



## A Computational Study on 1-silaallene and 2-silaallene

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### Abstract

The structural data and vibrational frequencies of 1- and 2-silaallenes have been studied computationally using the Gaussian 03 suite of programs. All of 15 normal modes were assigned to one of six types of motion (symmetrical stretching, antisymmetrical stretching, scissoring, rocking, wagging, twisting) determined by a group of quantum chemical analysis. Predicted geometric features, vibrational frequencies, and infrared intensities are also reported herein.

*Keywords:* 1-silaallene; 2-silaallene; vibrational frequencies; normal modes; IR

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### 1. Introduction

Compounds with multiple bonds to silicon have attracted more and more interest since their first isolation in 1981, due to their unique properties compared to carbon analogs [1]. Although chemists have made and afford to synthesize compound which include a cumulenenic double bond to silicon [2], the first 1-silaallene was synthesized and isolated as a stable compound by West and co-workers in 1993. It was stabilized by an extremely large steric hindrance around the Si=C=C moiety and characterized by X-ray crystallography, revealing that it is slightly bent ( $173.5^\circ$ ) in contrast to the carbon analogue allene, which is linear [3].

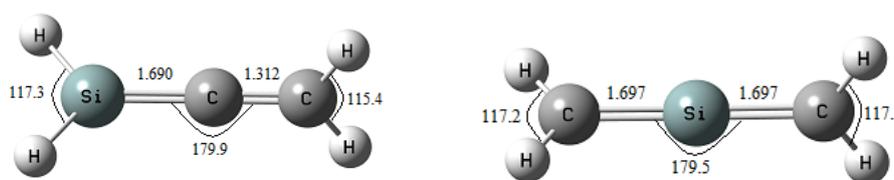
Interpretation of an experimental IR spectrum of silaallenes is a difficult task due to the problems encountered in their synthesis and isolation [1-5]. Literature survey also reveals that to the best of our knowledge no HF/DFT vibrational frequency calculations and corresponding normal mode assignments of 1- and 2-silaallenes without substituents have been reported to this date. Hence, we would like to present the geometric parameters, vibrational frequencies and characteristic normal mode frequencies of 1- and 2-silaallenes.

## 2. Computational methods

The computations were performed using the Gaussian 03 program package [6]. First of all, both structures (1-silaallene and 2-silaallene) were optimized at B3LYP/6-31G(d) level which is very successful in modeling for allenes [7,8,9]. The vibrational frequencies of 1- and 2-silaallene were calculated at the DFT (B3LYP) levels of theory with 6-31+G(d,p) and 6-31+G(d,p) basis sets. The computational method helped us to determine the normal modes of 1- and 2-silaallenes. Agreement among the method is a useful indicator that the vibrational modes have been correctly assigned for silaallenes. Each motion (symmetrical stretching, antisymmetrical stretching, scissoring, rocking, wagging, twisting) of normal modes were interpreted by means of visual inspection with help of GaussView program [11,12].

## 3. Result and discussion

The optimized structures of 1- and 2-silaallenes are shown in Figure 1. Although trisilaallene exhibit a very acute Si=Si=Si angle of  $136.5^\circ$  [13], the both studied molecules are linear with the bending angles of  $179.9^\circ$  and  $179.5^\circ$  at B3LYP/6-31G(d) level of theory, respectively. It is shows that the bond angles of 2-silaallene decreases slightly compared to 1-silaallene. The C=Si bonds on the 1- and 2-silaallenes are a little bit different from each other with 1.690 Å and 1.697 Å at B3LYP/6-31G(d) level of theory.



**Figure 1.** The optimized structures of 1-silaallene (*left*) and 2-silaallene (*right*) at B3LYP/6-31G(d) level of theory.

