

Structural Investigations of Substituted Silacyclopropylidenoids through Computational Techniques

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Abstract

The “*ab initio*” (MP2) level of theory using 6-311+G(d,p) basis set has been carried out to explore the isomeric structures, energies, and properties of substituted (-H, -CH₃, -SiH₃, -OH) LiBr-silacyclopropylidenoids. The resulting isomeric structures of LiBr-silacyclopropylidenes reveal three stationary structures: silylenoidal (**S**), inverted (**I**), and tetrahedral (**T**). The theoretical calculations indicate that all substituted LiBr-silacyclopropylidenoids have silylenoidal (**S**), inverted (**I**), and tetrahedral (**T**) forms except -OH substituted silylenoid. Interestingly we have obtained no tetrahedral structure as a minimum for the -OH substituted structure. The silylenoidal forms energetically more stable than the inverted (**I**) and tetrahedral (**T**) forms, whereas stability of the tetrahedral (**T**) forms for the title structures lower than the inverted (**I**) and silylenoidal (**S**) forms.

Keywords: *ab initio*, silacyclopropylidenoids

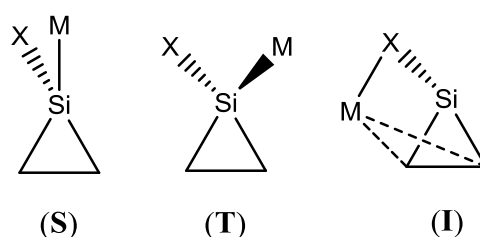
Introduction

Silylenoids, R₂SiMX (X=halogen, M=alkali metal), are important intermediates in silicon hybrid and organosilicon chemistry [1, 2]. As a kind of very reactive species, the preparation of silylenoids is very difficult. In recent decades, the synthesis and chemistry of silylenoids have attracted attention from the viewpoints of both fundamental and applied chemistry. Clark et al. [3] have carried out the first theoretical study on the simplest silylenoid H₂SiLiF, and then many silylenoids such as H₂SiMX (M = Li, Na, K; X = F, Cl, Br), R₂SiLiF

(R = CH₃, CH₂CH₃), and C₂H₄SiMX (where M=Li or Na and X= F, Cl, Br) [4-14] have been systematically investigated.

The silacyclopropylidenoid, the silicon analogue of cyclopropylidenoid, is a compound in which an electropositive metal (M) and a leaving group (X, usually halogen) are bound to the same silicon atom. Contrast to extensive experimental and computational studies on cyclopropylidenoids [15-17], only a few scientific work on silacyclopropylidenoids has been reported so far.

More recently, we have carried out a series of *ab initio* calculations on the isomeric structures, energies, and the properties of silacyclopropylidenoids, C₂H₄SiMX (where M=Li or Na and X= F, Cl, Br). The theoretical results reveal that three stationary structures for each of C₂H₄SiMXs, silacyclopropylidenoid (**S**), tetrahedral (**T**), and inverted (**I**), were located on the potential energy surfaces (PES) at the MP2/6-31+G(d,p) and MP2/aug-cc-pVTZ levels of theory (Scheme 1). Computed energy differences between them range from 0.70 to 8.70 kcal/mol at the MP2/6-31+G(d,p) level [14].



Scheme 1. The silacyclopropylidenoid (**S**), tetrahedral (**T**), and inverted (**I**) forms of C₂H₄SiMX (where M=Li or Na and X= F, Cl, Br) complexes.

In the present paper, we wish to provide the first computational study of the geometries, electronic structures, and the stabilities of substituted silacyclopropylidenoids (Figure 1, X=- H, -CH₃, -SiH₃, and -OH). The overall stabilities of silacyclopropylidenoid isomers are also compared and the main factors contributing to the stability of the isomers are simply discussed.

Computational Methods

Optimized geometries and energies for the stationary points were obtained using density functional theory at the MP2/6-311+G(d, p) level [19]. The corresponding harmonic vibrational frequency calculations were carried out in order to verify whether the stationary

points are local minima (no imaginary frequencies) or saddle points (one imaginary frequency) with help of Gaussian03 package program [20]. The computed structures were visualized by using the GaussView3.0 program [21].

