

DFT study on the unsaturated germylenoid $\text{H}_2\text{C}=\text{GeNaF}$

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Abstract

The unsaturated germylenoid $\text{H}_2\text{C}=\text{GeNaF}$ was studied by using the DFT B3LYP method in conjunction with the 6-311+G(d,p) basis set. Geometry optimization calculations indicate that $\text{H}_2\text{C}=\text{GeNaF}$ has three equilibrium configurations, in which the p-complex is the lowest in energy and is the most stable structure. Two transition states for isomerization reactions of $\text{H}_2\text{C}=\text{GeNaF}$ are located and the energy barriers are calculated. For the most stable one, vibrational frequencies and infrared intensities have been predicted.

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1. Introduction

Carbenoids, which are obtained by the reactions of carbenes and alkali halides, are important intermediates in some organic reactions and were used in many organic synthesis reactions [1–3]. Experimental study [1] indicated that carbenoids have many advantages such as good selectivity, simplification of products, and mild reaction conditions in organic synthesis reactions. Silylenoids, similar to carbenoids, which are obtained by the reactions of silylenes and alkali halides, are also important intermediates in some organic reactions and much attention was paid to them during the past four decades [4–7]. Compared with carbenes and silylenes, carbenoids and silylenoids are more stable. Germylene, similar to carbene and silylene, is an important active intermediate [8–10] and the research of germanium reaction is an interesting topic since many organic germanium compounds have been found to have biologic activity [11–17]. Germylenoid, similar to carbenoid and silylenoid, which can be denoted as $R_1R_2\text{GeMX}$, may be stable than germylene and have particular property. However, researches on germylenoid are scarce. To

our best knowledge, there are only two theoretical calculations on the simplest germylenoids H_2GeLiF [18] and H_2GeNaF [19]. The unsaturated germylenoids $R_1R_2\text{C}=\text{GeMX}$ are another kind of germylenoids. At present, their existence, structures, and chemical properties have not been studied either experimentally or theoretically. $\text{H}_2\text{C}=\text{GeNaF}$ is one of simplest unsaturated germylenoids similar to the $\text{H}_2\text{C}=\text{CLiF}$ [20] and $\text{H}_2\text{C}=\text{SiLiF}$ [21]. By using $\text{H}_2\text{C}=\text{GeNaF}$ as a model, a detail theoretical study on its structures and stability will be reported in present paper. We hope the results would be helpful for further experimental and theoretical studies on germylenoids.

2. Calculation details

The geometries of equilibrium configurations and transition states for isomerization reactions of $\text{H}_2\text{C}=\text{GeNaF}$ were optimized by using the density functional theory (DFT [22,23]) B3LYP (Becke's three-parameter hybrid function [24] with the non-local correlation of Lee–Yang–Parr [25]) method. To determine transition states, the frequencies and intrinsic reaction coordinate (IRC) calculations were performed. In all calculations the 6-311+G(d,p) basis [26] was used. The calculations were carried out using the GAUSSIAN03 suite of program [27].

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3. Results and discussion

Similar to the unsaturated carbene $\text{H}_2\text{C}=\text{C}:$ and silylene $\text{H}_2\text{C}=\text{Si}:$, the ground state of the unsaturated germylene $\text{H}_2\text{C}=\text{Ge}:$ is singlet [28]. The valence orbitals of the Ge atom in $\text{H}_2\text{C}=\text{Ge}:$ are sp hybridized, in which one sp hybrid orbital takes part in σ bonding with a carbon atom, and two electrons occupy another sp hybrid orbital. One of the two vertical p orbitals takes part in π bonding with the corresponding p orbital of the carbon atom; and another p orbital is an unoccupied orbital. The schematic diagram of unsaturated silylene $\text{H}_2\text{C}=\text{Ge}:$ is shown in Fig. 1. In the unsaturated germylene the empty p orbital has electrophilicity and the occupied sp hybrid orbitals have nucleophilicity.

3.1. Equilibrium structures

The B3LYP/6-311+G (d,p) calculations indicate that $\text{H}_2\text{C}=\text{GeNaF}$ has three equilibrium structures (**1–3** in Fig. 2). The optimized geometries of three isomers and transition states for isomerization reactions are given in Fig. 2. The total energies, relative energies, dipole moments, and number of the imaginary frequency of each isomer are listed in Table 1.

Structure **1** in Fig. 2, is a three-membered ring structure because there is a three-membered ring made of the Ge, Na, and F atoms in **1**. It is formed by the combination of a Na atom with a positive charge and the occupied sp hybrid orbital with two electrons of the Ge atom and the combination of an F atom with a negative charge and the empty p orbital of the Ge atom. In structure **1**, all atoms lie in the same plane and the molecule is in C_s symmetry. From the bond lengths it can be seen that the C=Ge bond of **1** is weaker than that in $\text{H}_2\text{C}=\text{Ge}$. The NaF bond length in the three-membered ring is 0.0126 nm longer than that in the NaF molecule. In structure **1**, the donating of part of σ electrons of the Ge atom to the Na atom with positive charge and the feedback of an electron lone pair of F atom to the p orbital of the Ge atom makes **1** have high stability. The associative energy of **1** ($\text{H}_2\text{C}=\text{Ge}({}^1\text{A}_1) + \text{NaF}$) is 132.29 kJ mol^{-1} . From Table 1, it can be seen that the energy of **1** is 44.84 kJ mol^{-1} higher than that of **2**, which is the lowest-energy structure.

