ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 7, pp. 1325–1329. © Pleiades Publishing, Ltd., 2014.
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# Conformational Flexibility of 4,4-Dimethyl-3,4-dihydro-2*H*-1,4-thiasiline and Its Monoheterocyclic Analogs

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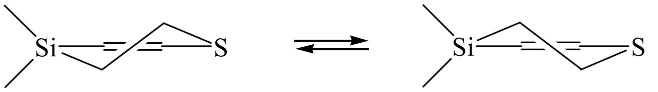
Received April 10, 2014

**Abstract**—Conformational behavior of the first cyclic organosilicon vinylsulfide, 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline as well as its monoheterocyclic analogs, 3,4-dihydro-2*H*-pyran, 3,4-dihydro-2*H*-thiopyran, and 1,1-dimethyl-1,2,3,4-tetrahydrosiline is studied in comparison with the carbocyclic analog, cyclohexene, using the methods of low-temperature NMR spectroscopy and theoretical calculations at the DFT and MP2 levels of theory. The barrier to the ring inversion with respect to that in cycloxene is increased in 3,4-dihydro-2*H*-pyran and 1,1-dimethyl-1,2,3,4-tetrahydrosiline, but, in contrast to the suggestions made in the literature, is decreased in 3,4-dihydro-2*H*-thiopyran. In 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline the barrier is intermediate between those in the corresponding monoheterocycles, 1,1-dimethyl-1,2,3,4-tetrahydrosiline and 3,4-dihydro-2*H*-thiopyran. The observed variations are rationalized from the viewpoint of the interaction of the π-electrons of the C=C double bond with the orbitals of heteroatoms in the ring. The structure of the transition state for the ring inversion is discussed.

**Keywords:** 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline, 1,1-dimethyl-1,2,3,4-tetrahydrosiline, 3,4-dihydro-2*H*-thiopyran, 3,4-dihydro-2*H*-pyran, onformational analysis

**DOI:** 10.1134/S1070363214070135

Recently we synthesized the first cyclic organosilicon vinylsulfide, 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline (**I**) by the Pummerer rearrangement of 4,4-dimethyl-1,4-thiasiline 1-oxide [1]. Molecule **I** is a heteroanalog of cyclohexene and also has a *semi-chair* conformation. The axial and equatorial protons $SCH_2$ and $SiCH_2$ are equivalent under the conditions of fast conformational equilibrium, but their signals may decoalesce if the exchange is slow in the NMR timescale.


(1)

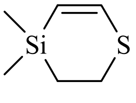
Using the same approach as we used for the earlier studied by us silaheterocyclohexanes [2–5] we tried to examine the conformational behavior of compound **I** by $^1$H NMR, but even at the lowest accessible temperature of 103 K we observed only broadening of the signals but not their decoalescence. This is indicative of a very low barrier to the ring inversion $\Delta G^{\neq}$ in molecule **I** (4–5 kcal/mol depending on the difference of the chemical shifts of the decoalescing signals $\Delta\nu$) which is in compliance with a higher flexibility of the cyclohexene ring ($\Delta G^{\neq}$ = 5.37 kcal/mol, [6]) as compared to the cyclohexane ring ($\Delta G^{\neq}$ = 10.3 kcal/mol, [7]).

Because of non-planar structure of the Si–$CH_2$–$CH_2$–S motif, molecule **I** has the axis of chirality, but whether the conformers in equilibrium (1) will be enantiomers depends on the mutual orientation of the

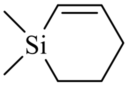
Me–Si–Me and Si–CH=CH–S planes. However, the analysis of the geometry of the two conformers optimized by MP2/6-311G(d,p) showed that the most planar in heterocycle **I** is the $CH_2$–Si–C=C fragment having the dihedral angle of less than 0.1° rather than the Si–CH=CH–S fragment where the Si–C–C–S dihedral angle is 8.4°. Structurally the two conformers are mirror images of each other (enantiomers), and their calculated total energies coincide. Hence, equilibrium (1) is degenerate.

