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Computational investigations on the electronic and structural properties of germacyclopropylidenoids

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This article is dedicated to Prof. Dr. Metin Balci on the occasion of his 65th birthday.

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ABSTRACT

DFT (B3LYP) and *ab initio* (MP2) levels of theories using standard 6-31+G(d,p) basis set have been carried out to investigate the isomeric structures, energies and properties of LiBr-germacyclopropylidenoids. The theoretical calculations indicate that **1**, **3**, and **5** have two stationary structures: germanoidal (**G**) and inverted (**I**). On the other hand, **2** and **4** have only one stationary structure, germanoidal (**G**). We also obtained no tetrahedral structure as a minimum for the title germacyclopropylidenoids. The inverted (**I**) forms for **3** and **5** are energetically more stable than the germanoidal (**G**) ones, whereas stability of the germanoidal (**G**) form for **1** higher than the inverted (**I**) one. Moreover, the Wiberg bond orders (WBO), frontier molecular orbitals (FMO), and the molecular electrostatic potential maps (MEP) have been achieved at the B3LYP/6-31+G(d,p) level of theory.

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1. Introduction

Germylenes, the heavy analogs of carbenes, are one of the most often occurring key intermediates in reactions of organogermanium compounds [1,2]. The chemistry of germylenes has enjoyed a few decades of explosive growth, and stable germylenes have been also reported [3–6]. Similar to carbenoid and silylenoid, germylenoid is the complex formed between free germylene and inorganic salt, which can be donated as R_1R_2GeMX (M: alkali metal, X: halogen). In 1991, Gaspar et al. suggested that germylenoid might be the intermediate in the reaction of dichlorodimethylgermane with substituted butadiene [7]. In some subsequent experiments, germylenoids are important active intermediates and they are difficult to be synthesized and stabilized [8,9]. The germacyclopropylidenoid, the germanium analogue of cyclopropylidenoid, is a compound in which an electropositive metal (M) and a leaving group (X, usually halogen) are bound to the same germanium atom. Contrast to extensive experimental and computational studies on cyclopropylidenoids and silacyclopropylidenoids [10–17], no scientific work on germacyclopropylidenoids 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, C_2H_4SiMX (where M = Li or Na and X = F, Cl, Br). The theoretical results reveal that three stationary structures for each of C_2H_4SiMXs, 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^{-1} at the MP2/6-31+G(d,p) level [17].

Likewise, it is necessary to be performed systematic theoretical study on germacyclopropylidenoids to penetrate their structures, properties, and reactions. In the present paper, we wish to provide the first computational study of the geometries, electronic structures, and the stabilities of germacyclopropylidenoids. The overall stabilities of germacyclopropylidenoid isomers are also compared and the main factors contributing to the stability of the isomers are simply discussed. Moreover, we have investigated their frontier molecular orbitals and molecular electrostatic potentials (MEP) related to the electronic density. Hopefully, the present results would be helpful for further experimental and theoretical studies on germacyclopropylidenes and germacyclopropylidenoids, especially for the development of organic germanium materials.

2. Computational details

The geometry optimizations of the title structures were performed using a combination of Becke's three-parameter hybrid functional and the Lee–Yang–Parr non-local correlation functional

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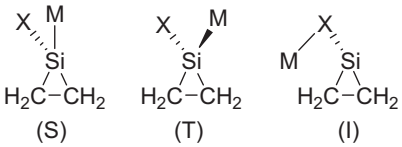
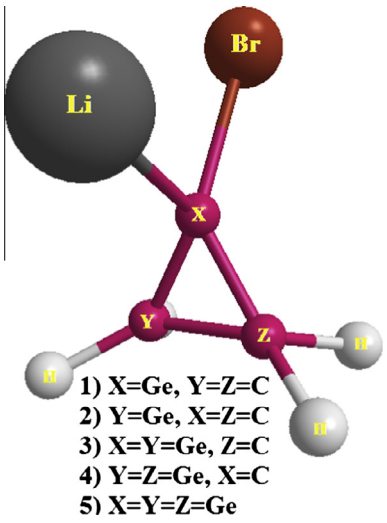


Scheme 1. The silacyclopropylidenoid (**S**), tetrahedral (**T**), and inverted (**I**) forms of C_2H_4SiMX (where M = Li or Na and X = F, Cl, Br) complexes.