Results and Discussion

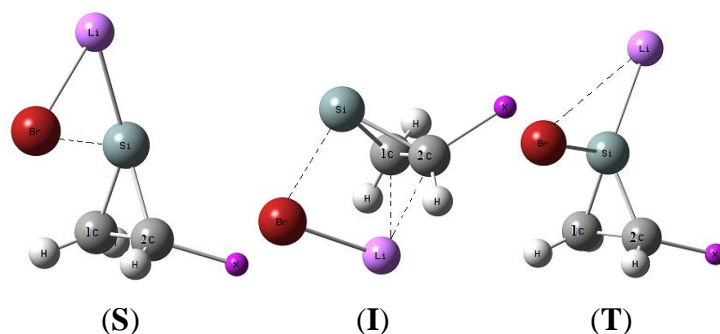


Figure 1. The general representation of silylenoidal (**S**), inverted (**I**), and tetrahedral (**T**) form of the title structures (X= -H, CH₃, -SiH₃, -OH).

C₃H₄LiBr can be regarded as a carbenoid formed by free cyclopropylidene and LiBr moieties. In this study, we studied substituted (X= -H, CH₃, -SiH₃, -OH) silicon analogues of cyclopropylidenoids are shown in Figure 1. The structure of silacyclopropylidenoid (C₂SiH₄LiBr) has three equilibrium configurations [14], in which the **S** form is the lowest in energy. The theoretical calculations depict that “-H, CH₃, and -SiH₃” substituted silacyclopropylidenoids have three stationary structures: silylenoidal (**S**), inverted (**I**), and tetrahedral (**T**). However, the tetrahedral (**T**) geometry could not be optimized for “-OH” substituted structure. To indicate that no suitable geometry and energy results were obtained, dashes (–) were placed into Table 2. From calculated energies of the title structures, the **S** forms are more stable than the **I** and **T** forms at MP2/6-311+G(d,p) theory of levels.

It is emphasized from the NBO analysis that positively charged ion, Li⁺, attach the carbonic Si atom to give minimal structures (**S**, **I**, and **T**) which have low-energy. In the inverted (**I**) form, the Li atom is positioned between the C1 and C2 atoms and interacts mostly with the C atoms. There is a non-bonding interaction between Br and Si atoms in silacyclopropylidene unit (Figure 1). However, the Li and Br atoms interact with Si atom in the silylenoidal (**S**) and tetrahedral (**T**) forms as it is seen from Figure 1.

Characteristic bond lengths of these minima are listed in Tables 1-4. We could not find comparable experimental bond lengths in our calculated structures. Quantum chemical calculations shows that the shortest Lithium-Bromine bond is found to be in the **I** form rather than **S** or **T** forms in the range of 2.325-2.336 Å and the Li-Br bond length of **I** forms is slightly larger than **G** forms. The calculations also indicate that, in the tetrahedral forms, the Li-Br distances change greatly with regard to the reference bond lengths [18]. When the Li atom leaves from Br in the **T** form, the LiSiBr bond angles sharply elongates to 111.0°, 112.3°, and 121.0° in -H, -CH₃, and -SiH₃, respectively. The results also indicate that the Si-Li bond of the **S** form decreases slightly compared to H₃Si-Li (2.479 Å), whereas the most strongly elongated bond in the studied molecule (**S**) is Si-Br with a increasing value in the range from 0.303 Å to 0.318 Å

In addition, we investigated the LiBr salt effect on bond lengths and angles of the free silacyclopropylidene moiety of the three complexes as compared to the bond length of SiH₃-CH₃ at the MP2/6-311+G(d,p) level of theory. Hence, we determined that the most elongation of the Si-C2 bond occurs on the **I** form of -SiH₃ with 0.093 Å as compared to reference bond length of the SiH₃-CH₃ bond, 1.876 Å [18]. On the other hand, the lowest elongation of the same bond is again on the -SiH₃ substituted structure. Concerning the Si-C1 distances in the **S** form of -SiH₃, the elongations, as compared to the bond length of SiH₃-CH₃ (1.876 Å), is found to be 0.011 Å. Moreover, the calculated C1SiC2 bond angles of the **S** and **T** forms of C₂H₄SiLiBr are higher than that of free silacyclopropylidene, 46.5°, whereas **I** forms have lowest ones.

From the energy results given in Tables 1-4, the relative stability of the **S**, **T**, and **I** forms are clear at the MP2/6-311+G(d,p) level. The **S** forms are more stable than the **I** and **T** forms for all of them. We have also found that the **I** forms are energetically more stable than the **T** forms by 7.66 kcal/mol, 7.40 kcal/mol, and 6.49 kcal/mol for -H, -CH₃, and -SiH₃ including zero-point energy at the MP2/6-311+G(d,p) level of theory, respectively.

