation of d-orbitals have been invoked to explain short Si—C bonds. Charge density distributions have been widely used in studies of molecular structure and bonding and several methods have been utilized for calculating atomic charges.[15–18,31] Silicon is relatively electropositive and bonds to silicon are generally considered to be rather polar. The hydrogen attached to an Si atom has an excess negative charge whereas the hydrogen attached to a carbon atom bears a slight positive charge. The atomic population gives a quantification of the charge transfer and an indication of the ionic contribution to the bond. The atomic charges for the chair conformers of the silathiacyclohexanes (**3a**, **4a**, **5a**) are given in the Supplementary Information (Fig. SI-1).

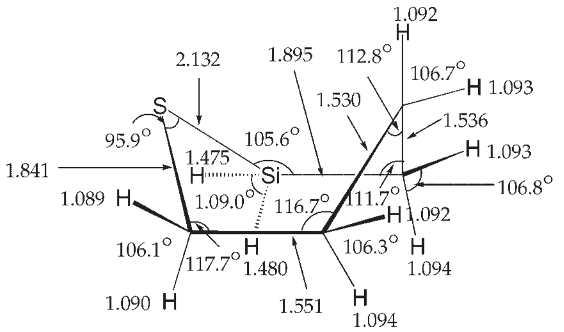
2-Silathiacyclohexane (3)

By analogy with cyclohexane, silacyclohexane (**1**) and thiacyclohexane (**2**), there are 19 conformations to be considered for the conformational interconversion of 2-silathiacyclohexane (**3**).[4,8,9,32–34] Seven of these conformations are shown in Fig. 3. Vibrational frequency calculations identified four minima [chair (**3a**), 1,4-twist (**3b**), 2,5-twist (**3c**), 3,6-twist (**3d**)] and three transition states (1,4-boat [**3e**]‡, 2,5-boat [**3f**]‡ and 3,6-boat [**3g**]‡) for 2-silathiacyclohexane.

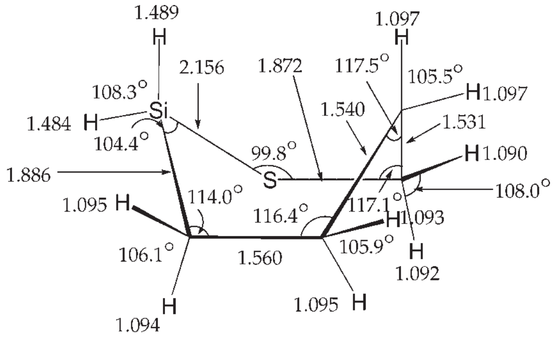
The three boat transition states of 2-silathiacyclohexane (**3**) are close in energy (Table 1). The calculated energy differences (ΔE, kcal mol^{-1}) between the chair conformer (**3a**) and the respective 1,4-boat ([**3e**]‡, $\Delta E = 4.98$), 2,5-boat ([**3f**]‡, $\Delta E = 4.81$), and 3,6-boat ([**3g**]‡, $\Delta E = 4.67$) transition states of 2-silathiacyclohexane are similar. The chair conformer (**3a**) of 2-silathiacyclohexane is 4.10, 3.00 and 3.81 kcal mol^{-1}, respectively, more stable than the 1,4-twist (**3b**), 2,5-twist (**3c**), and 3,6-twist (**3d**) conformers (Table 1). The long S—Si, Si—C and Si—H bonds help to minimize repulsive non-bonded interactions in the twist conformers (Table 2). Non-bonded interaction energies are difficult contributions to evaluate and may be attractive or repulsive. By analogy with some of the factors in acyclic systems, the relative stability of the twist conformers in the 2-silathiacyclohexane (**3c** < **3d** < **3b**), 3-silathiacyclohexane (**4d** < **4b** < **4d**) and 4-silathiacyclohexane (**5b** < **5c**) may be determined by a number of factors including hyperconjugation,[31a,b] an unfavorable overlap interaction between the bond orbitals in the eclipsed conformation,[31c] a favorable interaction (bonding–antibonding orbitals) in the staggered conformation,[31d–f] electrostatic interactions of weakly polarized bonds and the relative destabilizing non-bonded interactions in the eclipsed CH_2—CH_2 fragments. Non-bonded vicinal interactions in the CH_2—SiH_2 fragments are probably minimal since in the fully eclipsed conformation the H···H non-bonded distance is much longer than the

Table 1. Total energies and relative thermodynamic parameters for conformers and transition states of 2-silathiacyclohexane (**3**)

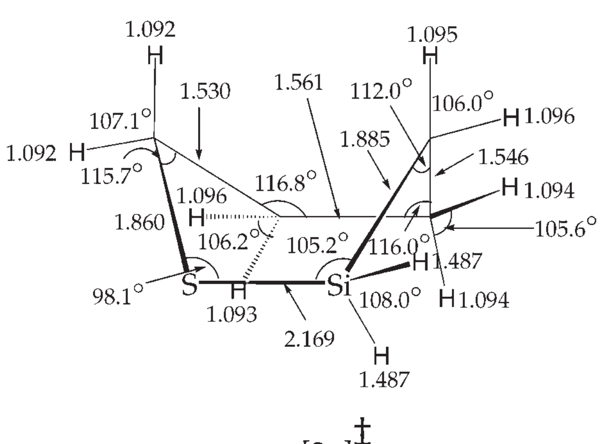
Conformer or transition state	Total energy (au)	ΔE (kcal mol^{-1})	$\Delta H°$ (kcal mol^{-1})	$\Delta G°$ (kcal mol^{-1})
3a	−846.261061			
3b	−846.254532	4.10	4.14	3.70
3c	−846.256285	3.00	3.05	2.84
3d	−846.254994	3.81	3.89	3.37
[**3e**]‡	−846.253124	4.98	4.50	5.07
[**3f**]‡	−846.253391	4.81	4.30	4.86
[**3g**]‡	−846.253623	4.67	4.19	4.97



