

Computational study of conformations and of sulfinyl oxygen-induced pentacoordination at silicon in 4-chloro-4-silathiacyclohexane 1-oxide and 4,4-dichloro-4-silathiacyclohexane 1-oxide

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Abstract

Second-order Møller–Plesset theory (MP2) and density functional theory (B3LYP) with the 6-311G(d,p) and 6-311+G(d,p) basis sets have been used to calculate the equilibrium geometries and relative energies of the chair, twist, and boat conformations of 4-chloro-4-silathiacyclohexane 1-oxide and 4,4-dichloro-4-silathiacyclohexane 1-oxide. The chair conformers of the axial sulfoxides are lower in energy than the chair conformers of the corresponding equatorial sulfoxides. MP2/6-311+G(d,p) predicted the chair conformer of axial *trans*-4-chloro-4-silathiacyclohexane 1-oxide (**4a**) to be 6.12, 0.44, and 0.45 kcal/mol, respectively, more stable than the corresponding 1,4-twist (**4b**), 2,5-twist (**4c**) and 1,4-boat (**4d**) conformers and 6.93 kcal/mol more stable than the 2,5-boat transition state (**[4e]**[‡]). Structures **4c** and **4d** are stabilized by intramolecular coordination of the sulfinyl oxygen with silicon that results in trigonal bipyramidal geometry at silicon. The 1,4-boat conformer (**7d**) of axial 4,4-dichloro-4-silathiacyclohexane 1-oxide is also stabilized by transannular coordination of the sulfinyl oxygen with silicon. The energy difference ($E_{\text{rel}} = 4.23$ kcal/mol) between the chair conformer (**7a**) and **7d** is larger than that between **4a** and **4d**. The relatively lower stability of the 1,4-boat conformer (**7d**) of axial 4,4-dichloro-4-silathiacyclohexane 1-oxide (**7a**) may be due to repulsive interactions of the axial halogen and sulfinyl oxygen atoms. The relative energies and structures of the conformers and transition states of *cis*- and *trans*-4-chloro-4-silathiacyclohexane 1-oxide and 4,4-dichloro-4-silathiacyclohexane 1-oxide are discussed in terms of hyperconjugative interactions, orbital interactions, nonbonded interactions, and intramolecular sulfinyl oxygen–silicon coordination.

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1. Introduction

Compounds of silicon with coordination number greater than four have been known for many years

and the synthesis, structure, and reactivity of organosilicon compounds continue to be areas of lively interest [1]. Although numerous studies of pentacoordinated silicon compounds have focused on the use of nitrogen (A), oxygen (B), and sulfur (C) ligands acting as donors which change the tetrahedral geometry at silicon toward trigonal bipyramidal (Fig. 1) [1a,1b], there appears to be only two reports [2] of acyclic sulfoxides coordinating

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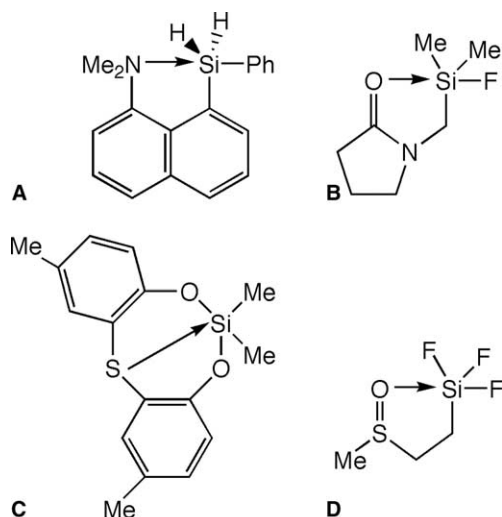
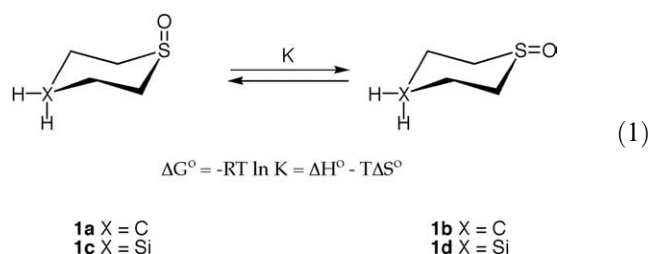


Fig. 1. Selected examples of nitrogen (A), oxygen (B), sulfur (C), and sulfinyl oxygen (D) donor action to form pentacoordinated trigonal bipyramidal geometry at silicon.

with silicon to generate hypervalent trigonal bipyramidal structures (D, Fig. 1) and only one report [3] of cyclic sulfoxides participating in pentacoordination at silicon (1e, 2, Fig. 2).

The preference by most substituents to occupy the equatorial position on a cyclohexane or heterocyclohexane ring is occasionally reversed [4] and examples are seen in the equilibria favoring the axial S=O group in thiacyclohexane 1-oxides [5], substituted thiacyclohexane 1-oxides, and silathiacyclohexane 1-oxides (Eq. (1)) [3]. There has been considerable discussion concern-

ing the magnitude of the conformational free energy (ΔG°) of thiacyclohexane oxides and the factors which contribute to the axial preference of the S=O group [3,5].



The cyclic organosilicon sulfoxides represent a relatively new class of compounds [6]. This study was undertaken in order to acquire information concerning hyperconjugative interactions, transannular sulfinyl oxygen–silicon coordination to form hypervalent silicon, structural properties, relative energies, and relative thermodynamic parameters of conformations, conformers, and transition states of axial *cis*-4-chloro-4-silathiacyclohexane 1-oxide (3, Fig. 3), axial *trans*-4-chloro-4-silathiacyclohexane 1-oxide (4, Fig. 4), equatorial *cis*-4-chloro-4-silathiacyclohexane 1-oxide (5, Fig. 5), equatorial *trans*-4-chloro-4-silathiacyclohexane 1-oxide (6, Fig. 6), axial 4,4-dichloro-4-silathiacyclohexane 1-oxide (7, Fig. 7), and equatorial 4,4-dichloro-4-silathiacyclohexane 1-oxide (8, Fig. 8).

