

Structures and N→Si Bond Characters of 1-Fluorosilatrane and the Silatranyl Cation<sup>†</sup>Hyo Sug Lee,<sup>‡</sup> Cheolbeom Bae, Youngkyu Do,<sup>\*</sup> and Yoon Sup Lee<sup>\*</sup>

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The structures of 1-fluorosilatrane and the silatranyl cation were calculated by Hartree-Fock (HF), Møller-Plesset second order (MP2), and various density functional theory (DFT) methods using many different basis sets, demonstrating that the Si-N bonds in two species are quite different. The N→Si bond distance of 1-fluorosilatrane from the hybrid DFT calculations (~2.32 Å) using the Perdew-Wang correlation functional agrees with the gas phase experimental value (2.324 Å), while other functionals yield larger distances. The MP2 bond distance (2.287 Å with 6-311G\*) is shorter, and the HF one (2.544 Å with 6-311G\*) larger than those of DFT calculations. The MP2 bond distance is in good agreement with experiment indicating that the electron correlations are crucial for the correct description of the N→Si interaction. The silatranyl cation is a stable local minimum on the potential energy surface in all methods employed suggesting that the cation could be a reaction intermediate. The Si-N bond length for the cation is about 1.87 Å for all calculations tested implying that the Si-N bond is mainly conventional. Bonding characteristics of the Si-N bond in two species derived from the natural bond orbital analysis support the above argument based on calculated bond lengths.

**Keywords :** 1-Fluorosilatrane, Silatranyl cation, Transannular bond, *Ab initio*, Density functional method.

## Introduction

Silatranes which constitute the unique and well studied class of pentacoordinated silicon derivatives<sup>1</sup> feature a hypervalent silicon atom with a transannular dative bonding interaction between the silicon and the bridged nitrogen atom. The structure and the stability of the silatranyl cation in gas phase are of interest from the theoretical point of view as a possible candidate of isolable cation and the reaction intermediate.<sup>2,3</sup> The nature of the substituents affects not only the range of biological activities<sup>4</sup> including antitumor properties<sup>5</sup> but also the strength of the transannular dative N→Si bonding.<sup>6</sup> The crystal structures of various substituted neutral silatranes have the Si-N distances in the range, 2.02-2.20 Å. The observed N→Si bonds of 1-methylsilatrane and 1-fluorosilatrane in gas phase are quite longer than those in solid state.<sup>7,8</sup> It is known that the N→Si interaction is weak and the potential energy surface is very flat. These observations lead to the expectation that there may be no actual Si-N bond in the gas phase and that the silicon and nitrogen are held more tightly in the solid due to the crystal forces.

Many theoretical studies have been reported on the equilibrium geometries of the 1-fluoro, 1-chloro, 1-methyl, hydroxysilatrane and 1-isothiocyatosilatrane.<sup>9-18</sup> The geometries of these molecules have been optimized by semiempirical (MNDO, PM3 and AM1), restricted Hartree-

Fock (RHF), and density functional theory (DFT) calculations. The calculated N→Si bond lengths were much longer than the experimental values in all these studies. Gordon *et al.*<sup>9,10</sup> have concluded that there is a dative bonding between Si and N atom using Boys localized density analysis developed by Bader<sup>19</sup> and Boys localized orbitals<sup>20</sup> although the calculated bond length is much longer than experimental values.

It is certain that the dative N→Si bond is present, but the nature of the bond has not been studied in detail. To the best

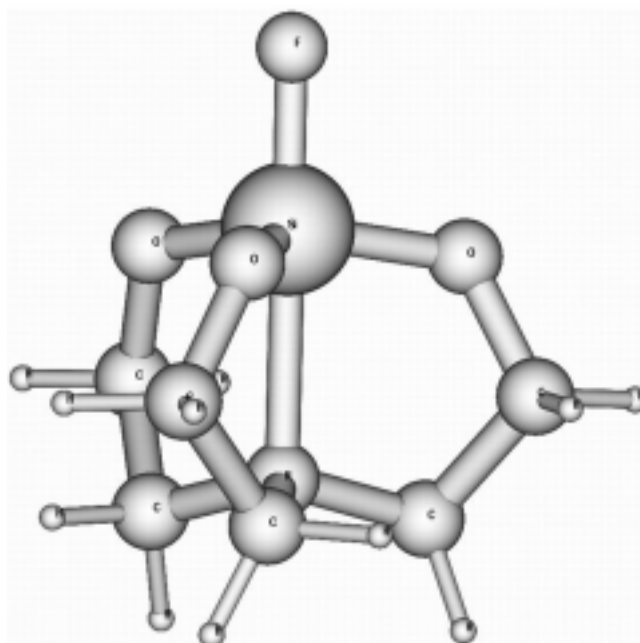
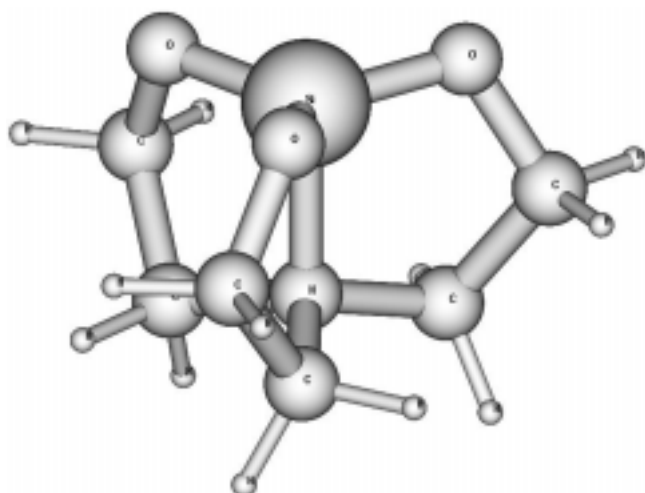


