

# DFT Study on The Sctructural Properties of Germacyclopropylidenoids

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## Abstract

DFT (B3LYP) levels of theory using 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 depict 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 have also obtained no tetrahedral structure as a minimum for all of the germacyclopropylidenoids. Inverted (I) forms are energetically more stable than germanoidal (G) forms for **3** and **5**, whereas stability of germanoidal (G) form higher than inverted (I) form for **1**. Moreover, natural bond orbitals (NBO) were achieved in this theoretical work.

**Keywords:** DFT, germacyclopropylidenoids, reactive intermediates

## Introduction

Germylene is an important organic reactive intermediate [1-3], which is similar to carbene and silylene. Germolenoid is very important analogue of germylene. Likewise, germacyclopropylidenoids, the germanium analogues of cyclopropylidenoids, are compound where an electropositive metal (Li) and a leaving group (Br) are bound the same carbenic atom. contrast to extensive experimental and theoretical studies on cyclopropylidenoids [4–9], there are no theoretical reports on germacyclopropylidenoids.

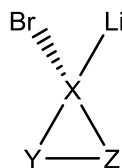
More recently, we have carried out a series of *ab initio* and DFT calculations on the silacyclopropylidenoids. We have found three stationary structures for silacyclopropylidenoid: silacyclopropylidenoid (S), tetrahedral (T), and (inverted (I) forms, which were obtained at the MP2/6-31+G(d,p) and MP2/aug-cc-pVTZ levels of theory. The theoretical results indicate that S-MX (where M = Li or Na and X = F, Cl or Br) forms are energetically the most stable ones in the gas phase, except for S-LiF. In contrast, all T-MX forms are the most unstable ones except for T-NaF [10].

In this work, we wish to report the results of structure, and the properties of the structure **1-5** with help of computational methods.

## Computational Methods

The geometry optimization of the title structures were performed using density functional theory (DFT) Becke's three-parameter hybrid function with the non-local correlation of Lee-Yang-Parr (B3LYP) method in gas phase [11-14]. The corresponding harmonic vibrational frequencies were computed at the same level of theory to characterize them as minima (no imaginary frequencies) with help of Gaussian03 package program [15]. All of above calculations were using 6-31+G(d,p) basis set. The energies reported herein include zero-point energy (ZPE) corrections at B3LYP/6-31+G(d,p) level of theory. Frontier molecular orbitals (FMOs) and molecular electrostatic potential maps (MEPs) were also calculated at the same level of theory. The computed structures were visualized by using the GaussView program [16].

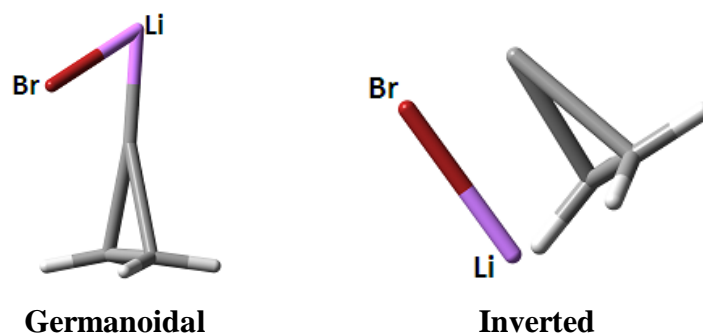
## Results and Discussions



- 1) X=Ge, Y=Z=C
- 2) Y=Ge, X=Z=C
- 3) X=Y=Ge, Z=X
- 4) Y=Z=Ge, X=C
- 5) X=Y=Z=Ge

**Fig. 1.** The illustration of Germanium Analogues of Cyclopropylidenoids.

$C_3H_4LiBr$  as a carbenoid, can be considered as a complex, which consists of free cyclopropylidene and LiBr moieties. In this study, we studied germanium analogues of cyclopropylidenoids are shown in Figure 1 (Structure 1-5). Contrary to fact structures of germylenoid has four isomeric structures [17], the theoretical calculations depict that **1**, **3**, and **5** have two stationary structures: germanoidal (G), and inverted (I) (Fig. 2.). On the other hand, **2** and **4** have only one stationary structure, germanoidal (G).



**Fig. 2.** The illustration of Germanoidal and Inverted Form of the Title Structures.

Positive ion,  $Li^+$ , attach the carbonic atom on the structures (**1-5**) in different positions to give the minimal structures which have low-energy. However, the structure of distorted tetrahedral could not be optimized for anyone at B3LYP/6-31+G(d,p) level of theory. The main geometric parameters of all stationary points calculated and also given in Table 1-5. It is easily understood from the tables, the optimized structures are local minima on PES (Potential Energy Surface), provided by stretching frequencies.