2. Computational methods and calculations

The calculations were carried out with the SPARTAN '02 Macintosh [7], SPARTAN '02 Unix [7], and GAUSSIAN 98 [8] computational programs. The equilibrium geometries were calculated at the B3LYP/6-311G(d,p) level followed by MP2/6-311+G(d,p) single point energy calculations. No constraints were imposed on the structures in the equilibrium geometry calculations and in the transition state structure optimizations. The B3LYP/6-311G(d,p) equilibrium geometry parameters and thermochemical data are given in the Supporting Information (SI).

Vibrational frequency analyses were carried out in order to assess the nature of the stationary points and to obtain zero point vibrational energies (ZPVE). The characteristics of local minima and transition states were verified by establishing that the matrices of the energy second derivatives (Hessians) have either zero (number of imaginary frequencies NIMAG = 0) or one negative eigenvalue (NIMAG = 1), respectively. B3LYP/6-311G(d,p) vibrational frequencies were computed on the geometry optimized structures. The zero point vibrational energies (ZPVE) were not scaled in the calculations of the relative thermodynamic parameters [8b,9]. The thermochemical data from the B3LYP/

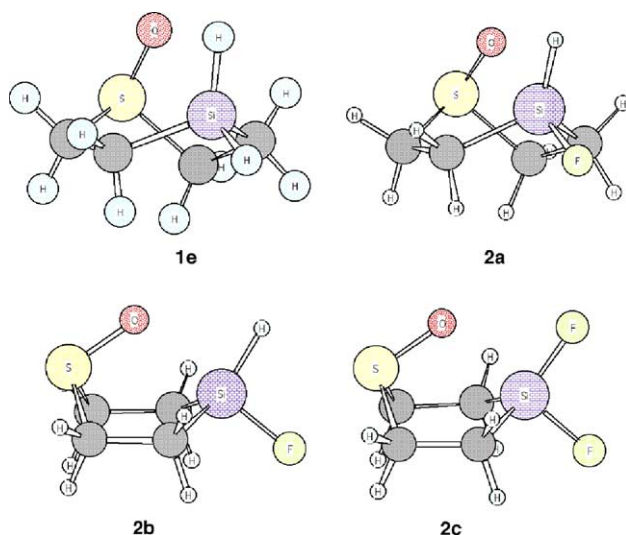


Fig. 2. The MP2/6-311+G(d,p) calculated 2,5-twist conformer (1e) of silathiacyclohexane, 2,5-twist (2a) and 1,4-boat (2b) conformers of *trans*-1-fluoro-4-silathiacyclohexane, and 1,4-boat conformer (2c) of 4,4-difluoro-4-silathiacyclohexane with sulfinyl oxygen-induced pentacoordination at silicon.

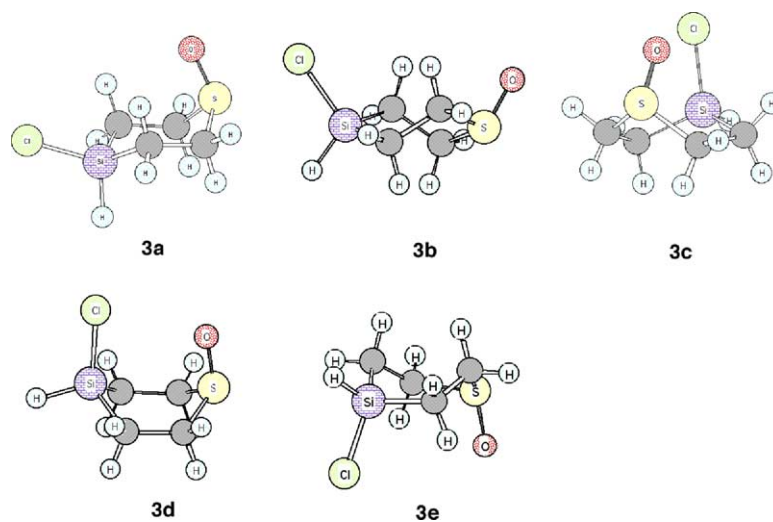


Fig. 3. Chair (**3a**), 1,4-twist (**3b**), 2,5-twist (**3c**), 1,4-boat (**3d**), and 2,5-boat (**3e**) conformations of axial *cis*-4-silathiacyclohexane 1-oxide.

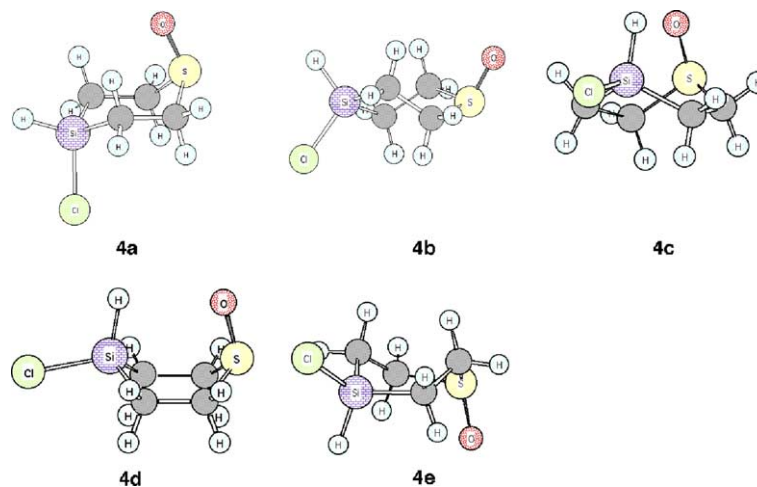


Fig. 4. Chair (**4a**), 1,4-twist (**4b**), 2,5-twist (**4c**), 1,4-boat (**4d**), and 2,5-boat (**4e**) conformations of axial *trans*-4-chloro-4-silathiacyclohexane 1-oxide.