The experimentally measured barrier to the ring inversion in cyclohexene is equal 5.37 kcal/mol and is increased to 6.6 and 7.32 kcal/mol upon introduction of one or two oxygen atoms in the α-position to the double bond [8, 9]. No experimental data are available for 3,4-dihydro-2*H*-thiopyran, but the effect of the sulfur atom was estimated at 3.4 kcal/mol, so that the barrier to the ring inversion in 3,4-dihydro-2*H*-thiopyran must be ~8.8 kcal/mol [10]. This estimation seems to be erroneous. First, it was made based on the results obtained for the intricately substituted 3,4-dihydro-2*H*-thiopyran containing two aryl and two cyano substituents, one amino group and one thioamide group, which obviously may distort the effect of the sulfur atom proper. Secondly, this estimation was made based on the fact that in the cyclohexane series the effect of the sulfur atom is thrice as that of the oxygen atom, so, in the studied compound the effect of the sulfur atom "purified" from the effects of other substituents, must also be three times stronger than that of the oxygen atom and, since introduction of oxygen into the cyclohexene ring increases the barrier from 5.37 to 6.6 kcal/mol, Brunskill et al. claimed that "sulfur atom in unsaturated ring sharply increases the barrier to inversion, apparently, due to conjugation of the π-orbital of the double bond and the lone electron pair of the sulfur atom" [10].

It must be noted that for the saturated compounds the trend is the opposite: the experimentally measured barrier to ring inversion in tetrahydro-2*H*-pyran and tetrahydro-2*H*-thiopyran is decreased relative to that in cyclohexane by 0.3 and 1.2 kcal/mol, respectively [10]. Even stronger is the decrease in the inversion barrier upon introduction of the silicon atom in the saturated ring. The lowering of the barrier in silacyclohexanes to 5–6 kcal/mol as compared to 10–11 kcal/mol in the cyclohexane derivatives was attributed to a longer Si–C bond (1.904 Å) in comparison with the C–C bond (1.534 Å) [11, 12], although stereoelectronic effects were also allowed to play an important role [13–16]. There are no data in the literature on the conformational properties of silacyclohexenes, to say nothing of thiasilacyclohexenes. Therefore, to evaluate the effect of the nature of the heteroatom on the value of the inversion barrier and the structure of stable conformers and transition states connecting them we performed theoretical analysis of equilibrium (1) for 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline (**I**) as well as for its monoheterocyclic analogs, 1,1-dimethyl-1,2,3,4-tetrahydrosiline (**II**), 3,4-dihydro-2*H*-thiopyran (**III**), and 3,4-dihydro-2*H*-pyran (**IV**), and their carbocyclic predecessor, cyclohexene (**V**).



**I**



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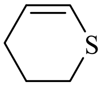

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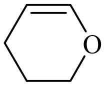
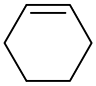


**IV**



**V**

All calculations were performed by the DFT method at the B3LYP level of theory and by the MP2 method using 6-311G(d,p), 6-311++G(d,p), cc-pVTZ basis sets with full geometry optimization including vibrational calculations by the use of Gaussian09 program package [17].

**Barriers to ring inversion.** The values of the barriers to the ring inversion in molecules **I–V** calculated by the aforementioned methods as differences between the total ($\Delta E^{\neq}$) or free energies ($\Delta G^{\neq}$) of the ground and transition states are presented in Table 1. The results of calculations are indicative of differently directed effect of heteroatom on the ease of the ring inversion. The introduction of the sulfur atom in the ring (compound **III**) decreases the inversion barrier by ~1 kcal/mol with respect to cyclohexene, whereas the oxygen atom (compound **IV**) increases it to nearly the same extent. This confirms the above assumption that the conclusion of Brunskill et al. [10] that in both cases the barrier is increased is wrong. Note, that the calculated barriers to ring inversion in compounds **IV** and **V** (Table 1) nicely coincide with the experimental values equal to 6.6±0.3 [8] and 5.37 kcal/mol [6].

