

The Isomeric Structures of H₂GeLiF, the Prototype Germylenoid

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Abstract: The structures of four isomeric forms of the model germylenoid, H₂GeLiF, have been examined by *ab initio* MO theory. The most stable structure is suggested to be the p-complex **1**. The other three species, three-membered ring **2**, σ -complex **3** and tetrahedron **4**, are also local minima on the potential energy surface, but are higher in energy.

Keywords: Germylenoid; p-complex; *ab initio*.

The properties and reactions of germylene, R₂Ge:, and its derivatives have been well studied¹. Germylene reactions, however, can be performed using intermediates of the type, RR'GeMX (M=alkali metal, X=halogen), analogous to carbenoids and silylenoids, RR'CMX and RR'SiMX^{2,3}. Recently, Gaspar and his coworker have suggested that germylenoid, Me₂GeLiCl, should be involved in the reaction of dichlorodimethyl-germane with substituted butadiene⁴, but little is known experimentally and theoretically about its energy, geometry or electronic structure. So it is necessary to investigate germylenoid, RR'GeMX, theoretically. For the sake of convenience, we start from H₂GeLiF, the prototype germylenoid, and investigate its structure using *ab initio* molecular orbital theory in order to exploit the new field of organogermanium chemistry.

The calculation shows that H₂GeLiF has four equilibrium structures, **1-4**, analogous to H₂SiLiF⁵ as depicted in **Figure 1**, and their molecular constants are listed in **Table 1**. The total energies and relative energies are given in **Table 2**.

Structure **1**, which is found to be the most stable and the lowest in energy, is called p-complex. It is formed by mutual approach of the electronegative F end of a LiF molecule and the empty p orbital of germylene. In this structure, the H atoms of Ge-H bond have negative charges, so there is an interaction between Li and electronegative H atoms with the Mulliken population between H and Li 0.074. An electronic circulation forms among Ge, F, H and Li atoms. This interaction makes the angle HGeH 4.2° smaller and the Ge-H bond 0.0062 nm longer than those of H₂Ge:, respectively. There is also a strong attractive interaction between electropositive Ge and electronegative F in the isomer **1**, and thus it is the most stable and experimentally detectable. The Ge-F

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bond is longer than the ordinary Ge-F bond in GeH₃F (0.1725 nm) at 3-21G* level, and this kind of loose bonding is an active bond for chemical reactions.

Figure 1. The depicted equilibrium structures of H₂GeLiF

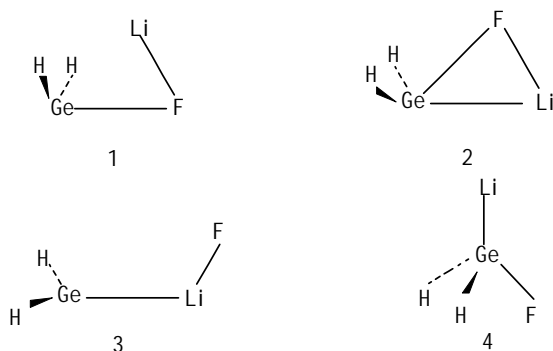


Table 1. 3-21G* optimized equilibrium geometry of various H₂GeLiF isomers

Parameters ^a	1	2	3	4
R(GeH)	0.1659	0.1579	0.1576	0.1577
R(GeLi)	—	0.2505	0.2698	0.2525
R(GeF)	0.1906	0.1916	—	0.1759
R(FLi)	0.1675	0.1664	0.1530	—
∠HGeH	87.8	98.8	97.0	101.3
∠FGeH	86.0	97.8	130.8 ^b	101.9
∠FGeLi	—	41.6	—	109.5
∠LiFGe	87.7	121.6 ^b	—	119.8 ^b
∠FLiGe	—	143.6 ^c	139.7	—

a Bond lengths are in nm and bond angles in degree.

b ∠HGeLi.

c ∠YGeLi. Y is a dummy atom, GeY is in the HGeH plane and is a bisector of ∠HGeH

Structure **2** has a three-membered ring and all the four ligands lie in a single hemisphere. It is formed when two ends of a LiF molecule simultaneously approach σ and p orbitals of H₂Ge; in this structure. Part of the negative charge on F atom enters the p orbital of H₂Ge, and the electropositive Li atom combines with the lone pair electron in σ orbital, which make the three-membered ring structure stable. At 3-21G* level, structure **2** is 21.8 kJ/mol less stable than structure **1**, although inclusion of

correlation increases this separation to 26.8 kJ/mol. In addition, the positive Mulliken population in Li-Ge, Li-F and F-Ge supports the three-membered structure. The Ge-F and Ge-Li bonds are all longer than those of H₃GeF and H₃GeLi, so structure **2** is also an active species in chemical reactions.

Table 2 Total energy (a.u.) and relative energy (kJ/mol) for H₂GeLiF isomers

Isomer	3-21G**//3-21G*		MP ₃ 6-31G**//3-21G* ^a	
	Total	Relative	Total	Relative
1	-2173.06634	0.0	-2173.94583	0.0
2	-2173.05800	21.8	-2173.93601	25.9
3	-2173.00047	173.2	-2173.88822	151.0
4	-2173.02869	98.7	-2173.91145	90.0
H ₂ Ge+LiF	-2172.97580	238.1	-2173.86660	207.9

a. 3-21G* for Ge atom, 6-31G** for other atoms

Structure **3** being called σ -complex is a H₂Ge: LiF complex in which H₂Ge: is acting as the donor and LiF closes to σ orbital with its electropositive Li end. The Li-F bond and Ge-H bond lengths are all close to those of free Li-F in LiF molecule and Ge-H in H₂Ge:, respectively, so the structure **3** is very unstable. At 3-21G* level, its energy is 173.2 kJ/mol higher than that of **1**, although this difference is decreased to 151.0 kJ/mol with inclusion of correlation.

Structure **4** is in classical “tetrahedral” form and seems to be the most common of the four isomers. However, although **4** is also a local minimum on the potential energy surface of H₂GeLiF, its energy is 98.7 kJ/mol higher than that of **1** at 3-21G* level. This difference is decreased to 90.0 kJ/mol if the correlation is included. The instability of **4** is attributed to the weak Ge-Li bond and the electrostatic attraction between Li and F atoms.

In addition, the calculations have shown that dissociative reaction of H₂GeLiF is largely endothermic.



This indicates that it is impossible for germylene to exist free when it coexists with LiF, while germynoid, H₂GeLiF, may be a reactive intermediate.

According to the above analysis, it is known that isomers **3** and **4**, are instable, isomer **2** has a short life time, and only isomer **1** is an equilibrium and experimentally detectable structure of H₂GeLiF. The stability of the equilibrium structures is in the order of **1**>**2**>**4**>**3**. The obtained results are of importance as reference to study the reaction of germynoids and to exploit the new fields of organogermanium chemistry. The study on a variety of germynoids, RR'GeMX, involving different metals, halogens, and organic groups has been undertaken in our laboratory.

All calculations were performed by using Gaussian-92 program, and structural

geometries were optimized by gradient technique at the 3-21G*⁶ (6d polarization function on germanium atom). The third-order MØller-Plesset correlation energy correction was computed with use of the frozen core approximation, which includes all single, double, triple and quadruple substitutions.

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