[**3e**]‡



[**3f**]‡



[**3g**]‡

Table 2. B3LYP/6–311+G(d,p) equilibrium geometry for the chair conformer (**3a**) of 2-silathiacyclohexane

Parameter	Value
Bond length (Å):	
S1—Si2	2.159
S1—C6	1.862
Si2—Hax	1.490
Si2—Heq	1.484
Si2—C3	1.885
C3—C4	1.545
C4—C5	1.539
C5—C6	1.531
C3—Hax	1.096
C3—Heq	1.096
C4—Hax	1.098
C4—Heq	1.095
C5—Hax	1.095
C5—Heq	1.097
C6—Hax	1.093
C6—Heq	1.091
Bond angle (°):	
S1—Si2—C3	106.7
S1—C6—C5	115.6
Si2—S1—C6	97.5
Si2—C3—C4	112.8
C3—C4—C5	114.7
C4—C5—C6	115.4
H—Si2—H	109.1
Torsional angle, τ (°):	
S1—Si2—C3—C4	49.7
S1—C6—C5—C4	−70.0
Si2—C3—C4—C5	−58.7
C3—C4—C5—C6	68.1

sum of the van der Waals radius for hydrogen. The two non-bonded vicinal H···H distances in **3b** are less than (2.36 Å) the sum of the van der Waals radius for hydrogen (2.40 Å).[35] The same is true for **3c** (2.38 Å) and **3d**, but in **3d** the non-bonded distances are shorter (2.35 Å).

The S—C bond (1.862 Å) in **3a** (Table 2) is longer than the S—C bond in thiacyclohexane (**2**) whereas the Si—C bond (1.885 Å) is similar to that in silacyclohexane (**1**). The C3—C4 bond (1.545 Å) is longer than the C4—C5 bond ($\Delta r = 0.006$ Å) and the C5—C6 bond ($\Delta r = 0.014$ Å). This is another example of when silicon is attached to a C_{sp^3}—C_{sp^3} bond it causes an elongation of that C_{sp^3}—C_{sp^3} bond. In the 1,4-twist conformer of 2-silathiacyclohexane (**3b**) the Si—S bond is 2.166 Å, which is longer than that in the chair conformer (**3a**), the same as in the 2,5-twist (**3c**) conformer and shorter than that in the 3,6-twist conformer (**3d**, 2.157 Å, Tables 3c–f in the Supplementary Information). The S—C bond in **3b** (1.867 Å) is longer than those in the chair (**3a**) and 2,5-twist (**3c**, 1.860 Å) conformers and shorter than that in the 3,6-twist conformer (**3d**, 1.869 Å). The Si—C bond (1.889 Å) in **3b** is longer than that in the chair conformer (**3a**) and shorter than those in **3c** (1.898 Å) and **3d** (1.899 Å). In **3b** the C3—C4 bond (1.551 Å) is longer than the C4—C5 bond (1.545 Å) and the C5—C6 bond (1.533 Å, Table 2).

Equal C—H or Si—H bonds may suggest an absence of stereoelectronic hyperconjugative interactions or that the interactions involving different bonds are present at the same time but are equal in magnitude. In the chair conformer of 2-silathiacyclohexane (**3a**) the Si—Hax bond (1.490 Å) is longer ($\Delta r = 0.006$ Å) than the Si—Heq bond ($n_S \rightarrow \sigma^*_{\mathrm{Si2\text{-}Hax}}$, $\sigma_{\mathrm{C3—Hax}} \rightarrow \sigma^*_{\mathrm{Si2—Hax}} > \sigma_{\mathrm{C6—S}} \rightarrow \sigma^*_{\mathrm{Si2—Heq}}$) and the C3—H bonds are equal (1.096 Å). The equal C3—H bonds in **3a** may be due to a competition between $\sigma_{\mathrm{C—Hax}} \rightarrow \sigma^*_{\mathrm{C—Hax}}$ which weakens the C3—Hax bond and an opposing homoanomeric effect ($n_{\mathrm{Sax}} \rightarrow \sigma^*_{\mathrm{C3—Heq}}$) that weakens the C3—Heq bond. Anderson and co-workers[13] proposed a homoanomeric hyperconjugation between the equatorial lone pair on the β-oxygen atom and C3—Heq in a W-arrangement in order to explain the weaker C3—Heq bonds in 1,2,4-trioxacyclohexane. Alabugin and co-workers[12] suggested that it is the axial (p-type) rather than the equatorial (s-type) lone pair at the β-oxygen atom that is involved in the stereoelectronic interaction. The C4—Hax bond in **3a** is shorter ($\Delta r = 0.003$ Å) than the C4—Heq bond, the C5—Heq bond is longer ($\Delta r = 0.002$ Å) than the C5—Hax bond ($\sigma_{\mathrm{S—C6}} \rightarrow \sigma^*_{\mathrm{C5—Heq}} > \sigma_{\mathrm{C6—Hax}} \rightarrow \sigma^*_{\mathrm{C5—Hax}}$, $\sigma_{\mathrm{C4—Hax}} \rightarrow \sigma^*_{\mathrm{C5—Hax}}$) and the C6—Hax bond is longer ($\Delta r = 0.002$ Å) than the C6—Heq bond ($\sigma_{\mathrm{C5—Hax}} \rightarrow \sigma^*_{\mathrm{C6—Hax}}$, $n_S \rightarrow \sigma^*_{\mathrm{C6—Hax}}$). Hence the proposed stereoelectronic hyperconjugative interactions in the chair conformer of 2-silathiacyclohexane (**3a**) are analogous to those suggested for the chair conformers of cyclohexane, silacyclohexane (**1a**)[2h] and thiacyclohexane (**2a**).[4,5,11,12]