(B3LYP) method in conjunction with the 6-31+G(d,p) basis set [18,19]. The results of calculations at the B3LYP/6-31+G(d,p) level were repeated with full geometry optimization at the MP2/6-31+G(d,p), M05-2X/6-31+G(d,p), and M06-2X/6-31+G(d,p) levels in the gas phase [20]. The corresponding harmonic vibrational frequencies were computed at all levels to characterize them as minima or saddle point with help of Gaussian03 package program [21]. The Intrinsic Reaction Coordinate (IRC) procedure was used for the identification of the connectivity of stationary points on the respective potential energy surfaces with the algorithm of Gonzalez and Schlegel [22–25]. The energies reported herein include zero-point energy (ZPE) corrections at all theoretical levels used herein. The frontier molecular orbitals (FMOs) and molecular electrostatic potential maps (MEPs) were also calculated at the B3LYP/6-31+G(d,p) level. The computed structures were visualized by using the GaussView3.0 program [26].

3. Results and discussion

C_3H_4LiBr can be regarded as a carbenoid formed by free cyclopropylidene and LiBr moieties. In this study, we studied germanium analogues of cyclopropylidenoids are shown in Scheme 2 (Structure **1**–**5**). Structure of germylenoid (H_2GeLiF) has three equilibrium configurations [27], in which p-complex is the lowest in energy, whereas the theoretical calculations depict that **1**, **3**, and **5** have two stationary structures: germanoidal (**G**) and inverted (**I**) (Fig. 1). On the other hand, **2** and **4** has only one stationary structure, germanoidal (**G**). In the inverted form, the Li atom is positioned between the Y and Z atoms and interacts mostly with the Y and Z atoms. Moreover, the Br atom shows only non-bonding interactions with the X atom in cyclopropylidene units. However, the Li and Br atoms interact with the X atom in the germanoidal (**G**) forms as it is seen from Fig. 1.



Scheme 2. Germanium analogues of cyclopropylidenoids.

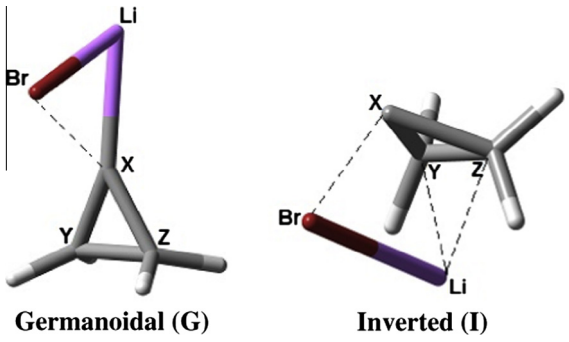


Fig. 1. The general representation of germanoidal (**G**) and inverted (**I**) form of the title structures.

Moreover, it is stated from the NBO (Natural Bond Orbital) analysis that positively charged ion, Li^+, attach the carbenic C atom for structure of **2** and **4** and the divalent Ge atom for structure of **1**, **3**, and **5** in different positions to give the minimal structures which have low-energy. However, the tetrahedral geometry could not be optimized for **1**–**5** at any levels used herein. Instead, all attempts to locate the tetrahedral forms for **1**–**5** lead directly to the germanoidal ones (**G**).