Tables 1 and 2 present the calculated vibrational frequencies for 1- and 2-silaallenes at DFT (B3LYP) level of theory using the standard 6-31G(d) and 6-31+G(d,p) basis sets, respectively. For the calculated frequencies of 1- and 2-silaallenes, there are very little variations of vibrational frequencies in the different symmetries within each level of theory. We can see easily from the results, the procedure cause to trustable estimations. However, as a result of calculations which are several levels of theory, there are a bit difference on the data of vibrational frequencies and IR intensities on the same band. For instance, the calculated frequency of C=Si=C bend ( $V_1$ ) of 2-silaallene is  $49.0\text{ cm}^{-1}$  at B3LYP/6-31G(d), whereas it is  $78.6\text{ cm}^{-1}$  at B3LYP/6-31+G(d,p). In addition, the increasing in the intensity of the C=Si=C bend for 2-silaallene can be easily seen from Table 2.

**Table 1.** The calculated Frequencies ( $\text{cm}^{-1}$ ) and IR intensities (km/mol) for 1-silaallene at B3LYP/6-31G(d) and B3LYP/6-31+G(d,p) levels of theory.

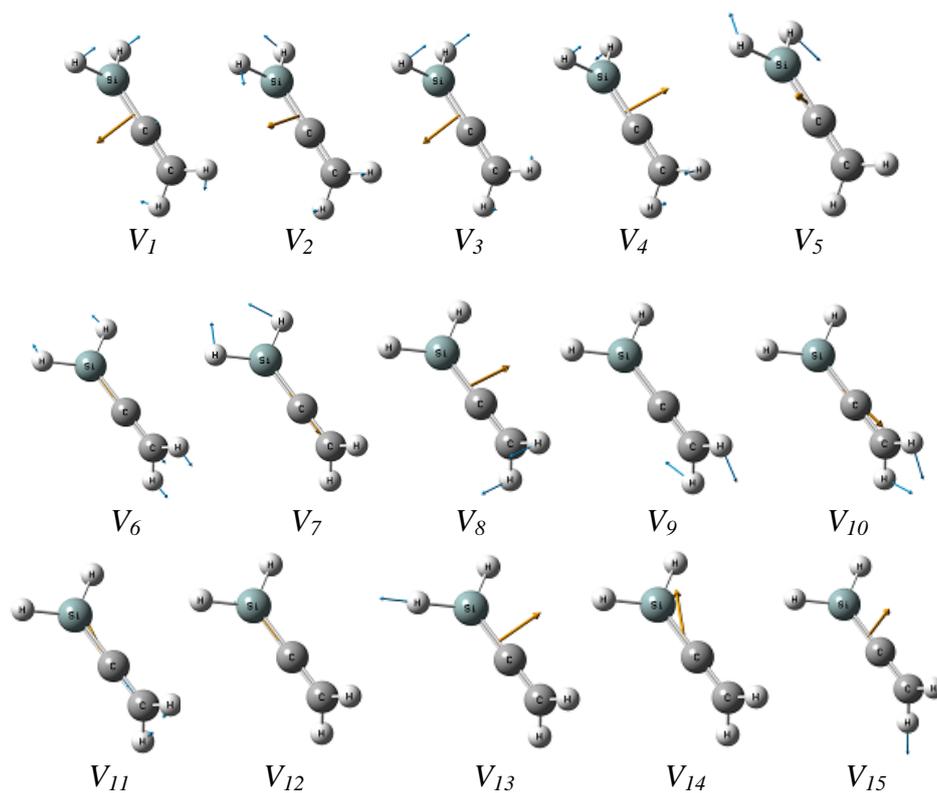
1-silaallene		B3LYP/6-31G(d)		B3LYP/6-31+G(d,p)	
Normal mode	Assignment	Calculated frequency	IR intensity	Calculated frequency	IR intensity
$V_1$	C=C=Si bend	172.9	8	180.1	17
$V_2$	C=C=Si bend	260.7	4	265.6	9
$V_3$	H-Si-H wag	392.8	2	391.5	3
$V_4$	H-Si-H twist	666.3	<1	660.3	<1
$V_5$	H-Si-H rock	667.9	70	663.7	78
$V_6$	Si=C stretch	775.4	<1	770.7	2
$V_7$	H-Si-H scissors	941.8	77	938.7	75
$V_8$	H-C-H wag	951.4	37	953.2	42
$V_9$	H-C-H rock	1021.5	<1	1012.1	<1
$V_{10}$	H-C-H scissors	1457.6	2	1437.33	<1
$V_{11}$	C=C stretch	1823.1	1	1808.3	4
$V_{12}$	H-Si-H stretch	2296.0	40	2287.5	37
$V_{13}$	H-Si-H Anti-stretch	2319.6	97	2309.9	85
$V_{14}$	H-C-H stretch	3100.1	25	3087.9	22
$V_{15}$	H-C-H Anti-stretch	3158.5	6	3150.9	5