Stereoelectronic hyperconjugative interactions are influenced by and depend on the geometric arrangements about the bonds involved. Hyperconjugative delocalization for $n \rightarrow \sigma^*$ interactions is maximized when the donor lone pair is antiperiplanar to the antibonding acceptor orbitals. Influences of geometric parameters on stereoelectronic hyperconjugative interactions are seen in a comparison of the torsional angles and the bond lengths in the chair (**3a**) and twist conformers (**3b–d**) of 2-silathiacyclohexane (Tables 3c–f in the Supplementary Information). In the 1,4-twist conformer (**3b**) the Si—Hax bond is longer ($\Delta r = 0.004$ Å) than the Si—Heq bond, the C3—H bonds are equal, the C4—H bonds are equal, the C5—H bonds are equal and the C6—Hax bond is longer ($\Delta r = 0.002$ Å) than the C6—Heq bond ($\sigma_{\mathrm{C5—Hax}} \rightarrow \sigma^*_{\mathrm{C6—Hax}}$, $n_S \rightarrow \sigma^*_{\mathrm{C6—Hax}}$). In the 2,5-twist conformer (**3c**), the respective C—H bonds at C3 and C4 are equal, the C5—H1iso bond is longer ($\Delta r = 0.004$ Å) than the C5—H2iso bond and the C6—HΨax bond (1.094 Å) is longer ($\Delta r = 0.002$ Å) than the C6—HΨeq bond. In the 3,6-twist (**3c**) conformer, the C—H bonds at C3, C4 and C5 are equal and the C6—H1iso bond (1.092 Å) is shorter ($\Delta r = 0.002$ Å) than the C6—H2iso bond.

The Si—HΨax bond is longer than the Si—HΨeq bond and the C5—HΨax bond is longer than the C5—HΨeq bond in the 1,4-boat transition state [**3e**]‡ of

2-silathiacyclohexane, the Si—HΨax bond is longer than the Si—HΨeq bond and the C6—HΨax bond is longer than the C6—HΨeq bond in the 2,5-boat transition state [**3f**]‡ and the Si—H bonds are equal and the C6—HΨax bond is shorter than the C6-HΨeq bond in the 3,6-boat transition state [**3g**]‡.

The Si—C3—C4 bond angle in the chair conformer (**3a**) of 2-silathiacyclohexane is larger than the Si—C2—C3 bond angle in the chair conformer of silacyclohexane (**1a**) and the S—C6—C5 bond angle in **3a** is larger than the S—C2—C3 bond angle in the chair conformer of thiacyclohexane (**2a**). With the exception of the 1,4-twist conformer (**3b**), the C3—C4—C5 bond angles in **3a**, **c** and **d** are larger than the C4—C5—C6 bond angles.

3-Silathiacyclohexane (4)

The 19 conformations considered for involvement in the conformational interconversion of 3-silathiacyclohexane (**4**) are shown in Figs 4 and 5. Frequency calculations identified four minima [chair (**4a**), 1,4-twist (**4b**), 2,5-twist (**4c**), 3,6-twist (**4d**)] and five transition states (1,4-boat [**4e**]‡, 2,5-boat [**4f**]‡, 3,6-boat [**4g**]‡, half-chair [**4k**]‡, four atoms coplanar, sofa [**4s**]‡, five atoms coplanar) for 3-silathiacyclohexane.