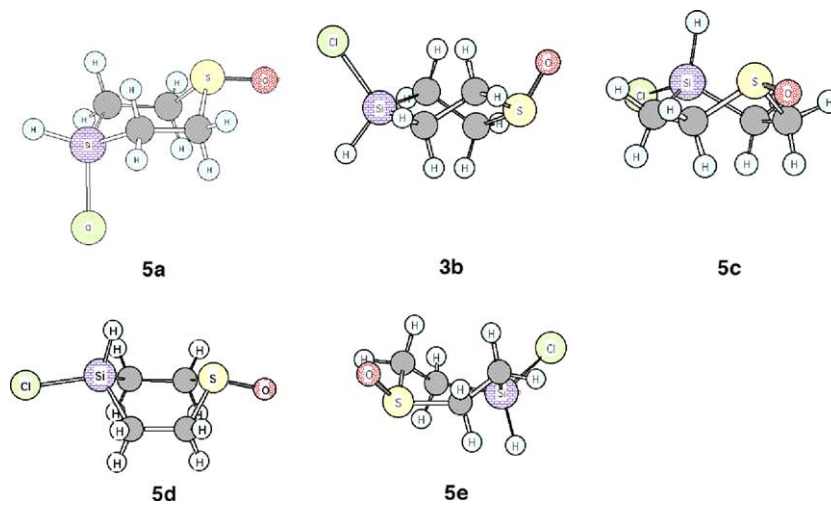


Fig. 5. Chair (**5a**), 1,4-twist (**5b**), 2,5-twist (**5c**), 1,4-boat (**5d**), and 2,5-boat (**5e**) conformations of equatorial *cis*-4-chloro-4-silathiacyclohexane 1-oxide.

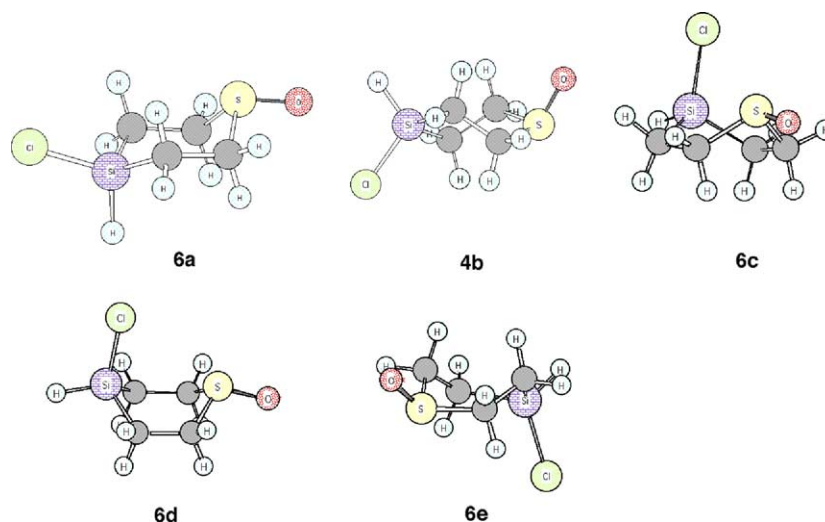


Fig. 6. Chair (**6a**), 1,4-twist (**4b**), 2,5-twist (**6c**), 1,4-boat (**6d**), and 2,5-boat (**6e**) conformations of equatorial *trans*-4-chloro-4-silathiacyclohexane 1-oxide.

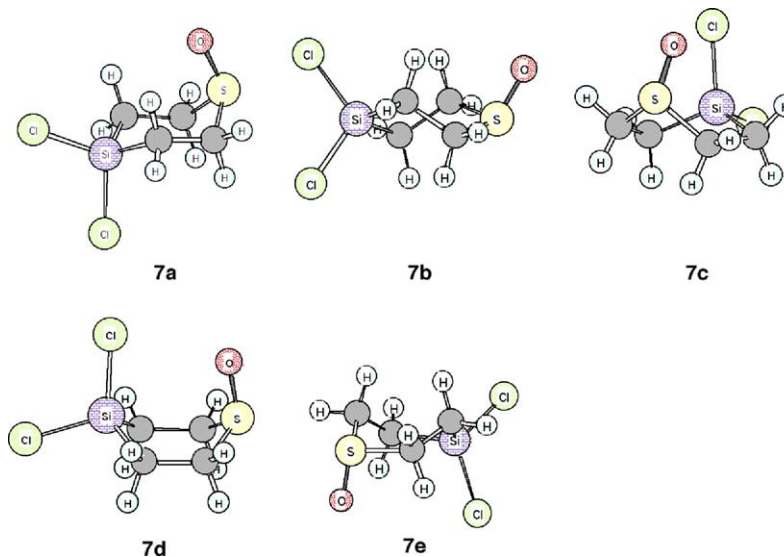


Fig. 7. Chair (**7a**), 1,4-twist (**7b**), 2,5-twist (**7c**), 1,4-boat (**7d**), and 2,5-boat (**7e**) conformations of axial 4,4-chloro-4-silathiacyclohexane 1-oxide.

6-311G(d,p) frequency calculations were used in the MP2/6-311+G(d,p) single point energy calculations of the relative thermodynamic parameters. The relative energy (E_{rel}) is the difference in calculated energy without zero-point or other corrections. The $H(0)_{\text{rel}}$ is the difference in enthalpy at 0 K ($H(0)_{\text{rel}} = E_{\text{rel}} + \text{ZPVE correction}$), which is also the difference in free energy [$G(0)_{\text{rel}}$] at that temperature. $H(298)_{\text{rel}}$ and $G(298)_{\text{rel}}$ are the enthalpy and free energy differences corrected to 298 K.

Transition states were located using the linear synchronous transit method [7] and the Berny algorithm [8]. The atomic charges were obtained at the MP2/6-311G(d) level of theory [8b]. The van der Waals radii (r_{vdW}) of H = 1.20 Å, C = 1.70 Å, O = 1.52 Å, F = 1.47 Å, Cl = 1.84 Å, Br = 1.96 Å, Si = 2.10 Å, and S = 1.80 Å are used in the discussion [10]. Repulsive ste-

ric interactions arise when the nonbonded distance between the atoms is less than the sum of the van der Waals radii of the atoms.

Total energies are in hartree [H, atomic units (au)] and the other energies are in kcal/mol. Bond angles are in degrees, bond lengths are in angstroms (Å), dipole moments (μ) are given in debyes (D), atomic charges are given in electrons, and entropies are given in cal/mol K.