Structure **2** in Fig. 2 can be regarded as the structure that forms when the F ends with a negative charge attack the empty p orbital of the Ge atom. In this structure, the electrons transfer from the F atom to the empty p orbital of the Ge atom. Structure **2** can be named as a p-complex structure. It is noticed that **2** is a nonplanar structure. In structure **2** the Na atom interacts not only with the F atom,

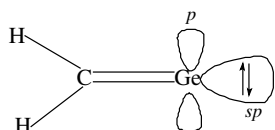


Fig. 1. Schematic diagram of unsaturated germylene $\text{H}_2\text{C}=\text{Ge}$.

but also with C and Ge atoms. Similar to $\text{H}_2\text{C}=\text{SiLiF}$ [21], structure **2** can be regarded as the $[\text{H}_2\text{C}-\text{Ge}-\text{F}]^-\text{Na}^+$ complex geometry and there is a bent delocalized π bond with three atoms and four electrons in **2**. The C=Ge bond length of **2** is 0.0064 nm longer than that of $\text{H}_2\text{C}=\text{Ge}$, and the NaF bond length is 0.0174 nm longer than that in the NaF molecule. From Table 1, it can be seen that the structure **2** is the lowest in energy among the three structures. The associative energy of **2** is 177.13 kJ mol^{-1} . Structure **2** may be experimentally detectable and is the structure in which $\text{H}_2\text{C}=\text{GeNaF}$ mainly exists.

Structure **3** in Fig. 2 can be named as σ complex, which is regarded as the complex formed when the positive Na end of the NaF molecule approaches the σ occupied orbital of the Ge atom and results in a Ge \rightarrow Na bond combination. The C, Ge, Na, and F atoms of **3** are in a line, and **3** is in C_{2v} symmetry. The C=Ge bond length of **3** is 0.0014 nm shorter than that of $\text{H}_2\text{C}=\text{Ge}$, and the NaF bond length is only 0.0009 nm longer than that in the NaF molecule. The energy of **3** is 116.73 kJ mol^{-1} higher than that of **1**, and **3** is the highest in energy among the three structures of $\text{H}_2\text{C}=\text{GeNaF}$.

The theoretical calculations [21] predicted that unsaturated silylenoid $\text{H}_2\text{C}=\text{SiLiF}$ has four isomers, in which isomer **4** (see Fig. 1 in Ref. [21]) is a 'classical' silene in C_s symmetry. However, B3LYP/6-311+G(d,p) calculations indicated that $\text{H}_2\text{C}=\text{GeNaF}$ has not the similar structure as '4'. We carried out geometry optimization calculations with the initial structure like '4' and at last only got the geometry **1** in Fig. 2. And we conclude that $\text{H}_2\text{C}=\text{GeNaF}$ has only three isomers. According to the analysis on the energies (see Table 1), the order of the thermodynamic stability of the three structures of $\text{H}_2\text{C}=\text{GeNaF}$ is $2 > 1 > 3$.

3.2. Isomerization reactions

Structures **4** and **5** (see Fig. 2) are the two transition states on the potential energy surface of $\text{H}_2\text{C}=\text{GeNaF}$. It is known from the reaction vectors (the eigenvector corresponding to the unique negative eigenvalue of the second derivative of energy) and the IRC calculation results that they are the transition states for isomerization reactions between structures **2** and **1**, and **3** and **1**, respectively. Vibration analysis calculations indicated that the unique imaginary frequencies of structure **4** and **5** were 50.5i and 21.4i, respectively, at the B3LYP/6-311+G (d,p) level.

Generally speaking, the stability of each structure depends on its energy and the activation energy of the isomerization reactions. From Table 1 it can be seen that the potential barrier from structure **1** to structure **3** is 116.84 kJ mol^{-1} and the inverse is only 0.11 kJ mol^{-1} , so structure **3** easily isomerizes to structure **1**. The potential barrier from structure **1** to structure **2** is 1.83 kJ mol^{-1} and the inverse is 46.67 kJ mol^{-1} , so structure **1** easily isomerizes to structure **2**. Structure **2** should be the main existent structure of $\text{H}_2\text{C}=\text{GeNaF}$ and would be searched in future experiments.