The intrinsic reaction coordinates (IRC) have been also performed to investigate the energy profiles between the tetrahedral form and the germanoidal form, the correct local minima. As can be seen from Fig. 2, the isomerization from the tetrahedral to germanoidal form passes from point 0.0 to point 8.0 with the step size, 0.1. In the region of 1.5–6.5, the X(Ge)–Br bond distance increases and Li–Br distance decreases. This leads to the fracturing of the Ge–Br (Step 17) and the formation of Li–Br (Step 63) for structure **1**. Besides, this finding means that no energy barrier for the conversion of the tetrahedral (**I**) to the germanoidal (**G**) actually exists (Fig. 2).

The structures of **1**–**5** have been calculated as low-spin (singlet) molecules. There is, to best of our knowledge, no experimental and theoretical data for these kinds of species are available for comparison. The main geometric parameters of all stationary points (**G** and **I**) were calculated and also given in Tables S1–S5 (in Supplementary material). The frequency analyses of the **G** and **I** forms of **1**, **2**, **3**, **4**, and **5** indicated the presence of have no imaginary frequencies except the germanoidal (**G**) form of **4** due to the calculated stretching frequency of $-40.7\ cm^{-1}$, $-28.0\ cm^{-1}$, and $-16.6\ cm^{-1}$ at the MP2/6-31+G(d,p), M05-2X/6-31+G(d,p), and M06-2X/6-31+G(d,p) levels, respectively. In addition, the germanoidal (**G**) form of **5** also could not be stated as a local minima with $-12.5\ cm^{-1}$ stretching frequency at the M05-2X/6-31+G(d,p) level. Hence, all of the optimized structures are local minima at all the levels used herein on the PES (Potential Energy Surface) with two exceptions.

We have obtained the geometric parameters and energies of these minima using DFT and *ab initio* methods along with the 6-31+G(d,p) basis set (Tables S1–S5, given in Supplementary material). It can be noticed that all of them have C_s symmetry. These Tables 1–5 give us a chance to compare some of geometric parameters to reference values [28]. In this part, a positive percentage value depicts an elongation, whereas a negative percentage value means shortening. For example, the bond lengths of the X–Li for the **G** forms are elongated 0.28% and 0.73% for **3** and **5**, respectively. On the other hand, the related bond lengths are altered −0.53%, −1.66%, and −2.4% for **1**, **2**, and **4** at B3LYP/6-31+G(d,p) level with regard to the reference bond lengths, respectively. The elongation is determined for the Ge–Li bond length of the **G** for **3** and **5** which have the divalent Ge atom, except for structure **1**. If the divalent X atom is carbon for **2** and **4**, the bond length of the

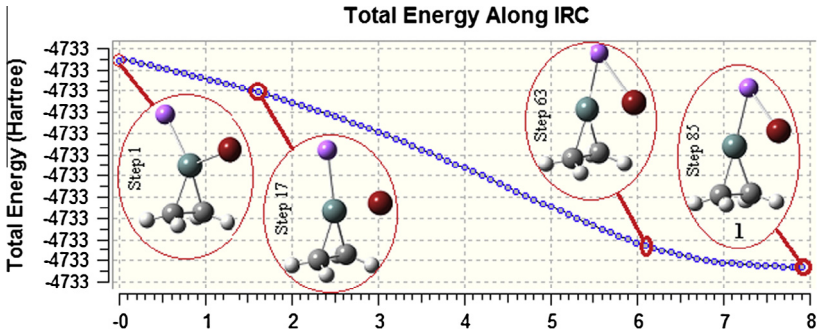


Fig. 2. IRC plot of structure **1**.