**Table 2.** The calculated Frequencies ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{km/mol}$ ) for 2-silaallene at B3LYP/6-31G(d) and B3LYP/6-31+G(d,p) levels of theory.

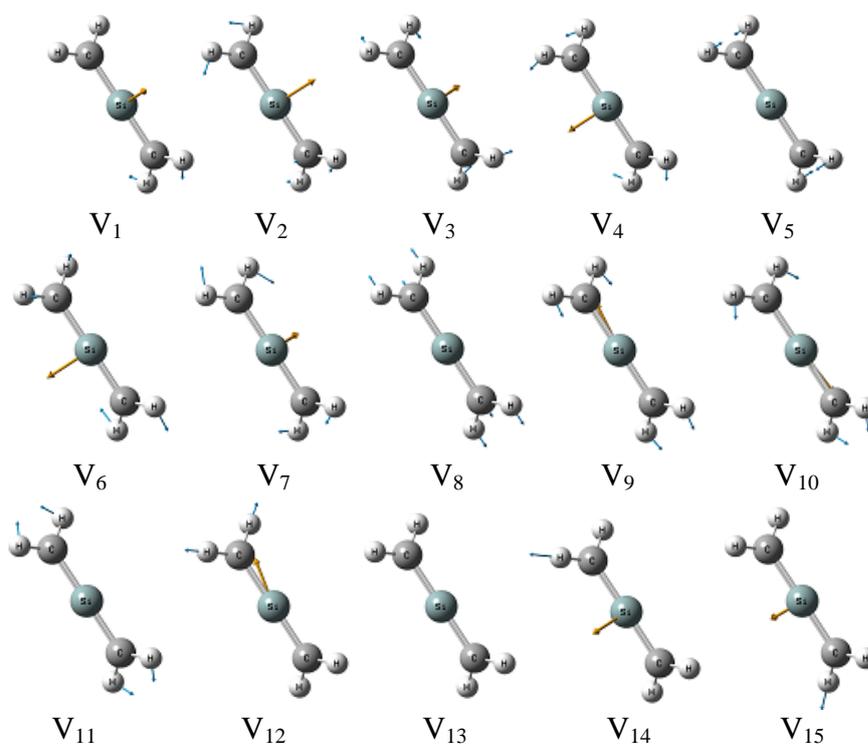
2-silaallene		B3LYP/6-31G(d)		B3LYP/6-31G(d,p)	
Normal mode	Assignment	Calculated frequency	IR intensity	Calculated frequency	IR intensity
V <sub>1</sub>	C=Si=C bend	49.0	4	78.6	7
V <sub>2</sub>	C=Si=C bend	49.0	4	78.6	7
V <sub>3</sub>	H-C-H wag	583.1	54	584.6	64
V <sub>4</sub>	H-C-H rock	583.3	54	584.6	64
V <sub>5</sub>	H-C-H twist	662.7	<1	641.2	<1
V <sub>6</sub>	H-C-H wag	755.9	1	749.2	2
V <sub>7</sub>	H-C-H rock	755.9	1	749.2	2
V <sub>8</sub>	C=Si stretch	820.6	<1	815.4	<1
V <sub>9</sub>	C=Si stretch	1157.6	25	1149.1	47
V <sub>10</sub>	H-C-H scissors	1368.2	12	1363.9	19
V <sub>11</sub>	H-C-H scissors	1390.1	<1	1369.2	0
V <sub>12</sub>	H-C-H stretch	3180.9	2	3196.3	2
V <sub>13</sub>	H-C-H stretch	3183.3	<1	3171.7	0
V <sub>14</sub>	H-C-H Anti-stretch	3277.1	1	3270.9	2
V <sub>15</sub>	H-C-H Anti-stretch	3277.3	1	3270.9	2