Unexpectedly, the introduction of the silicon atom into the cyclohexene ring (compound **II**), in contrast to expectations based on a high conformational flexibility of silacyclohexanes [11–16], increases the barrier to inversion by 1–1.5 kcal/mol with respect to cyclohexene. The presence of two heteroatoms in the molecule (compound **I**) results in the values of the barrier to inversion intermediate between those of compounds **II** and **III**.

In the case of 3,4-dihydro-2*H*-pyran (**IV**) the reason for the increase in the barrier to ring inversion is quite evident: it is the conjugation effect of the lone electron pair of the oxygen atom with the double bond. This effect is stronger in the ground state than in the transition state as follows from different degree of polarization of the double bond calculated as the difference of the charges on the olefin carbon atoms and equal to 0.485*e* in molecule **IV** and 0.446*e* in TS-**IV** (hereinafter the charges given are calculated by the MP2/6-311G** method). For 3,4-dihydro-2*H*-thiopyran (**III**) the situation is inverted: the similarly calculated charge difference is 0.091*e* in molecule **III** and 0.162*e* in TS-**III**, that is, the effect of conjugation is stronger in the transition state. Moreover, in contrast to molecule **IV**, the double bond is polarized in the opposite direction, to the sulfur atom. This allows rationalizing the differently directed variation of the barrier to inversion upon introduction of oxygen or sulfur atom into the ring. Less evident is the case of 1,1-dimethyl-1,2,3,4-tetrahydrosiline (**II**). In this case, the double bond, as in molecule **III**, is polarized towards the heteroatom, the degree of polarization is 0.430*e*, which is close to that in molecule **IV** but in the opposite direction. The total charge on the C=C bond in molecule **II** is –0.604*e*, while in the sulfur-containing heterocycle **III** it is equal –0.391*e*, and in the oxygen analog **IV** it is as low as –0.097*e*. A high electron density on the double bond in molecule **II** is caused by the strong electron-releasing effect of the dimethylsilyl group, while its polarization towards the silicon atom is due to the conjugation of the π-electrons of the C=C bond with vacant orbitals of the two Si–Me bonds, $\pi_{C=C}\rightarrow\sigma^*_{Si-Me}$. This conjugation is notably higher in the ground state of molecule **II** than in transition state TS-**II** as follows from different angles between the plane of the π-bond and the plane of the Me–Si–Me bonds. In the ground state, these planes are almost parallel providing maximum conjugation of the $\pi_{C=C}$ and $\sigma^*_{Si-Me}$ orbitals, whereas in the transition state the angle is equal to ~30° and the effectiveness of conjugation is substantially lower. This explains the increase of the barrier to ring inversion in molecule **II** relative to cyclohexene. Finally, in 4,4-dimethyl-3,4-dihydro-2*H*-1,4-thiasiline (**I**) the barrier to inversion is averaged between the values for 1,1-dimethyl-1,2,3,4-tetrahydrosiline and 3,4-dihydro-2*H*-thiopyran, as a result of a compromise between the conjugation of the π-electrons of the C=C bond with two $\sigma^*_{Si-Me}$ orbitals and the lone electron pair of the sulfur atom. The electron density on the double bond in molecule **I** is maximum in the investigated series and equals to –0.624*e*, and the degree of polarization of the double bond decreases relative to that in molecule **II** and becomes equal to 0.324*e* towards the silicon atom.

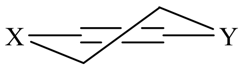
**Table 1.** Calculated barriers to ring inversion (kcal/mol) in cyclohexene and its heteroanalogs