3. Results and discussion

The chair conformer (**1a**) of axial thiacyclohexane 1-oxide is more stable than the equatorial chair conformer (**1b**, Table 1, Tables 1a, 1b in the Supporting Information). Attractive interactions between the axial sulfinyl oxygen and the partially positive axial hydrogens at

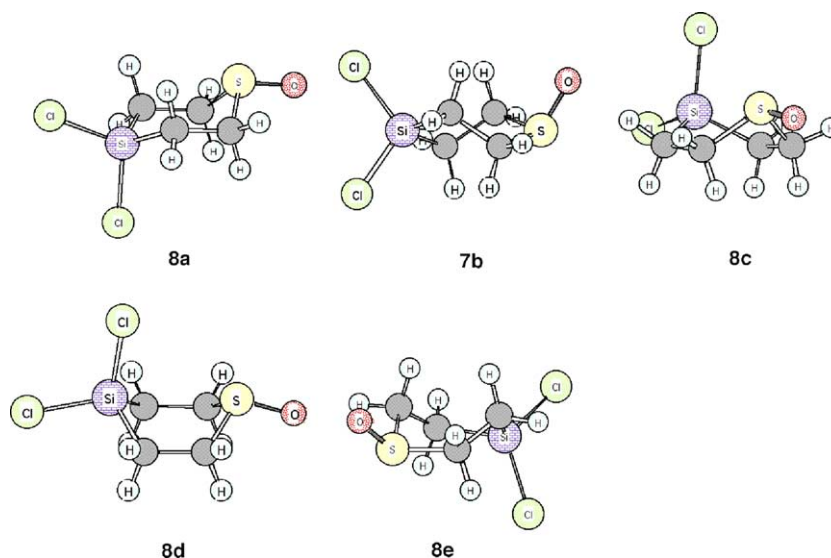


Fig. 8. Chair (**8a**), 1,4-twist (**7b**), 2,5-twist (**8c**), 1,4-boat (**8d**), and 2,5-boat (**8e**) conformations of equatorial 4,4-dichloro-4-silathiacyclohexane 1-oxide.

Table 1

Conformational free energies (Eq. (1)) and relative thermodynamic parameters for the chair conformers of axial and equatorial thiacyclohexane 1-oxide (**1a**, **1b**) and 4-silathiacyclohexane 1-oxide (**1c**, **1d**)

Chair conformer	E_{rel}	$H(298)_{\text{rel}}$	$G(298)_{\text{rel}}$
1a _{ax}			
1b _{eq}	1.03	1.03	0.82
1c _{ax}			
1d _{eq}	1.88	1.69	1.38
3a _{ax}			
5a _{eq}	1.27	1.19	1.10
4a _{ax}			
6a _{eq}	3.89	3.66	3.25
7a _{ax}			
8a _{eq}	3.15	3.00	2.70

C3 and C5 have been invoked to explain the predominance of the axial conformer (**1a**, Fig. 9) [5a,5j,5l]. The MP2/6-311+G(d,p) calculated relative free energy ($G(298)_{\text{rel}}$) is 0.82 kcal/mol ($E_{\text{rel}} = 1.03$ kcal/mol, Eq. (1), Table 1) is in agreement with experimental data ($\Delta G^0 = 0.75$ kcal/mol) and shows that the axial conformer **1a** is favored.

The conformational free energy ($\Delta G^0 = 1.50$ kcal/mol; $E_{\text{rel}} = 1.79$ kcal/mol; Eq. (1), Table 1) between the axial (**1c**) and equatorial (**1d**) chair conformers of 4-silathiacyclohexane 1-oxide is larger than that between **1a** and **1b**. Thus replacement of the 4-CH₂ group in thiacyclohexane 1-oxide (**1a**, **1b**) with a SiH₂ group leads to a greater preference for the axial conformer (**1c**). As in thiacyclohexane 1-oxide (**1a**, **1b**), the greater stability of the axial chair conformer **1c** as compared to **1d** is due in part to stabilizing attractive electrostatic interactions between the sulfinyl oxygen and axial hydrogen atoms at C3 and C5 in **1c** (Fig. 9). The S=O...H intramolecular separation (2.546 Å) in **1c** is less than the sum

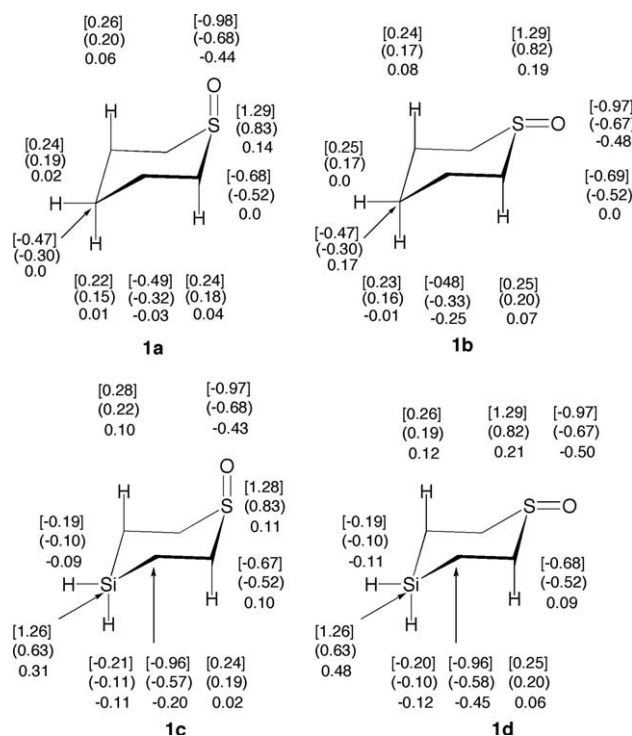


Fig. 9. Selected atomic charges for the chair conformers of thiacyclohexane 1-oxide (**1a**, **1b**) and 4-silathiacyclohexane 1-oxide (**1c**, **1d**): electrostatic, Mulliken (), and Natural [].

of the van der Waals radii (2.72 Å) for the hydrogen and oxygen atoms [10].

The 2,5-twist conformer (**1e**) of axial 4-silathiacyclohexane 1-oxide is stabilized by a transannular interaction between the sulfinyl oxygen and silicon that leads to a pentacoordinate silicon (Fig. 2) [3]. The geometry at silicon in **1e** corresponds to a distorted trigonal bipyramid with the sulfinyl oxygen and pseudoequatorial

hydrogen substituents axial. The $\text{S}=\text{O} \cdots \text{Si}$ distance in **1e** (2.788 Å) is shorter than the sum of the van der Waals radii for the oxygen and silicon atoms (3.62 Å) but is longer than the distances (1.75–2.40 Å) found in silanes undergoing oxygen-induced pentacoordination [1j,2b]. The S–O bond in **1e** (1.520 Å) is longer than those in the axial chair (**1c**, $\Delta r = 0.007$ Å) and equatorial chair (**1d**, $\Delta r = 0.010$ Å) conformers of 4-silathiacyclohexane 1-oxide. The $\text{O}-\text{Si}-\text{H}_{\text{eq}}$ bond angle in **1e** is 176.1° . Orbital analysis leads to the conclusion that it is the electrostatic interaction between the electronegative sulfinyl oxygen and electropositive silicon atom as well as the $n_{\text{O}}-\sigma_{\text{Si-Cl}}^*$ hyperconjugative interaction which are responsible for pentacoordination. Noteworthy is the seminal role of the electronegative substituent X at silicon, which lowers the antibonding $\sigma_{\text{Si-Cl}}^*$ orbital thus facilitating negative hyperconjugation with the lone pair of the donor atom (sulfinyl oxygen). The observed bond length variations are satisfactorily rationalized within this model.