IRC calculations at the HF/6–31+G(d,p) level of theory showed that half-chair transition state [**4k**]‡ connected the chair (**4a**) and 1,4-twist (**4b**) conformers of 3-silathiacyclohexane. The HF/6–31+G(d,p) imaginary frequency at $-61\,\mathrm{cm}^{-1}$ suggests that the 2,5-boat transition state [**4f**]‡ is the barrier to the interconversion of the enantiomers of the 1,4-twist conformer (**4b**). The HF/6–31+G(d,p) energy difference between the chair conformer (**4a**) and half-chair transition state [**4k**]‡ is 5.14 kcal mol^{-1}. At the B3LYP/6–31+G(d,p) and B3LYP/6–311+G(d,p) levels of theory, the sofa transition state [**4s**]‡ was located. Intrinsic reaction path calculations at the B3LYP/6–311+G(d,p) level of theory showed that the sofa transition state [**4s**]‡ connects the chair (**4a**) and 2,5-twist (**4c**) conformers of 3-silathiacyclohexane (Fig. 8). The imaginary frequency at $-79\,\mathrm{cm}^{-1}$ for the 3,6-boat transition state [**4g**]‡ suggests that it is the barrier to the interconversion of the enantiomers of the 2,5-twist conformer (**4c**). The B3LYP/6–31+G(d,p) and B3LYP/6–311+G(d,p) energy differences (ΔE) between the chair conformer (**4a**) and sofa transition state [**4s**]‡ are 5.14 and 5.58 kcal mol^{-1}, respectively (Table 3). The chair–chair interconversion path for 3-silathiacyclohexane (**4a**, Fig. 8) is similar to that for cyclohexane and thiacyclohexane (**2a**) but different than that for silathiacyclohexane (**1a**, Fig. 7) and 4-silathiacyclohexane (**5a**, Fig. 9). It is of interest that the barrier to the chair–chair interconversion of 3-silathiacyclohexane is closer to those for silacyclohexane (**1a**, 5.47 kcal mol^{-1}) and 4-silathiacyclohexane (**5a**, 4.82 kcal mol^{-1}) than those for cyclohexane (10.2 kcal mol^{-1}) and thiacyclohexane (**2a**, 9.4 kcal mol^{-1}). Hence it is seen that when a ring carbon in a cyclohexane or thiacyclohexane (**2**) is substituted by a silicon atom, the resulting chair conformer becomes more flexible owing to the longer Si—C bond and the flattening of the ring at the silicon atom. This leads to lower barriers for the conformational interconversion processes although the paths may be different (cf. Figs 7–9).

There are relatively small energy differences among the twist conformers of 3-silathiacyclohexane (Table 3). The chair conformer (**4a**) is 3.91, 4.02 and 3.47 kcal mol^{-1}, respectively, more stable than the 1,4-twist (**4b**), 2,5-twist (**4c**) and 3,6-twist (**4d**) conformers. As for the twist conformers of 2-silathiacyclohexane (**3c** < **3d** < **3b**, see above), the relative stability of the twist conformers is determined by a number of factors including orbital interactions, electrostatic interactions and the relative destabilizing non-bonded interactions in the eclipsed $\mathrm{CH_2}$—$\mathrm{CH_2}$ fragments.[33] In **4c** there are four repulsive vicinal H···H non-bonded interactions (2.36 to 2.38 Å), whereas **4d** and **4b** have only one such interaction, the H···H non-bonded distance being shorter in the latter.

In the chair conformer of 3-silathiacyclohexane (**4a**), the S—C2 bond is longer ($\Delta r = 0.004$ Å) than the S—C6 bond, the Si—C bonds are equal and the C4—C5 bond is longer ($\Delta r = 0.011$ Å) than the C5—C6 bond (Table 4). This is another example of when silicon is attached to a $\mathrm{C_{sp^3}}$—$\mathrm{C_{sp^3}}$ bond it causes an elongation of the $\mathrm{C_{sp^3}}$—$\mathrm{C_{sp^3}}$ bond. In the 1,4-twist conformer (**4b**), the S—C2 bond is shorter ($\Delta r = 0.007$ Å) than the S—C6 bond, the Si—C2 bond is shorter ($\Delta r = 0.010$ Å) than the Si—C4 bond and the C4—C5 bond is longer ($\Delta r = 0.012$ Å) than the C5—C6 bond. In contrast to the 1,4-twist conformer **4b**, in the 2,5-twist conformer (**4c**), the S—C2 bond is longer ($\Delta r = 0.006$ Å) than the S—C6 bond, the Si—C2 bond is longer ($\Delta r = 0.010$ Å) than the Si—C4 bond and the C4—C5 bond is longer ($\Delta r = 0.010$ Å) than the C5—C6 bond (Tables 4c–f in the Supplementary Information). In the 3,6-twist conformer (**4d**) the S—C2 bond is shorter ($\Delta r = 0.011$ Å) than the S—C6 bond, the Si—C bonds are equal and the C4—C5 bond is longer ($\Delta r = 0.006$ Å) than the C5—C6 bond.

In the chair conformer of 3-silathiacyclohexane (**4a**), the Si—Hax bond is shorter ($\Delta r = 0.004$ Å) than the Si—Heq bond (homoanomeric effect $n_{\mathrm{Sax}} \rightarrow \sigma^*_{\mathrm{Si—Heq}}$, $\sigma_{\mathrm{S–C2}} \rightarrow \sigma^*_{\mathrm{Si—Heq}} > \sigma_{\mathrm{C2—Hax}} \rightarrow \sigma^*_{\mathrm{Si—Hax}}$ and $\sigma_{\mathrm{C4—Hax}} \rightarrow \sigma^*_{\mathrm{Si—Hax}}$), which is in contrast to what is observed in the chair conformers of silacyclohexane (**1a**), 2-silathiacyclohexane (**3a**) and 4-silathiacyclohexane (**5a**), but is similar to C3 in the chair conformer of thiacyclohexane (**2a**). In the 1,4-twist conformer (**4b**) the Si—HΨax bond is shorter ($\Delta r = 0.003$ Å) than the Si—HΨeq bond, in the 2,5-twist conformer (**4c**) the Si—HΨax bond is longer ($\Delta r = 0.002$ Å) than the Si—HΨeq bond and in the 3,6-twist conformer (**4d**) the Si—H1iso bond is