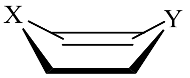
| Comp. no. | Method[a] | $\Delta E^{\neq}$ | $\Delta G^{\neq}$ (103 K) |
|---|---|---|---|
| **I** | B3LYP/6-311G** | 5.9 | 5.5 |
| | B3LYP/6-311++G** | 5.9 | 5.5 |
| | MP2/6-311G** | 6.3 | 6.0 |
| | MP2/cc-pVTZ | 6.1 | 5.7 |
| **II** | B3LYP/6-311G** | 6.4 | 6.1 |
| | B3LYP/6-311++G** | 6.4 | 6.1 |
| | MP2/6-311G** | 6.9 | 6.6 |
| | MP2/cc-pVTZ | 6.6 | 6.3 |
| **III** | B3LYP/6-311G** | 4.6 | 4.2 |
| | B3LYP/6-311++G** | 4.7 | 4.4 |
| | MP2/6-311G** | 3.9 | 3.6 |
| | MP2/cc-pVTZ | 4.4 | 4.1 |
| **IV**[b] | B3LYP/6-311G** | 6.9 | 6.4 |
| | B3LYP/6-311++G** | 6.8 | 6.3 |
| | MP2/6-311G** | 7.5 | 6.9 |
| | MP2/cc-pVTZ | 7.5 | 6.9 |
| **V**[c] | B3LYP/6-311G** | 5.5 | 5.5 |
| | B3LYP/6-311++G** | 5.4 | 5.0 |
| | MP2/6-311G** | 5.5 | 5.0 |
| | MP2/cc-pVTZ | 5.5 | 5.0 |

[a] At the MP2/cc-pVTZ level of theory, $\Delta G^{\neq}$ values for compounds **I–IV** were calculated using MP2/6-311G** thermodynamic parameters. [b] Experimental value is 6.6 kcal/mol [8]. [c] $\Delta E^{\neq}$(ZPE) values calculated by different methods vary from 5.33 to 6.28 kcal/mol [18]. Experimental value is 5.37 kcal/mol [6]

*Structure of the ground and transition states*. The degenerate inversion of the cyclohexene ring in molecule **V** occurs through the transition state which is non-planar, that is, not averaged between the two

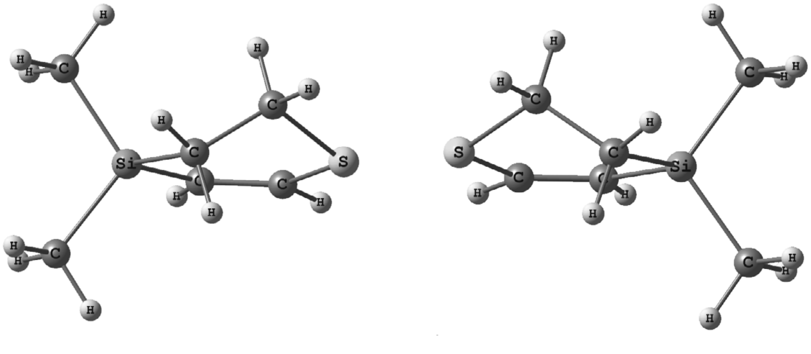
**Table 2.** Selected structural characteristics of the calculated molecules and transition states and imaginary frequencies in the latter





| Method | X | Y | Angles in molecules | | | Angles in transition states | | | ν, cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | XC=CY | CXC=C | C=CYC | XC=CY | X–CH$_2$–CH$_2$ | CH$_2$–CH$_2$–Y | |
| B3LYP/6-311G** | Si | S | 6.3 | 3.0 | 14.5 | 1.8 | 117.0 | 119.8 | 127*i* |
| | Si | C | 3.2 | 4.0 | 20.5 | 7.9 | 114.4 | 118.2 | 126*i* |
| | S | C | 2.4 | 9.6 | 15.8 | 1.7 | 115.7 | 114.5 | 83*i* |
| | O | C | 3.6 | 12.2 | 13.1 | 3.4 | 115.5 | 113.3 | 139*i* |
| | C | C | 1.7 | 13.8 | 13.8 | 2.1 | 113.9 | 113.5 | 35*i* |
| B3LYP/6-311++G** | Si | S | 6.4 | 3.2 | 14.2 | 1.6 | 117.0 | 120.0 | 128*i* |
| | Si | C | 3.2 | 4.0 | 20.6 | 7.9 | 114.3 | 118.2 | 126*i* |
| | S | C | 2.5 | 9.2 | 16.2 | 2.1 | 115.7 | 114.6 | 80*i* |
| | O | C | 3.5 | 12.2 | 13.2 | 3.2 | 115.5 | 113.4 | 140*i* |
| | C | C | 1.6 | 13.8 | 13.8 | 2.3 | 114.0 | 113.5 | 34*i* |
| MP2/6-311G** | Si | S | 8.4 | 0.1 | 16.4 | 3.5 | 115.6 | 118.9 | 111*i* |
| | Si | C | 3.7 | 4.2 | 21.2 | 11.0 | 112.0 | 117.2 | 136*i* |
| | S | C | 3.3 | 11.1 | 14.8 | 1.5 | 115.6 | 113.1 | 93*i* |
| | O | C | 4.5 | 13.6 | 12.4 | 4.0 | 114.3 | 111.2 | 96*i* |
| | C | C | 2.0 | 14.4 | 14.4 | 7.7 | 113.4 | 111.7 | 43*i* |
| MP2/cc-pVTZ | Si | S | 8.4 | 2.2 | 14.3 | 2.4 | 115.3 | 119.1 | |
| | Si | C | 4.2 | 4.9 | 19.9 | 10.7 | 111.7 | 117.5 | |
| | S | C | 3.5 | 9.8 | 15.6 | 0.3 | 115.4 | 113.2 | |
| | O | C | 4.6 | 12.8 | 12.7 | 3.3 | 114.6 | 111.8 | |
| | C | C | 2.4 | 14.1 | 14.1 | 8.5 | 113.9 | 111.8 | |