We have obtained geometric parameters and energies of these minima using DFT method along with 6-31+G(d,p) basis set (Table 1-5). It can be noticed that all of them have  $C_s$  symmetry. These tables give us a opportunity to compare some of geometric parameters to references. For example, the bond length of X-Li in the germanoidal forms are elongated 0.28 and 0.73% for **3** and **5**, respectively. On the other hand, the same bond length are altered -0.53, -1.66, and -2.4% for **1**, **2**, and **4**, respectively. A positive percentage value depicts an elongation, whereas a negative percentage value means shortening with regard to reference bond. It is interesting that, when the carbenic atom was carbon, shortening of the bond length of C-Li were occurred for germanoidal structures at B3LYP/6-31+G(d,p) level of theory. Otherwise, elongation determined for the Ge-Li bond length of **3** and **5** which have carbonic Ge atom, except for structure **1**.

<b>X=Ge, Y=Z=C</b>	<b>Germanoidal</b>	<b>Inverted</b>
X-Li	2.432	2.954
X-Br	2.690	2.676
X-Y	1.979	2.041
X-Z	1.979	2.041
Y-Z	1.518	1.528
Li-Br	2.343	2.312
XLiBr	68.5	59.6
YXZ	45.1	43.9
$\nu$ X-Br	58.6	53.2
$E_{rel}$	-4732.889817	-4732.888436

**Table 1** Selected bond lengths and angles ( $\text{\AA}$ ), stretching frequencies  $\nu$ X-Br, and ZPVE-corrected relative energies (a.u) for structure of **1** at B3LYP/6-31+G(d,p) level.

<b>Y=Ge, X=Z=C</b>	<b>Germanoidal</b>	<b>Inverted</b>
X-Li	1.952	
X-Br	2.167	
X-Y	1.923	
X-Z	1.539	
Y-Z	1.947	
Li-Br	2.389	
XLiBr	58.8	
YXZ	67.4	
$\nu$ X-Br	118.2	
E <sub>rel</sub>	-4732.791833	

**Table 2** Selected bond lengths and angles (Å), stretching frequencies  $\nu$ X-Br, and ZPVE-corrected relative energies (a.u) for structure of **2** at B3LYP/6-31+G(d,p) level.

<b>X=Y=Ge, Z=C</b>	<b>Germanoidal</b>	<b>Inverted</b>
X-Li	2.452	3.066
X-Br	2.649	2.605
X-Y	2.421	2.549
X-Z	2.011	2.017
Y-Z	1.955	2.010
Li-Br	2.361	2.372
XLiBr	66.7	55.5
YXZ	51.3	50.6
$\nu$ X-Br	51.9	90.8
E <sub>rel</sub>	-6769.811398	-6769.823144

**Table 3** Selected bond lengths and angles (Å), stretching frequencies  $\nu$ X-Br, and ZPVE-corrected relative energies (a.u) for structure of **3** at B3LYP/6-31+G(d,p) level.

<b>Y=Z=Ge, X=C</b>	<b>Germanoidal</b>	<b>Inverted</b>
X-Li	1.937	
X-Br	2.120	
X-Y	1.969	
X-Z	1.969	
Y-Z	2.355	
Li-Br	2.434	
XLiBr	56.6	
YXZ	73.4	
$\nu$ X-Br	32.4	
E <sub>rel</sub>	-6769.721276	

**Table 4** Selected bond lengths and angles (Å), stretching frequencies  $\nu$ X-Br, and ZPVE-corrected relative energies (a.u) for structure of **4** at B3LYP/6-31+G(d,p) level.

<b>X=Y=Z=Ge</b>	<b>Germanoidal</b>	<b>Inverted</b>
X-Li	2.463	3.483
X-Br	2.634	2.614
X-Y	2.498	2.554
X-Z	2.498	2.554
Y-Z	2.414	2.476
Li-Br	2.374	2.415
XLiBr	65.9	48.5
YXZ	57.7	58.0
$\nu$ X-Br	24.4	92.7
E <sub>rel</sub>	-8806.748095	-8806.761597

**Table 5** Selected bond lengths and angles (Å), stretching frequencies  $\nu$ X-Br, and ZPVE-corrected relative energies (a.u) for structure of **5** at B3LYP/6-31+G(d,p) level.

We have investigated the molecular orbitals of the title structures with help of NBO analysis at B3LYP/6-31+G(d,p) theory of level. Charge distribution of molecules determined by NBO method.

## **Conclusions**

In the present study, we have carried out a DFT study of germanium analogues of cyclopropylidenoids. The molecules have two stationary structures: Germanoidal (G) and Inverted (I). The theoretical results indicate that inverted forms of **3** and **5** have lower energies than germanoidal forms of **3** and **5**, whereas germanoidal form is more stable for **1**.

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