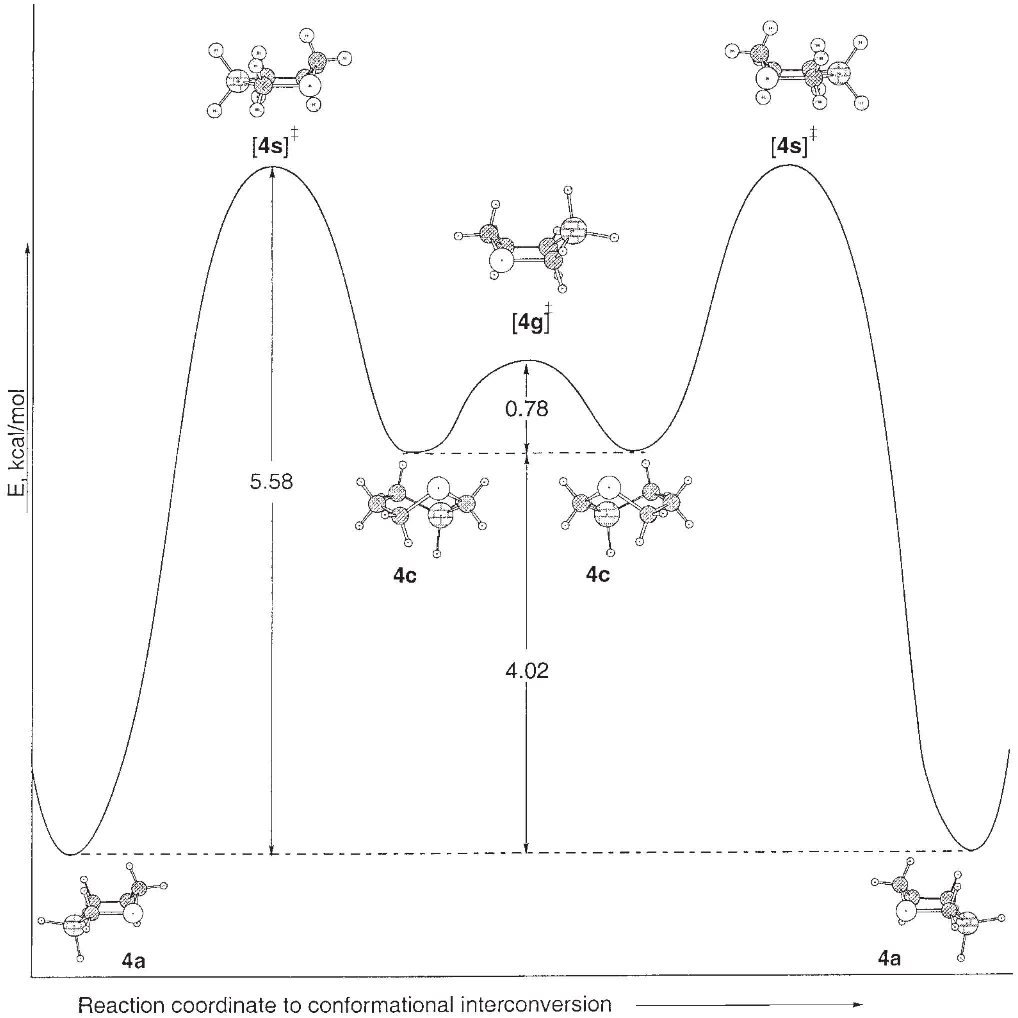


Figure 8. B3LYP/6–311+G(d,p) potential energy diagram for the chair–chair interconversion of 3-silathiacyclohexane (**4**)

shorter ($\Delta r = 0.007$ Å) than the Si—H2iso bond (Tables 4d–f in the Supplementary Information).

In the chair conformer of 3-silathiacyclohexane (**4a**), at C2 ($\Delta r = 0.002$ Å), C4 ($\Delta r = 0.003$ Å) and C6 ($\Delta r = 0.003$ Å) the respective C—Hax bonds are longer than the C—Heq bonds ($\sigma_{\text{C—Hax}} \rightarrow \sigma^*_{\text{C—Hax}}$). In the 1,4-twist conformer (**4b**), at C2 and C4 the respective C—H bonds are equal. In the 2,5-twist conformer (**4c**), the C2—Hiso bonds are equal, the C4—HΨax bond is longer ($\Delta r = 0.002$ Å) than the C4—HΨeq bond and the C6—HΨax bond is longer ($\Delta r = 0.002$ Å) than the C6—HΨeq bond. In the 3,6-twist conformer (**4d**), the C2—H bonds are equal and the respective C—H bonds at C4, C5, and C6 are equal.