forms, but rather has, according to the literature, the *boat* conformation and $C_s$ symmetry [18]. Calculations of the transition states using the methods presented in Table 1 confirm the *boat* conformation for compounds **I–IV** with heteroatoms in the flagpole position. In Table 2, structural parameters calculated by different methods for the ground and transition states are presented, which characterize the deviation of the X–C=C–Y fragment in the ground state from planarity and the distortion of the *boat* conformation in the



Enantiomers of compound **I**.

transition state due to the deviation of the "bottom" of the *boat* from planarity (dihedral angle CCCC).

The analysis of the obtained results shows a slight dependence of the structure on the method of calculation (DFT or MP2) and the lack of dependence on the basis set used. The deviation of the X–C=C–Y fragment in the ground state from planarity is negligible for cyclohexene (~2°), somewhat larger for its monoheteroatomic derivatives **II–IV**, S < Si < O (2.4°–4.5°), and is maximal for compound **I** (6.3°–8.4°). An interesting structural feature of the silicon-containing heterocycles **I** and **II** is the conformation close to *sofa*, that is, with almost planar C–Si–C=C–Y fragment and the $YCH_2$ group substantially deviating from this plane (see figure and angles CXC=C and C=CYC in Table 2). Molecules **III–V** possess the *semi-chair* conformation.

For transition states the distortion of the ideal *boat* conformation (deviation of the CCCC angle from zero) in the DFT method in both bases is negligible for TS-**I**, TS-**III**, TS-**V** (1.6°–2.3°), slightly larger for TS-**IV** (~3.3°), and is quite notable for TS-**II** (7.9°). In MP2 method, it is also negligible for TS-**III** (0.3°–1.5°), slightly larger for TS-**I** and TS-**IV** (2.6°–3.5° and 3.7°–4.0°), unexpectedly large for TS-**V** (7.7°–8.5°), and is maximal for TS-**II** (10.7°–11.0°). In transition states TS-**III** and TS-**IV** the degree of the ring folding at the heteroatom (angle between the C*X*C plane and the averaged plane of the bottom of the *boat*) it smaller than that at the carbon atom. In transition state TS-**I** the degree of the ring folding at silicon is larger than at sulfur. In case of TS-**II** such estimation would be incorrect because of large distortion of the *boat* conformation.

All calculated transition states are characterized by only one imaginary frequency (Table 2). For the studied structures, both DFT and MP2 calculations give minimal values of this frequency for cyclohexene, intermediate values for 3,4-dihydro-2*H*-thiopyran (**III**), and maximal values for 3,4-dihydro-2*H*-pyran (**IV**) (in DFT methods) or 1,1-dimethyl-1,2,3,4-tetrahydrosiline (**II**) (in MP2 method).

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