Table 1. Selected bond lengths (Å), bond angles (°), and ZPVE-corrected energies (E, a.u.) for the Silylenoidal (**S**) and Inverted (**I**) forms of the C₂H₃XSiLiBr (where X=-H) at the MP2/6-311+G(d,p) level

X=-H	S	I	T
Si-Li	2.446	3.021	2.437
Si-Br	2.547	2.569	2.316
Li-Br	2.337	2.327	3.918

Si-C1	1.892	1.946	1.893
Si-C2	1.892	1.947	1.893
C1-C2	1.529	1.539	1.531
C2-X	1.088	1.087	1.088
SiLiBr	64.2	55.6	33.5
C1SiC2	47.6	46.5	47.7
SiC2X	117.9	119.0	118.9
V	76.45	151.33	78.72
E _{rel}	-2947.333433	-2947.331979	-2947.319771

Table 2. Selected bond lengths (Å), bond angles (°), and ZPVE-corrected energies (E, a.u.) for the Silylenoidal (**S**) and Inverted (**I**) forms of the C₂H₃XSiLiBr (where X=-OH) at the MP2/6-311+G(d,p) level

X=-OH	S	I	T
Si-Li	2.452	3.072	-
Si-Br	2.532	2.534	-
Li-Br	2.343	2.336	-
Si-C1	1.904	1.949	-
Si-C2	1.896	1.961	-
C1-C2	1.521	1.519	-
C2-X	1.419	1.417	-
SiLiBr	63.7	54.0	-
C1SiC2	47.2	45.7	-
SiC2X	116.0	122.6	-
V	64.91	91.48	-
E _{rel}	-3022.400007	-3022.399002	-

Table 3. Selected bond lengths (Å), bond angles (°), and ZPVE-corrected energies (E, a.u.) for the Silylenoidal (**S**), Inverted (**I**), and Tetrahedral (**T**) forms of the C₂H₃XSiLiBr (where X=-CH₃) at the MP2/6-311+G(d,p) level

X=-CH ₃	S	I	T
Si-Li	2.447	3.022	2.438
Si-Br	2.541	2.561	2.315
Li-Br	2.340	2.326	3.950
Si-C1	1.898	1.958	1.901
Si-C2	1.899	1.947	1.898
C1-C2	1.525	1.534	1.526
C2-X	1.518	1.520	1.516
SiLiBr	64.0	55.4	32.8
C1SiC2	47.3	46.2	47.3

SiC2X	120.4	119.1	121.5
V	66.74	107.55	75.83
E _{rel}	-2986.502474	-2986.501245	-2986.489437

Table 4. Selected bond lengths (Å), bond angles (°), and ZPVE-corrected energies (E, a.u.) for the Silylenoidal (**S**), Inverted (**I**), and Tetrahedral (**T**) forms of the C₂H₃XSiLiBr (where X=-SiH₃) at the MP2/6-311+G(d,p) level

X=-SiH ₃	S	I	T
Si-Li	2.453	3.007	2.442
Si-Br	2.546	2.569	2.300
Li-Br	2.340	2.325	4.128
Si-C1	1.887	1.942	1.891
Si-C2	1.901	1.969	1.912
C1-C2	1.538	1.541	1.536
C2-X	1.853	1.859	1.844
SiLiBr	64.1	55.8	28.5
C1SiC2	47.9	46.4	47.6
SiC2X	119.1	118.2	117.2
V	66.37	84.34	30.30
E _{rel}	-3237.530471	-3237.529050	-3237.518699

Conclusion

In the present study, we have carried out a high level *ab initio* study of the C₂H₃XSiLiBr (where X= H, -CH₃, -SiH₃, and -OH) types of molecules. C₂H₃XSiLiBr has three stationary structures: silacyclopropylidenoid (**S**), tetrahedral (**T**), and inverted (**I**), which were obtained at the MP2/6-311+G(d,p) level of theory. The theoretical results indicate that the **S** forms are energetically the most stable ones in the gas phase. Our calculations also depict that the **T** form of -OH could not be optimized, whereas the others are found to be minima with no imaginary frequencies at the MP2/6-311+G(d,p) computational level.

Acknowledgments

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