Table 3. Total energies and relative thermodynamic parameters for conformers and transition states of 3-silathiacyclohexane (**4**)

Conformer or transition state	Total energy (au)	ΔE (kcal mol^{-1})	ΔH° (kcal mol^{-1})	ΔG° (kcal mol^{-1})
4a	−846.237481			
4b	−846.231243	3.91	4.01	3.33
4c	−846.231069	4.02	4.10	3.62
4d	−846.231952	3.47	3.54	3.13
[4e]‡	−846.229373	5.09	4.93	5.21
[4f]‡	−846.231100	4.00	3.95	4.32
[4s]‡	−846.228589	5.58	5.37	5.36

In the chair conformer of 3-silathiacyclohexane (**4a**), the C5—Hax bond is shorter ($\Delta r = 0.003$ Å) than the C5—Heq bond ($\sigma_{\text{S—C6}} \rightarrow \sigma^*_{\text{C5—Heq}} > \sigma_{\text{C6—Hax}} \rightarrow \sigma^*_{\text{C5—Hax}}$, $\sigma_{\text{C4—Hax}} \rightarrow \sigma^*_{\text{C5—Hax}}$). The shorter C5—Hax bond in **4a** is similar to that observed in the chair conformer (**2a**) of thiacyclohexane. In the 1,4-twist conformer (**4b**), the C5—H bonds are equal, in the 2,5-twist conformer (**4c**) the C5—1Hiso bond is longer ($\Delta r = 0.002$ Å) than the C5—2Hiso bond and in the 3,6-twist conformer (**4d**) the C5—H bonds are equal.

4-Silathiacyclohexane (5)

The 12 conformations considered for involvement in the conformational interconversion path of 4-silathiacyclo-

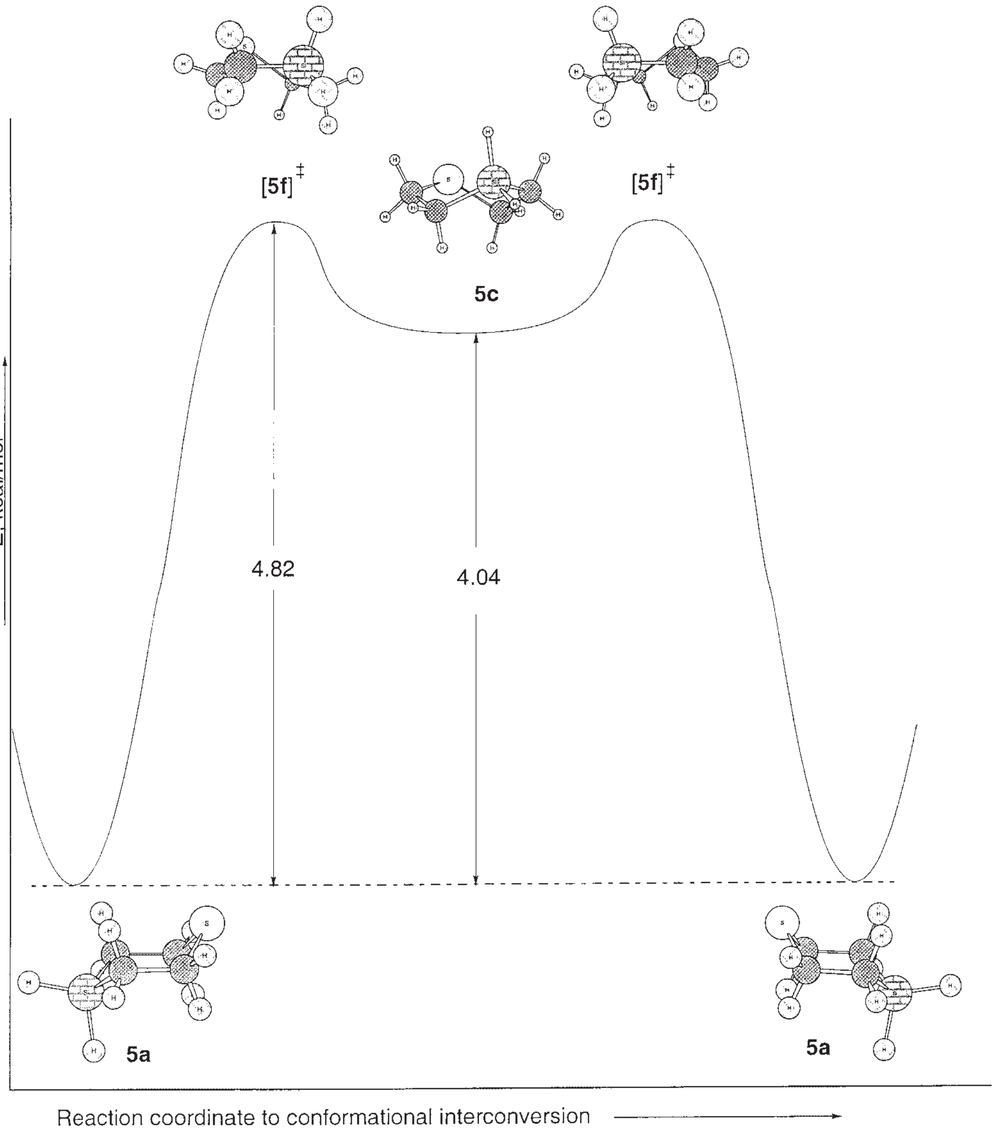
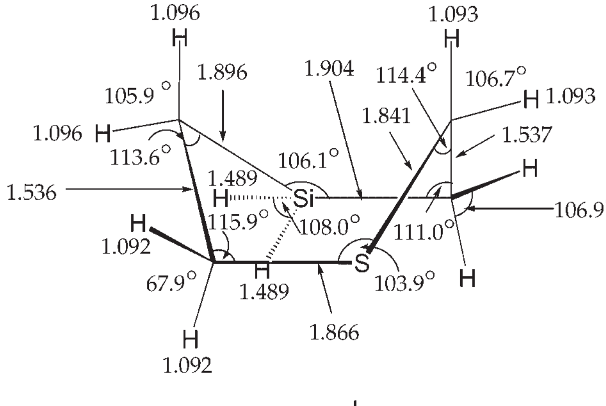