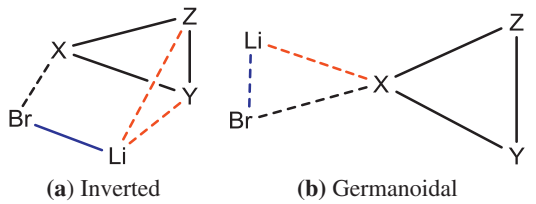
C-Li is shortened for the germanoidal (**G**) forms at the B3LYP/6-31+G(d,p) level of theory. Concerning the Li–Br distances in the **G** and **I** forms of the title structures, the elongations are between 5.33% and 10.88% as compared to the bond length in the Li–Br salt (2.195 Å) at the B3LYP/6-31+G(d,p) level of theory. Moreover, the calculated XLiBr bond angles of the **G** forms for **1**, **3**, and **5** are higher than for **2** and **4** (Tables S1–S5). When compared to the YXZ bond angels of the title structures, the smallest one is found to be the **I** form of **1** with 43.9°. However, the largest one is determined to be the **G** form of **4** at the B3LYP/6-31+G(d,p) theory of level.

We can describe chemical bond disruption and formation by the Wiberg bond order (WBO), give us knowledge of electron density between two relevant atoms [29]. The WBO of several bonds of title molecules calculated at the B3LYP/6-31+G(d,p) level of theory with the help of the NBO analyses [30,31] are tabulated in Tables S1–S5 (in parentheses). A WBO value is directly proportional to the strength of covalent bonding between two related atoms. For instance, a large WBO value depicts a strong covalent bonding interaction between two relevant atoms. The theoretical results show that the X–Li bond of the two optimized forms, **G** and **I**, of **1**–**5** have the ionic character rather than the covalent nature due to the estimated WBO values, which are in the range of 0.0158 and 0.1278. In addition, the X–Z bond of the **G** form of **2** has the strongest covalent character with the WBO value of 1.0834. For the Y–Z bond of title molecules, the **G** form of **1** has a substantial covalent bond interaction due to the 1.0687 WBO value at B3LYP/6-31+G(d,p) level.

The molecular orbitals of the studied structures with the help of the NBO (Natural Bond Orbital) analysis were also examined at the B3LYP/6-31+G(d,p) level. We can determine the charge distribution in molecules based on creating atomic natural orbitals with the NBO analysis. The Li *anti lone pair* (n^*_{Li}) interacts with the both X *lone pair* (n_X) and Br *lone pair* (n_{Br}) for the **G** forms of the title structures. It is determined that the strongest delocalization of the **G** form involves the interaction of the X (divalent atom) *lone pair* (n_X) with the Li *anti lone pair* (n^*_{Li}). In NBO analysis, large stabilization energy value, called as *E(2)*, shows the intensive interaction between electron-donors and electron-acceptors, and greater the extent of conjugation of the whole system. The $n_X \rightarrow n^*_{Li}$ interactions between the X *lone pair* and the Li *anti lone pair* are identified as the strongest stabilization, by 16.3 kcal/mol, 14.5 kcal/mol, 14.9 kcal/mol, 13.3 kcal/mol, and 13.9 kcal/mol for **1**, **2**, **3**, **4**, and **5**, respectively at the B3LYP/6-31+G(d,p) level of theory (Fig. 3b, colored in red[1]). On the other hand, the interaction between the Li *anti lone pair* (n^*_{Li}) and Br *lone pair* (n_{Br}) has the second highest value. These interactions stabilize the germanoidal (**G**) forms of **1**, **2**, **3**, **4**, and **5** by 12.5 kcal/mol, 6.5 kcal/mol, 11.6 kcal/mol, 6.0 kcal/mol, and 11.1 kcal/mol, respectively. On the contrary, the *lone pairs* of the Br atoms in direct interaction with the *anti lone pairs* of the Li atoms ($n_{Br} \rightarrow n^*_{Li}$) to minimize energy of the inverted **I** forms of **1**, **3**, and **5**, by 26.7 kcal/mol, 23.9 kcal/mol, and 21.5 kcal/mol, respectively (Fig. 3a, colored in blue). The stabilization energies of the inverted (**I**) forms for **3** and **5** are 7.65 kcal/mol (Bonding H1–Ge_7/LP∗Li_8) and 9.09 kcal/mol (Bonding Ge_7–Ge_9/LP∗Li_5), respectively. The Li–Ge coordination energies of inverted (**I**) forms for both **3** and **5** are higher than the Li–C in the **I** form of **1** (Fig. 3a, colored in red).