Five conformations of axial *cis*-4-chloro-4-silathiacyclohexane 1-oxide (chair, **3a**, C_s ; 1,4-twist, **3b**; 2,5-twist, **3c**; 1,4-boat, **3d**, C_s ; 2,5-boat, **3e**, Fig. 3) and five conformations of axial *trans*-4-chloro-4-silathiacyclohexane 1-oxide (chair, **4a**, C_s ; 1,4-twist, **4b**; 2,5-twist, **4c**; 1,4-boat, **4d**, C_s ; 2,5-boat, **4e**, Fig. 4) were considered. Vibrational frequency calculations verified that the chair (**3a** and **4a**), 1,4-twist (**3b** and **4b**), 2,5-twist (**3c**), and 1,4-boat (**4d**) structures are minima and that the 2,5-boat structure (**4e**)[‡] is a transition state (one imaginary vibrational frequency). The 1,4-boat structure (**4d**) is exceptional since in cyclohexane and in unsubstituted monoheterocyclohexanes and diheterocyclohexanes the boat structures are generally transition states [4]. The 1,4-boat (**3d**) and 2,5-boat (**3e**) structures of axial *cis*-4-chloro-4-silathiacyclohexane 1-oxide did not optimize at the levels of theory used. Presumably repulsive electrostatic interactions between the partially negative oxygen and chlorine atoms contribute to the higher energy of **3d** and **3e** in addition to repulsive interactions between the eclipsed C–H bonds in the CH_2CH_2 fragments in **3d**.

The calculated relative free energy ($G(298)_{\text{rel}} = 1.10$ kcal/mol; $E_{\text{rel}} = 1.27$ kcal/mol) for (**3a**) and (**5a**) (Table 1) is larger than that for the thiacyclohexane 1-oxide equilibrium (**1a**–**1b**) and smaller than that for the silathiacyclohexane 1-oxide equilibrium (**1c**–**1d**, Table 1). The greater stability of the axial chair conformer (**3a**) as compared to the equatorial chair conformer (**5a**) is due in part to nonbonded stabilizing attractive electrostatic interactions between the sulfinyl oxygen and axial hydrogen atoms at the C3 and C5 in **3a** (Fig. 10). The $\text{S}=\text{O} \cdots \text{H}$ nonbonded distances (2.571 Å) in **3a** are less than the sum of the van der Waals radii for the hydrogen and oxygen atoms. The energy differences (E_{rel}) between the chair conformer (**3a**) and the

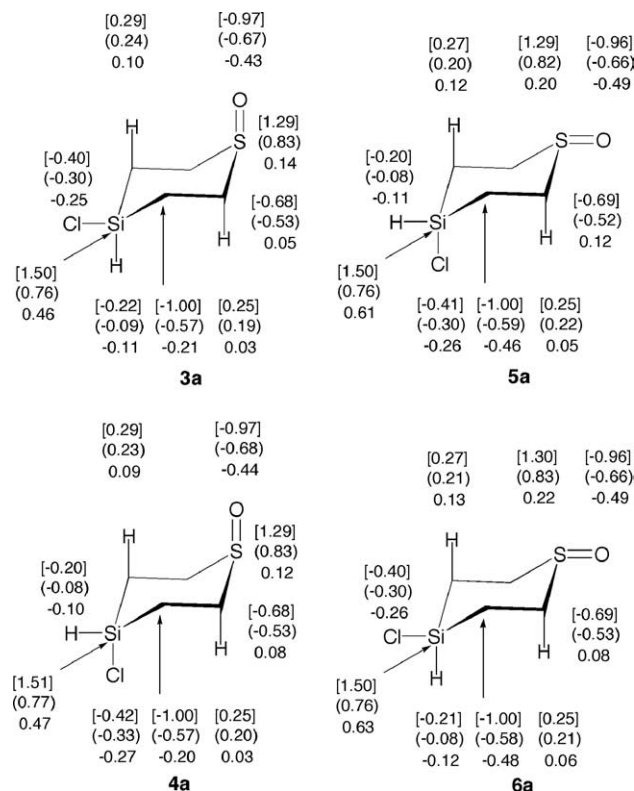


Fig. 10. Selected atomic charges for the chair conformers of 4-chloro-4-silathiacyclohexane 1-oxide: electrostatic, Mulliken ($()$), and Natural ($[\]$).

1,4-twist (**3b**) and 2,5-twist (**3c**) conformers are 4.69 and 4.88 kcal/mol, respectively (Table 2). There is little interaction between the partially negative sulfinyl oxygen and the partially negative chlorine in the 2,5-twist conformer (**3c**) since the nonbonded $\text{S}=\text{O} \cdots \text{Cl}$ distance (3.720 Å) is greater than the sum of the van der Waals radii (3.20 Å) for the chlorine and oxygen atoms.