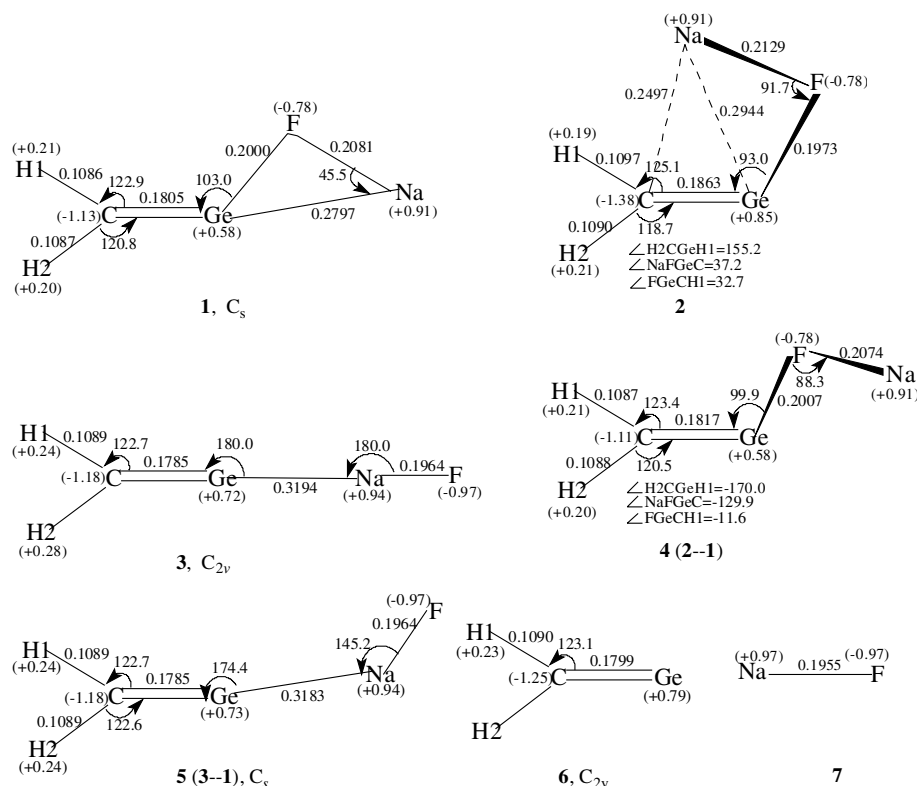


Fig. 2. The equilibrium configurations and the transition states for isomerization reactions of $\text{H}_2\text{C}=\text{GeNaF}$ calculated at B3LYP/6-311+G(d,p) level (Bond lengths are given in nm and angles in degrees, values in parentheses are the natural charges).

Table 1

The B3LYP/6-311+G (d,p) calculated total energies (E_{tot} , in a.u.), relative energies (E_{rel} , in kJ mol^{-1}), dipole moments (μ , in C m), and number (N_{imag}) of imaginary frequency of the geometries for $\text{H}_2\text{C}=\text{GeNaF}$

| Geometries | E_{tot} | E_{rel} | $10^{30}\mu$ | N_{imag} |
|------------|------------------|------------------|--------------|-------------------|
| 1 | -2378.5382207 | 0.0 | 29.26 | 0 |
| 2 | -2378.5552992 | -44.84 | 20.23 | 0 |
| 3 | -2378.4937589 | 116.73 | 31.80 | 0 |
| 4 | -2378.5375237 | 1.83 | 27.76 | 1 |
| 5 | -2378.4937174 | 116.84 | 30.62 | 1 |
| 6 | -2116.2659508 | - | 1.42 | 0 |
| 7 | -262.2218839 | - | 27.52 | 0 |

Table 2

The B3LYP/6-311+G(d,p) calculated vibrational frequencies (ν , in cm^{-1}) and infrared intensities (I , in km mol^{-1}) of configuration 2 in Fig. 2

| ν | I | ν | I |
|--------|--------|--------|--------|
| 129.0 | 18.39 | 613.4 | 15.08 |
| 213.86 | 13.77 | 671.2 | 34.17 |
| 254.8 | 4.57 | 729.1 | 169.47 |
| 344.2 | 49.64 | 1378.2 | 10.80 |
| 402.6 | 103.60 | 3023.0 | 32.44 |
| 567.0 | 49.15 | 3139.6 | 13.55 |

3.3. The vibrational frequencies and infrared intensities of configuration 2

It is known from the above calculation results that structure 2 is the main existent structure of unsaturated germylenoid $\text{H}_2\text{C}=\text{GeNaF}$. The vibrational frequencies and

infrared intensities of structure 2 calculated at the B3LYP/6-311+G (d,p) level are listed in Table 2, to provide evidence for geometric analysis of unsaturated germylenoid $\text{H}_2\text{C}=\text{GeNaF}$. This gives the theoretical evidence for analysis of the infrared spectrum of $\text{H}_2\text{C}=\text{GeNaF}$.

4. Conclusions

The B3LYP/6-311+G(d,p) calculation results show that the unsaturated germylenoid $\text{H}_2\text{C}=\text{GeNaF}$ has three equilibrium structures, their energies are in the order of p-complex < three-membered < σ -complex. The p-complex has the lowest energy and should be experimentally detectable and is the structure in which $\text{H}_2\text{C}=\text{GeNaF}$ exists and takes part in chemical reactions. Though the three-membered structure has the lower energy, it easily isomerizes to 2 with a barrier of only 1.83 kJ mol^{-1} . The σ -complex structure has the highest energy and may also isomerize to the three-membered structure with small barrier.

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