The Si-H group is readily identified by a strong band in the range 2280-2080. There is no interference from other bands in this part of group [14]. In addition, the vibrational frequencies of C-H stretch, and C=C stretch are found, 3079, 1423  $\text{cm}^{-1}$  experimentally, respectively [14]. There are very close results which are compared to experimental data in this study. For example, the Si-H stretch, C-H stretch, and C=C stretch of 1 silaallene were calculated 2296.0  $\text{cm}^{-1}$ , 3100.1  $\text{cm}^{-1}$ , 1823.1  $\text{cm}^{-1}$  at B3LYP/6-31G(d), respectively (Table 1).

Figure 2 and 3 present a view of the normal modes of 1- and 2-silaallenes using GaussView 3.0 program [12]. The arrows on the figures show dipole derivative unit vector (in *red color*) and displacement vectors (in *blue color*). Table 3 presents the calculated geometric parameters for 1- and 2-silaallenes at B3LYP/6-31G(d) and B3LYP/6-31+G(d,p) levels. Figure 4 also depicts the illustration of IR spectra analyses of 1- and 2-silaallenes. The spectra analyses were computed at B3LYP/6-31G(d) level of theory with help of Gaussian set of electronic structure program.



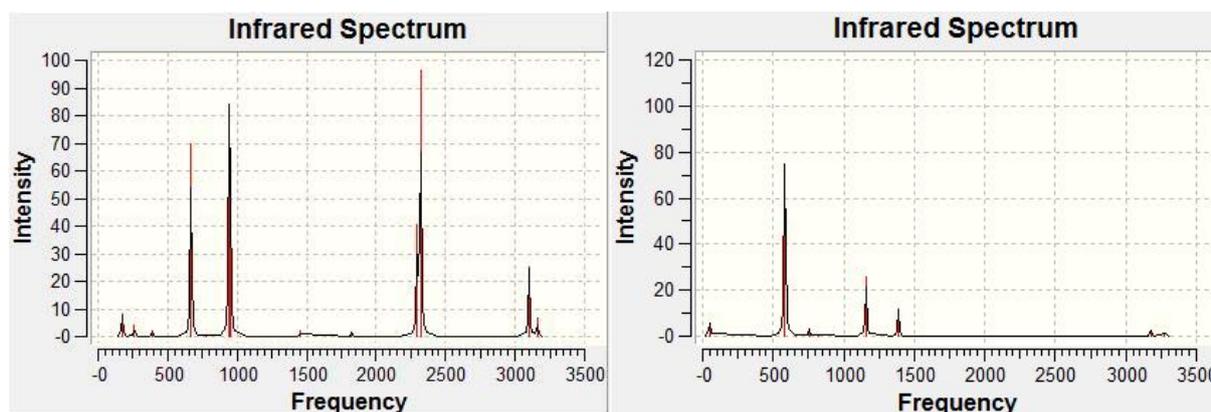
**Figure 2.** Normal Modes of 1-silaallene at B3LYP/6-31G(d) visualized with the help of Gaussview 3.0 program.



**Figure 3.** Normal Modes of 2-silaallene at B3LYP/6-31G(d) visualized with the help of Gaussview 3.0 program

**Table 3.** Calculated Bond Lengths (Å) and Bond Angles (degree) at B3LYP/6-31G(d), B3LYP/6-31+G(d,p) levels of theories for 1- and 2-silaallenes.