Figure 9. B3LYP/6–311+G(d,p) potential energy diagram for the chair–chair interconversion of 4-silathiacyclohexane

hexane (**5**) are shown in Fig. 6. Vibrational frequency calculations identified three minima [(chair **5a**, C_s symmetry), 1,4-twist (**5b**, C_2 symmetry), 2,5-twist (**5c**)] and two transition states, (2,5-boat, [**5e**]‡, half-chair transition state ([**5f**]‡, Fig. 9) for 4-silathiacyclohexane.

The energy difference between the chair conformer (**5a**) and the 2,5-boat transition state ([**5e**]‡) is 4.13 kcal mol^{-1} (Table 5). IRC calculations at the HF/6–311+G(d,p) and B3LYP/6–311+G(d,p) levels of theory showed that the half-chair transition state [**5f**]‡ connected the enantiomeric chair conformers (**5a**) via the 2,5-twist conformer (**5c**). The HF/6–311+G(d,p) and B3LYP/6–311+G(d,p) energy differences (ΔE) between the chair conformer (**5a**) and the half-chair transition structure [**5f**]‡ were 5.67 and 4.82 kcal mol^{-1}, respectively. Hence it is seen that the path for the chair–chair interconversion of 4-silathiacyclohexane (**5a**, Fig. 9) is different to that for cyclohexane (**1a**) but similar to those for silacyclohexane(**1a**)[2g,h] and thiacyclohexane (**2a**).[4] The barrier (ΔE) to the chair–chair interconversion of **5a** is similar to those of silacyclohexane (**1a**) and 3-silathiacyclohexane (**4a**) and significantly smaller than those of cyclohexane and thiacyclohexane (**2a**).



[5e]‡

Table 4. B3LYP/6–311+G(d,p) equilibrium geometry for the chair conformer (**4a**) of 3-silathiacyclohexane

Parameter	Value
Bond length (Å):	
S1—C2	1.844
S1—C6	1.840
C2—Si3	1.892
Si3—Hax	1.487
Si3—Heq	1.491
Si3—C4	1.893
C4—C5	1.543
C5—C6	1.532
C2—Hax	1.094
C2—Heq	1.092
C4—Hax	1.098
C4—Heq	1.095
C5—Hax	1.095
C5—Heq	1.098
C6—Hax	1.095
C6—Heq	1.092
Bond angle (°):	
S1—C2—Si3	110.2
S1—C6—C5	115.6
C2—S1—C6	101.1
C2—Si3—C4	107.1
Si3—C4—C5	113.8
C4—C5—C6	113.9
Hax—Si—Heq	108.7
Torsional angle, τ (°):	
S1—C2—Si3—C4	50.4
S1—C6—C5—C4	−69.1
C2—Si3—C4—C5	−48.1
Si3—C4—C5—C6	57.2

The chair conformer (**5a**) of 4-silathiacyclohexane is 3.05 and 4.04 kcal mol^{-1}, respectively, more stable than the 1,4-twist (**5b**) and 2,5-twist (**5c**) conformers (Table 5). The relative stability of the conformers (**5a** < **5b** < **5c**) may be determined by a number of causes, including relative repulsive non-bonded interactions in the eclipsed CH$_2$—CH$_2$ fragments.[31] The relative energies of conformers **5a** < **5b** < **5c** follow the same order as the degree of eclipsing of C—H bonds in the H—C2—C3—H fragments. The chair conformer (**5a**) is virtually staggered, the 1,4-twist conformer (**5b**) is slightly eclipsed (the smallest H—C2—C3—H torsional angle is 52.4°) and the 2,5-twist conformer (**5c**) is eclipsed more considerably (the smallest H—C2—C3—H torsional angles are 48.8° and 46.3°).

In the chair (**5a**) and 1,4-twist (**5b**) conformers of 4-silathiacyclohexane, the respective S—C and Si—C bonds are equal (Table 6). However, in the 2,5-twist conformer (**5c**), the S—C2 bond is significantly longer ($\Delta r = 0.018$ Å) than the S—C6 bond, the Si—C3 bond is shorter ($\Delta r = 0.009$ Å) than the Si—C5 bond and the C—C bonds are equal.

In the chair conformer (**5a**) of 4-silathiacyclohexane, the C2—H bonds are equal, the C3—Heq bond is longer ($\Delta r = 0.002$ Å) than the C3—Hax bond and the Si—Hax bond is longer ($\Delta r = 0.004$ Å) than the Si—Heq bond. In the 1,4-twist conformer (**5b**), the respective C2—H bonds and C3—H bonds are equal. In the 2,5-twist conformer (**5c**), the C2—Hiso bonds are equal, the C3—H bonds are equal, the Si—HΨeq bond is longer ($\Delta r = 0.003$ Å) than the Si—HΨax bond and the C5—H1iso bond is longer ($\Delta r = 0.003$ Å) than the C5—H2iso bond (Tables 5c–e in the Supplementary Information).