We also investigated the molecular orbitals of the title structures with the help of the NBO analysis at the B3LYP/6-31+G(d,p) theory of level. The charge distributions of the title molecules were also determined by the NBO method. The frontier molecular orbitals (HOMO and LUMO) are very important to define reactivity of the structures. In addition, the optical, electrical, and the other properties can be discussed with help of the FMOs. The HOMO–LUMO energy gaps give us a chance to determine chemical reactivity and kinetic stability of molecules. A molecule which has a small frontial orbital gap is more polarizable and generally associated with a high chemical reactivity, low kinetic stability and also called as soft molecule [32–38]. Fig. 4 indicates the illustration of the HOMO and LUMO orbitals with calculated energies at the B3LYP/6-31+G(d,p) theory of level for the two local minima. The **I** form of structure **1** has the biggest HOMO–LUMO gap with 0.162 eV, whereas the lowest ones are on the **I** and **G** forms of **5** with the same value, 0.131 eV. The NBO analysis also indicate that the main part of the HOMOs is located on the divalent Ge or C atoms with −0.202, −0.188, −0,195, −0.187, and −0.196 eV, whereas the LUMOs is situated on the Li atoms with −0.053, −0.049, −0.058, −0.053, and −0.065 eV for the germanoidal forms of **1**, **2**, **3**, **4**, and **5** at B3LYP/6-31+G(d,p) level, respectively. In consequence, $XYZH_4$ part of the title structures, considered as a free germylene show nucleophilic character.

The MEP (Molecular Electrostatic Potential) is related to the electronic density. The MEP is very useful method to determine nucleophilic and electrophilic sites of molecules [39–41]. For instance, the MEPs of the optimized forms of the structure **1** at the B3LYP/6-31+G(d,p) level of theory are depicted in Fig. 5. The nega-



(**a**) Inverted (**b**) Germanoidal

Fig. 3. The illustration of interactions for Li–Y/Z, Li–X, and Li–Br.

[1] For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

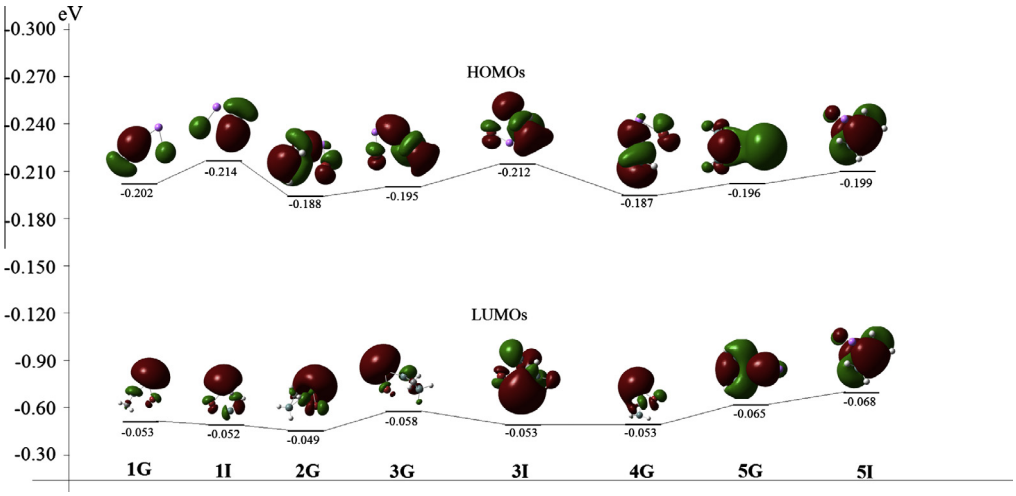


Fig. 4. HOMOs and LUMOs of two minimum forms (**G** and **I**) of title molecules with energies (eV) at the B3LYP/6-31+G(d,p) theory of level.