<i>Molecules</i>		<b>B3LYP/6-31G(d)</b>	<b>B3LYP/6-31+G(d,p)</b>
<b>1-silaallene</b>	<i>Bond length</i>		
	C-H	1.092	1.092
	Si-H	1.475	1.472
	C=C	1.312	1.314
	Si=C	1.690	1.692
	<i>Bond angle</i>		
	Si-C-C	179.9	179.9
H-Si-C-H	-90	-90	
<b>2-silaallene</b>	<i>Bond length</i>		
	C-H	1.084	1.084
	C-Si	1.697	1.698
	<i>Bond angle</i>		
	C-Si-C	179.5	179.6
H-C-C-H	-90	-90	



**Figure 4.** The IR spectra of 1-silaallene (*left*) and 2-silaallenes (*right*) at B3LYP/6-31G(d) level of theory

#### 4. Conclusions

The normal mode geometries and corresponding vibrational frequencies in *C<sub>s</sub>* symmetry were studied theoretically using the Gaussian 03W set of quantum chemistry codes. All normal modes were successfully determined in accordance with six of motion (symmetrical stretching, antisymmetrical stretching, scissoring, rocking, wagging, twisting) with help of a group of theoretical analysis. In addition to that infrared intensities are reported in this study. These findings would be helpful for further studies of 1- and 2-silaallenes.

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## References

- [1] For reviews, see: (a) G. Raabe, J. Michl, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, vol. 1, Wiley, Chichester (1989) Chapter 17; (b) T. Müller, W. Ziche, N. Auner, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organosilicon Compounds*, vol. 2, Wiley, Chichester (1998) Chapter 16; (c) Y. Apeloig, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Organosilicon Compounds*, Wiley, Chichester (1989) Chapter 2; (d) A.G. Brook, M.A. Brook, *Adv. Organomet. Chem.* 39 (1996) 71; (e) J. Escudie', C. Couret, H. Ranaivonjatovo, *Coord. Chem. Rev.* 178 (1998) 565; (f) R. Okazaki, R. West, *Adv. Organomet. Chem.* 39 (1996) 231; (g) T. Tsumuraya, S.A. Bathceler, S. Masamune, *Angew. Chem. Int. Ed. Engl.* 32 (1991) 902.
- [2] For reviews, see: (a) B. Eichler, R. West, *Adv. Organomet. Chem.* 46 (2001) 1; (b) J. Escudie, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* 100 (2000) 3639.
- [3] (a) G.E. Miracle, J.L. Ball, D.R. Powell, R. West, *J. Am. Chem. Soc.* 115 (1993) 11598; (b) M. Trommer, G.E. Miracle, B.E. Eichler, D.R. Powell, R. West, *Organometallics* 16 (1997) 737.
- [4] N. Sigal, Y. Apeloig, *Organometallics* 21 (2002) 5486-5493..
- [5] J.E. Rode, J.C. Dobrowolski, *J. Mol. Struct. (THEOCHEM)* 635 (2003) 151.
- [6] Gaussian 03, Revision C.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J.C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin,

R.L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

[7] A. Azizoglu, O. Demirkol, T. Kilic, Y.K. Yildiz, *Tetrahedron* 63 (2007) 2409–2413.

[8] A. Azizoglu, R. Ozen, T. Hokelek, M. Balci, *J. Org. Chem.* 69 (2004) 1202–1206.

[9] J.-L. Mieusset, U. H. Brinker, *J. Org. Chem.* 70 (2005) 10572–10575.

[11] A. Frisch, A.B. Nielsen, A.J. Holder, *Gaussview Users Manual*, Gaussian, Inc., Pittsburgh, 2000.

[12] Silverstein R.M., Webster F.X.: *Spectroscopic Identification of Organic Compounds*, sixth ed., John Wiley&Sons Inc., New York 2005.

[13] M. Kosa, M. Karni, Y. Apeloig, *J. Am. Chem. Soc.* 126 (2004) 10544-10545.

[14] (a) D.R. Anderson, in “*Analysis of Silicones*”, A. L. Smith, Wiley-interscience, New York, (1974), Chapter 10.; (b) L. J. Belamy, “*The Infrared Spectra of Complex Molecules*”, 3rd ed., Chapman and Hall London, (1975), Chapter 20.; (c) A. L. Smith, *Spectrochim. Acta A* 16 (1960) 87.