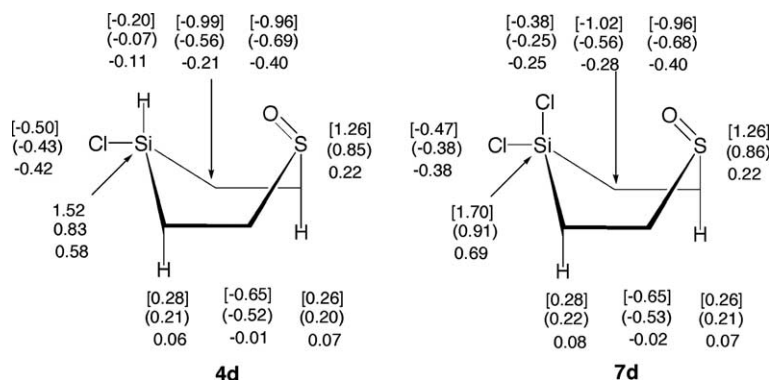
The calculated relative free energy ($G(298)_{\text{rel}} = 3.25$ kcal/mol; $E_{\text{rel}} = 3.89$ kcal/mol) for the chair conformers (**4a**) and (**6a**) (Table 1) is significantly larger than those for the respective **1a**–**1b**, **1c**–**1d**, or **3a**–**5a** equilibrium. The energy differences (E_{rel}) between the chair conformer (**4a**) and the 1,4-twist (**4b**), 2,5-twist (**4c**), and 1,4-boat (**4d**) conformers and the 2,5-boat (**4e**)[‡] transition state are 6.12, 0.44, 0.45, and 6.93 kcal/mol, respectively (Table 2). The 2,5-twist (**4c**) and 1,4-boat (**4d**) conformers have very similar structural properties and are very close in energy (Table 1 and Tables 2d and 2e in the Supporting Information). MP2/6-31G(d) and MP2/6-311+G(d,p)//MP2/6-31G(d), respectively, also calculated **4c** and **4d** to have similar geometrical parameters and to be very close in energy [11].

The 1,4-boat conformer (**4d**) is almost as stable as the chair conformer (**4a**) in spite of the absence of a nonbonded stabilizing electrostatic interaction between the sulfinyl oxygen and axial hydrogen on silicon

Table 2

Relative thermodynamic parameters for conformers and transition state of axial *cis*- and *trans*-4-chloro-4-silathiacyclohexane 1-oxide (**3** and **4**)^a

Conformer or transition state	Total energy	E_{rel}	$H(298)_{\text{rel}}$	$G(298)_{\text{rel}}$
Axial <i>cis</i> -4-chloro-4-silathiacyclohexane 1-oxide				
3a	-1378.800224			
3b, 5b	-1378.792755	4.69	4.54	3.94
3c	-1378.792450	4.88	4.77	4.23
Axial <i>trans</i> -4-chloro-4-silathiacyclohexane 1-oxide				
4a	-1378.803036			
4b, 6b	-1378.793283	6.12	5.94	5.36
4c	-1378.802401	0.44	0.47	0.32
4d	-1378.802326	0.45	0.47	0.18
[4e][‡]	-1378.791994	6.93	6.14	5.49

^a MP2/6-311+G(d,p).Fig. 11. Selected atomic charges for the 1,4-boat conformers of axial *trans*-4-chloro-4-silathiacyclohexane 1-oxide (**4d**) and axial 4,4-dichloro-4-silathiacyclohexane 1-oxide (**7d**): electrostatic, Mulliken ($()$), and Natural [$]$.

($\text{S}=\text{O} \cdots \text{H} = 2.401 \text{ \AA}$) and the destabilizing interactions between the eclipsed C–H bonds (Fig. 11 and Tables 2d and 2e in the Supporting Information). The relative stability of the 1,4-boat (**4d**) conformer is due to stabilizing transannular interaction between the sulfanyl oxygen and silicon that leads to a pentacoordinate trigonal bipyramidal silicon. The distance from the silicon atom to the equatorial plane formed by C3, (Si)H, and C5 is 0.241 Å. The angle between the plane of the four carbons and the C–S–C plane in (**4d**) is 72.6° whereas the angle between this plane and the C–Si–C plane is 33.6°. The O–Si–H ψ_{ax} , O–Si–Cl ψ_{eq} , O–Si–C3, and O–Si–C5 bond angles in the 1,4-twist conformer (**4d**) are 81.3°, 177.0°, 82.3°, and 82.3°, respectively. Another indication of the intramolecular sulfanyl oxygen–silicon coordination in **4d** is its relatively large dipole moment ($\mu = 6.50 \text{ D}$).

The S=O–Si bond length in **4d** (2.138 Å) is shorter than the sum of the van der Waals radii (3.62 Å) for the oxygen and silicon atoms (Tables 2c, 2d, and 2e in the Supporting Information) [1j,2b]. The respective Si–Cl bonds in **4c** and **4d** are significantly longer than those in the chair (**3a**, **4a**) and 1,4-twist (**3b**, **4b**) conformers. The S–O bonds in **4c** and **4d** (1.555 Å) are longer than those in the chair (**4a**) and 1,4-twist (**4b**) conformers. The S–C bonds in **3a**, **4a**, **4c**, and **4d** are equal and the

S–C2 bonds in **3b** and **4b** are longer than the respective S–C6 bonds. The Si–C bonds in **3a**, **4a**, **4c**, and **4d** are equal and the Si–C3 bonds are longer than the respective Si–C5 bonds in the 1,4-twist conformers **3b** and **4b**.

In the chair (**3a** and **4a**) and 1,4-twist (**3b** and **4b**) conformers the respective C–H ax bonds are longer than or equal to the corresponding C–H eq bonds ($\sigma_{\text{C-Hax}} \rightarrow \sigma_{\text{C-Hax}}^*$, $\sigma_{\text{Si-Hax}} \rightarrow \sigma_{\text{C-Hax}}^*$, $\sigma_{\text{Si-Clax}} \rightarrow \sigma_{\text{C-Hax}}^*$) which is consistent with hyperconjugative interactions [3,12–18]. In the chair conformers **3a** and **4a**, the Si–H ax and Si–Cl ax bonds are longer than the corresponding Si–H eq and Si–Cl eq bonds ($\sigma_{\text{C-Hax}} \rightarrow \sigma_{\text{Si-Hax}}^*$, $\sigma_{\text{Si-Hax}} \rightarrow \sigma_{\text{C-Hax}}^*$, $\sigma_{\text{C-Hax}} \rightarrow \sigma_{\text{Si-Clax}}^*$, $\sigma_{\text{Si-Clax}} \rightarrow \sigma_{\text{C-Hax}}^*$). The C–H bonds are equal in the 2,5-twist (**4c**) and 1,4-boat (**4d**) conformers which is consistent with geometry playing a role in hyperconjugative interactions.