Table 5. Total energies and relative thermodynamic parameters for conformers and transition states of 4-silathiacyclohexane (**5**)

Conformer or transition state	Total energy (au)	ΔE (kcal mol^{-1})	$\Delta H°$ (kcal mol^{-1})	$\Delta G°$ (kcal mol^{-1})
5a	−846.236751			
5b	−846.231173	3.50	3.57	3.10
5c	−846.230310	4.04	4.10	3.44
[**5e**]‡	−846.230168	4.13	3.65	4.49
[**5f**]‡	−846.229070	4.82	4.31	4.74

The chair conformer of 2-silathiacyclohexane (**3a**) is lower in energy (ΔE) than the chair conformers of 3-silathiacyclohexane (**4a**, −846.237481 au, $\Delta E = 15.4$ kcal mol^{-1}) and 4-silathiacyclohexane (**5a**, −846.236751 au, $\Delta E = 15.9$ kcal mol^{-1}). Hence the most stable isomer (**3a**) is the one with the silicon–sulfur bond. One can attribute this greater stability in part to the electrostatic interactions between the electropositive silicon and electronegative sulfur since the charge differences follow the

Table 6. B3LYP/6–311+G(d,p) equilibrium geometry for the chair conformer (**5a**) of 4-silathiacyclohexane

Parameter	Value
Bond length (Å):	
S1—C2	1.840
S1—C6	1.840
C2—C3	1.538
C3—Si4	1.894
Si4—C5	1.894
C5—C6	1.538
C2—Hax	1.094
C2—Heq	1.093
C3—Hax	1.095
C3—Heq	1.097
Si4—Hax	1.492
Si4—Heq	1.488
Bond angle (°):	
S1—C2—C3	114.5
S1—C6—C5	114.5
C2—S1—C6	100.7
C2—C3—Si4	112.3
C3—Si4—C5	107.6
Hax—Si4—Heq	108.3
Torsional angle, τ (°):	
S1—C2—C3—Si4	60.5
S1—C6—C5—Si4	−60.5
C2—C3—Si4—C5	−45.9
C3—Si4—C5—C6	45.9

same order: $\Delta q = q_{\mathrm{Si}} - q_{\mathrm{S}} = 0.701$, 0.422 and 0.402 for **3a**, **4a** and **5a**, respectively (Fig. SI-1 in the Supplementary Information). It is worth noting in the 3,6-twist conformer (**3d**) of 2-silathiacyclohexane, the 1,4- and 2,5-twist conformers of 3-silathiacyclohexane (**4b**) and (**4c**) and the 2,5-twist conformer of 4-silathiacyclohexane (**5c**) that the silicon-containing fragment of the respective molecule deviates only slightly from planarity. The 'ideal' torsional angle C2—C3—C4—C5 in the twist conformer of cyclohexane is 30°, whereas the corresponding angles in **3d** (S—Si—C3—C4, 16.5°), in **4b** (C2—Si—C4—C5, 15.2°), in **4c** (S—C2—Si—C4, 17.5°) and in **5c** (C3—Si—C5—C6, 12.3°) are significantly smaller than 30°. The reason has to do with the much longer Si—H bond length compared with the C—H bond.

CONCLUSIONS

Stereoelectronic hyperconjugative interactions, relative energies and geometric parameters for conformers and transition states of 2-, 3- and 4-silathiacyclohexane were calculated at the B3LYP/6–311+G(d,p) level of theory. The chair conformer of 2-silathiacyclohexane is 15.4 and 15.9 kcal mol^{-1}, respectively, lower in energy than the chair conformers of 3- and 4-silathiacyclohexane. IRC calculations were used to connect the transition state between the chair and 2,5-twist conformers of 3-silathiacyclohexane. The chair–chair interconversion path for 3-silathiacyclohexane, which is similar to those for cyclohexane and thiacyclohexane, is chair → $[\mathrm{sofa}]^{\ddagger}$ → 2,5-twist → $[3,6\text{-boat}]^{\ddagger}$ → 2,5-twist → $[\mathrm{sofa}]^{\ddagger}$ → chair, with the barrier height being associated with the step of chair → $[\mathrm{sofa}]^{\ddagger}$. The path for the chair–chair conformational interconversion of 4-silathiacyclohexane is similar to that for silacyclohexane and proceeds via the 2,5-twist conformer (intermediate) without going through a boat conformation. The barriers (ΔE, kcal mol^{-1}) to the chair–chair conformational interconversions in 3-silathiacyclohexane (5.15) and 4-silathiacyclohexane (4.62) are significantly smaller than those for cyclohexane and thiacyclohexane (9.47), but similar to that for silacyclohexane (5.47). The S—Si bond lengths in the chair, 1,4-twist, 2,5-twist and 3,6-twist conformers of 2-silathiacyclohexane are 2.159, 2.166, 2.166 and 2.157 Å, respectively. Stereoelectronic hyperconjugative interactions were predicted for the chair and twist conformers and boat transition states of 2-, 3- and 4-silathiacyclohexane.

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