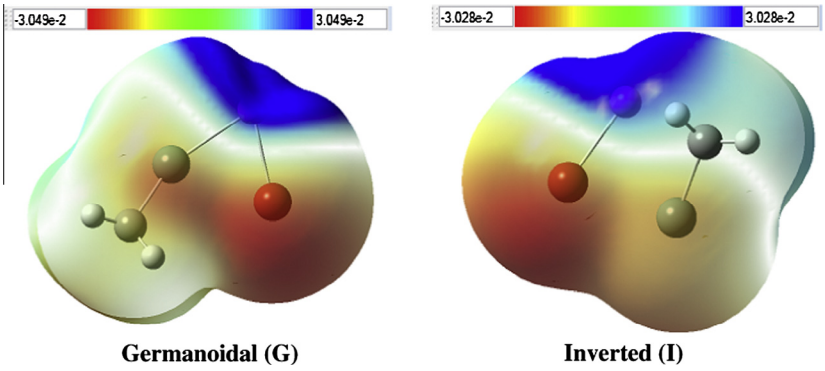


Fig. 5. MEP maps of **G** and **I** forms of **1** calculated at the B3LYP/6-31+G(d,p) level.

tive (red and yellow) and the positive (blue) regions in the MEP were related to the electrophilic and nucleophilic reactivity, respectively. As can be seen Fig. 5, the negative region of the title structures were localized on the Ge and Br atoms, whereas the positive regions are observed around the Li atoms for the germanoidal (**G**) and inverted (**I**) forms of **1**. The molecular electrostatic potential maps provide that the divalent Ge atom of the **I** and **G** forms of the title structures have nucleophilic character in accordance with the HOMO–LUMO analyses.

The relative stabilities of the title structures **1–5,** are clear from the energy results at the B3LYP/6-31+G(d,p), MP2/6-31+G(d,p), M05-2X/6-31+G(d,p), and M06-2X/6-31+G(d,p) levels, summarized in Tables S1–S5 (in Supplementary material). The germanoidal form of **1** has lower energy than inverted one with 0.86 kcal/mol, whereas the germanoidal forms have higher energy than inverted forms for **3** and **5** with 7.37 and 8.47 kcal/mol at the B3LYP/6-31+G(d,p) level, respectively. As can be seen from Scheme 2, the structure **1** is the constitutional isomer of **2**, and **3** also is isomer of **4**. When we compare the energies of the isomers, it is obtained that **2** and **4** have higher energy than **1** and **3** for the **G** form. From their calculated energy values, **1** and **3** are more stable, by 61.4 kcal/mol 56.5 kcal/mol, than **2** and **4** for the **G** form at the B3LYP/6-31+G(d,p) level.

4. Conclusions

We have carried out a series of DFT and *ab-initio* calculations on the germanium analogue of cyclopropylidenoids. The optimized molecules of **1**, **3**, and **5** have two stationary structures, germanoidal (**G**) and inverted (**I**), whereas that of **2** and **4** have only one stationary structure, germanoidal (**G**). The theoretical WBO values indicate that the X–Li bond of the two considered forms, **G** and **I**, of **1**–**5** have ionic character rather than covalent nature which are in the range of 0.0158 and 0.1278. Moreover, the X–Z bond of the **G** form is the strongest bond having a substantial covalent character with a WBO value of 1.0834 for **2**. The computational results also show that the **I** forms of **3** and **5**, have lower energies than the **G** forms of **3** and **5**, whereas the **G** form is more stable for **1**. From the frontier molecular orbital analysis one can easily conclude that the **I** form of structure **1** has the biggest HOMO–LUMO gap with 0.162 eV, whereas the lowest ones are located on the **I** and **G** forms of **5** with 0.131 eV. The present quantum chemical study may further play an important role in understanding of the molecular properties of these interesting compounds.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2013.09.009.

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