The vibrational frequency calculations on 4-chloro-4-silathiacyclohexane 1-oxide (Figs. 5 and 6) verified that the chair (**5a**, C_s; **6a**, C_s), 1,4-twist (**3b**, **4b**) and 2,5-twist (**5c**, **6c**) structures are minima and that the 2,5-boat structures are transition states ([**5e**][‡] and [**6e**][‡]) [19–22]. The energy difference (E_{rel}) between the chair (**5a**) and the 1,4-twist (**3b**) and 2,5-twist (**5c**) conformers and the 2,5-boat transition state ([**5e**][‡]) are 3.42, 5.22, and 5.98 kcal/mol, respectively (Table 3). The energy difference (E_{rel}) between the chair (**6a**) and the 1,4-twist

Table 3

Relative thermodynamic parameters for conformers and transition states of equatorial *cis*- and *trans*-4-chloro-4-silathiacyclohexane 1-oxide (**5** and **6**)^a

Conformer or transition state	Total energy	E_{rel}	$H(298)_{\text{rel}}$	$G(298)_{\text{rel}}$
Equatorial <i>cis</i> -4-chloro-4-silathiacyclohexane 1-oxide				
5a	-1378.798208			
3b, 5b	-1378.792755	3.42	3.34	2.83
5c	-1378.789891	5.22	5.17	4.39
[5e] [‡]	-1378.788684	5.98	5.17	5.89
Equatorial <i>trans</i> -4-chloro-4-silathiacyclohexane 1-oxide				
6a	-1378.796840			
4b, 6b	-1378.793283	2.23	2.29	2.11
6c	-1378.790250	4.14	4.16	3.76
[6e] [‡]	-1378.789603	4.54	3.77	4.68

^a MP2/6-311+G(d,p).

(**4b**), 2,5-twist (**6c**) conformers and 2,5-boat transition state ([**6e**][‡]) are 2.23, 4.14, and 4.54 kcal/mol, respectively (Table 3).

The S–C bonds in the chair conformer **5a** are equal and the S–C2 bonds in the 1,4-twist (**5b**, **6b**) and 2,5-twist (**5c**, **6c**) conformers are longer than the respective S–C6 bonds (Tables 3c, 3d, and 3e in the Supporting Information). The Si–C bonds in **5a** are equal, the C3–Si bonds in **3b** and **4b** are longer than the Si–C5 bonds, and the C3–Si bonds in **5c** are shorter than the Si–C5 bonds. In the chair (**5a**) and 1,4-twist (**3b**) conformers the respective C–H_{ax} bonds are longer than or equal to the corresponding C–H_{eq} bonds ($\sigma_{\text{C-H}_{\text{ax}}} \rightarrow \sigma_{\text{C-H}_{\text{ax}}}^*$, $\sigma_{\text{C-Cl}_{\text{ax}}} \rightarrow \sigma_{\text{C-H}_{\text{ax}}}$) which suggest the presence of hyperconjugative interactions. In the chair conformers **5a** and **6a**, the Si–H_{ax} and Si–Cl_{ax} bonds are longer than the corresponding Si–H_{eq} and Si–Cl_{eq} bonds ($\sigma_{\text{C-H}_{\text{ax}}} \rightarrow \sigma_{\text{Si-H}_{\text{ax}}}^*$, $\sigma_{\text{Si-H}_{\text{ax}}} \rightarrow \sigma_{\text{C-H}_{\text{ax}}}^*$, $\sigma_{\text{C-H}_{\text{ax}}} \rightarrow \sigma_{\text{Si-Cl}_{\text{ax}}}^*$, $\sigma_{\text{Si-Cl}_{\text{ax}}} \rightarrow \sigma_{\text{C-H}_{\text{ax}}}$).

Vibrational frequency calculations verified that the chair (**7a**, C_s; **8a**, C_s), 1,4-twist (**7b**), 2,5-twist (**8c**), and 1,4-boat (**7d**, C_s) structures are minima and that the 2,5-boat structures are transition states ([**7e**][‡] and [**8e**][‡]) (Figs. 7 and 8). The atomic charges for **7a**, **7d**, and **8a** are given in Fig. 12. The calculated relative free energy

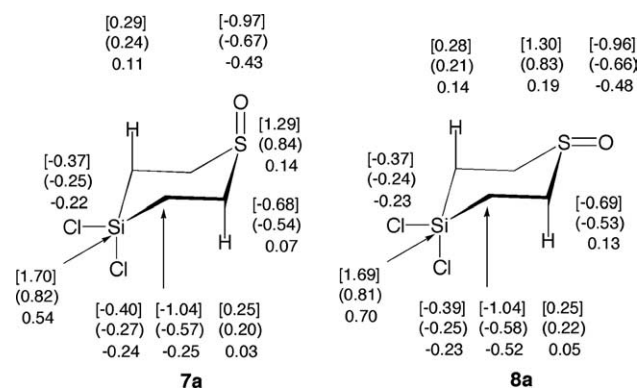


Fig. 12. Selected atomic charges for the chair conformers of 4,4-dichloro-4-silathiacyclohexane 1-oxide: electrostatic, Mulliken (), and Natural [].

($G(298)_{\text{rel}}$) for **7a** and **8a** is 2.71 kcal/mol ($E_{\text{rel}} = 3.15$ kcal/mol; Eq. (1), Table 1) which is smaller than that between **4a** and **6a** but larger than those for the **1a** to **1b**, **1c** to **1d**, and **3a** to **5a** equilibria. The energy differences (E_{rel}) between the chair (**7a**) and the 1,4-twist (**7b**) and 1,4-boat (**7d**) conformers and 2,5-boat transition state ([**7e**][‡]) are 6.14, 4.23, and 6.90 kcal/mol, respectively (Table 4). The energy differences (E_{rel}) between the chair

Table 4

Relative thermodynamic parameters for conformers and transition states of axial and equatorial 4,4-dichloro-4-silathiacyclohexane 1-oxide (**7** and **8**)^a

Conformer or transition state	Total energy	E_{rel}	$H(298)_{\text{rel}}$	$G(298)_{\text{rel}}$
Axial 4,4-dichloro-4-silathiacyclohexane 1-oxide				
7a	-1837.917846			
7b, 8b	-1837.908067	6.14	6.00	5.51
7d	-1837.911098	4.23	4.35	3.83
[7e] [‡]	-1837.906855	6.90	6.10	6.94
Equatorial 4,4-dichloro-4-silathiacyclohexane 1-oxide				
8a	-1837.912821			
7b, 8b	-1837.908067	2.98	3.00	2.81
8c	-1837.904281	5.36	5.31	4.37
[8e] [‡]	-1837.904070	5.49	4.79	5.63

^a MP2/6-311+G(d,p).

(**8a**) and the 1,4-twist (**7b**) and 2,5-twist (**8c**) conformers and the 2,5-boat transition state ($[\mathbf{8e}]^\ddagger$) are 2.98, 5.36, and 5.49 kcal/mol, respectively (Table 4).

As with the 1,4-boat conformer (**4d**), the relative stability of the 1,4-boat conformer (**7d**) is due to stabilizing transannular interaction between the sulfinyl oxygen and silicon that leads to a pentacoordinate silicon. The silicon atom adopts a trigonal bipyramidal structure with the sulfinyl oxygen and chlorine substituents axial. The distance from silicon to the equatorial plane formed by the C3, (Si)Cl ψ_{ax} , and C5 atoms is 0.281 Å. The plane of the four carbons in **7d** forms the angle of 71.1° with the C–S–C plane and of 29.9° with the C–Si–C plane. The O–Si–Cl ψ_{ax} , O–Si–Cl ψ_{eq} , O–Si–C3, and O–Si–C5 bond angles in **7d** are 83.5°, 179.4°, 80.9°, and 80.9°, respectively. As expected for trigonal bipyramid geometry, the O–Si–Cl ψ_{eq} angle in **7d** is almost linear (179.4°). Another indication of the intramolecular sulfinyl oxygen–silicon coordination in **7d** is the relatively large dipole moment ($\mu = 7.59$ D).

The Si–Cl ψ_{ax} bond in **7d** is 0.099 and 0.109 Å, respectively, longer than the Si–Cl ψ_{ax} and Si–Cl ψ_{eq} bonds in the chair conformer **7a** (Tables 4c, 4d, and 4e in the Supporting Information). The S=O... (Si)Cl ψ_{eq} non-bonded distances (2.882 Å) in **7d** are less than the sum of the van der Waals radii for oxygen and chlorine. The S=O–Si bond in **7d** (2.149 Å) is longer than that in **4d** (2.138 Å) owing in part to the repulsive S=O... (Si)Cl ψ_{ax} interaction. This effect probably outweighs the influence of the increased positive charge on silicon atom induced by the two chlorines (Fig. 12). Thus, since silanes undergoing oxygen-induced pentacoordination have O–Si lengths that range from 1.75 to 2.40 Å [1] S=O–Si bonding is operative in **7d**.

The S–O bond in **7d** (1.554 Å) is longer than those in the chair (**6a**, **8a**), 1,4-twist (**7b**), and 2,5-twist (**8c**) conformers. The respective S–C bonds in **7a** and **7d** are equal, but not in the twist conformers (**7b**, **8c**) where the S–C2 bond is longer than the S–C6 bond. The C–H ψ_{ax} and Si–Cl ψ_{ax} bonds in **7a** and **8a** are longer than the corresponding C–H ψ_{eq} and Si–Cl ψ_{eq} bonds ($\sigma_{C-H_{ax}} \rightarrow \sigma_{Si-H_{ax}}^*$, $\sigma_{Si-H_{ax}} \rightarrow \sigma_{C-H_{ax}}^*$, $\sigma_{C-H_{ax}} \rightarrow \sigma_{Si-Cl_{ax}}^*$, $\sigma_{Si-Cl_{ax}} \rightarrow \sigma_{C-H_{ax}}^*$). In the twist conformer (**7b**) the C–H ψ_{ax} bonds are longer than the C–H ψ_{eq} bonds and the Si–Cl ψ_{iso} bond is shorter than the Si–Cl ψ_{iso} bond, and in the 2,5-twist conformer (**8c**) the C–H ψ_{ax} bonds are longer than the corresponding C–H ψ_{eq} bonds. Also in **8c**, the Si–Cl ψ_{ax} bond is longer than the Si–Cl ψ_{eq} bond. Thus, hyperconjugative interactions are predicted for conformers of the 4,4-dichloro-4-silathiacyclohexane 1-oxides (**7**, **8**).

Analysis of atomic charges in Figs. 9–12 allows one to draw the following conclusions. First, the negative charge on the axial halogen atoms is higher than on equatorial (cf. **3a** versus **4a**, **5a** versus **6a**, and **7a** versus **8a**). This is a manifestation of hyperconjugative interactions ($\sigma_{C-H_{ax}} \rightarrow \sigma_{C-Cl_{ax}}^*$). Second, hydrogen atoms in the

3,5-positions, when involved in 1,3-diaxial interactions, become more positive (**3a** versus **6a**, **4a** versus **5a**, **7a** versus **8a**). Third, pentacoordination results in an increase of the negative charge on the equatorial halogen atom (Cl ψ_{eq}) and of the positive charge on silicon, that is, in polarization of the Si–Cl ψ_{eq} (**4d** versus **3a**, **7d** versus **7a**). Interestingly, the electrostatic and natural charges on the sulfinyl oxygen decrease upon pentacoordination, whereas the Mulliken charges increase [7b,23]. As was discussed recently, the best agreement with chemical reasoning for nonclassical partial bonding formed by silicon is obtained with electrostatic atomic charges [24].

4. Conclusions

The theoretical calculations successfully characterize the intramolecular coordination of the sulfinyl oxygen with silicon that results in trigonal bipyramidal geometry at silicon. The chair conformers of the axial sulfoxides are lower in energy than the corresponding equatorial sulfoxides. The chair conformer (**4a**) of axial *trans*-4-chloro-4-silathiacyclohexane 1-oxide is 6.12, 0.45, 0.44, and 6.93 kcal/mol more stable than the 1,4-twist, 2,5-twist, and 1,4-boat conformers and the 2,5-boat transition state. The 2,5-twist and 1,4-boat conformers are stabilized by intramolecular coordination of the sulfinyl oxygen with silicon. The chair conformer **7a** of axial 4,4-dichloro-4-silathiacyclohexane 1-oxide is 6.14, 4.23, and 6.90 kcal/mol more stable than its 1,4-twist and 1,4-boat (**7d**) conformers and 2,5-boat transition state. The 1,4-boat conformer **7d** is also stabilized by transannular coordination of the sulfinyl oxygen with silicon.

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Appendix A. Supplementary data

Tables of relative energies, geometries, relative thermodynamic parameters, and thermochemical data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.06.013.

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