Figure 1. Structure of 1-fluorosilatrane.

<sup>†</sup>Dedicated to Professor Kyung-Hoon Jung in appreciation of his great contribution to physical chemistry

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**Figure 2.** Structure of the silatranyl cation.

of our knowledge, there have been no study on the silatranyl cation. In this study the structures of 1-fluorosilatrane and the silatranyl cation have been obtained from HF, hybrid DFT, and the second order Møller-Plesset perturbation (MP2) calculations with various basis sets. Figure 1 and Figure 2 show the structure of 1-fluorosilatrane and the silatranyl cation, respectively. Extensive set of DFT functionals was tested in an effort to assess the performance of DFT for the silatrane-type molecules which have flat potential energy surface near minimum. We analyzed the character of N→Si tansannular bond using the natural bond orbital (NBO) analysis.<sup>21</sup>

### Method and Computational Details

HF, hybrid DFT, and MP2 calculations have been performed to optimize geometries of the 1-fluorosilatrane and the silatranyl cation. As the hybrid DFT methods, Becke's one parameter hybrid functional with the Lee-Yang-Parr (LYP) correlation functional as implemented by Adamo and Barone (B1LYP),<sup>22,23</sup> Becke's three parameter hybrid functional with the LYP correlation functional (B3LYP),<sup>24</sup> Becke's three parameter hybrid functional with Perdew-Wang91 (PW91) correlation functional (B3PW91), and Barone and Adamo's Becke-style one parameter hybrid functional with modified Perdew-Wang exchange and Perdew-Wang91 correlation functional (mPW1PW91)<sup>25</sup> were employed with 6-31G\*, 6-31+G\*, 6-311G\*, 6-311+G\* basis sets. The MP2 calculations were performed with 6-31G\*, 6-31+G\*, 6-311G\* basis sets. We use the natural bond analysis (NBO) methods<sup>21</sup> to analyse the nature of the N→Si tansannular dative bond. Calculations have been performed on the CRAY-C90 computers at KISTI using the Gaussian98 program.<sup>26</sup>

### Results and Discussion

Table 1 shows the optimized geometry of 1-fluorosilatrane at the HF, MP2, and various hybrid DFT levels of theory using 6-31G\*, 6-31+G\*, 6-311G\*, and 6-311+G\* basis sets.

**Table 1.** Calculated bond lengths(in Å) of 1-fluorosilatrane

Basis set	Method	R(Si-N)	R(Si-F)	R(Si-O)
6-31G*	HF	2.555	1.581	1.633
	MP2	2.283	1.615	1.679
	B1LYP	2.466	1.603	1.661
	B3LYP	2.428	1.605	1.664
	B3PW91	2.358	1.606	1.667
	mPW1PW91	2.307	1.604	1.667
6-31+G*	HF	2.523	1.588	1.634
	MP2	2.251	1.629	1.684
	B1LYP	2.404	1.617	1.666
	B3LYP	2.394	1.619	1.669
	B3PW91	2.285	1.620	1.673
	mPW1PW91	2.271	1.616	1.669
6-311G*	HF	2.544	1.583	1.627
	MP2	2.287	1.612	1.669
	B1LYP	2.473	1.609	1.658
	B3LYP	2.458	1.611	1.661
	B3PW91	2.355	1.611	1.664
	mPW1PW91	2.364	1.607	1.659
6-311+G*	HF	2.537	1.584	1.628
	B1LYP	2.439	1.614	1.660
	B3LYP	2.424	1.616	1.663
	B3PW91	2.310	1.616	1.667
	mPW1PW91	2.294	1.613	1.664
	<i>exp.</i>	crystal	2.042	1.622
gas phase		2.324	1.568	1.652

In the silatrane molecules the most interesting parts are the Si-N bond length and whether there is a bonding between Si and N. In the gas phase experiment, the Si-N bond length of 1-fluorosilatrane is 2.324 Å, longer by 0.282 Å than that of the solid state. The Si-N distance at the HF level is longer than the gas phase experimental value by about 0.2 Å. As the electron correlation effects strongly contract the Si-N distance, the Si-N distance at the MP2 level is shorter than that of the gas phase experimental value but longer than that of the solid state. The optimized Si-N bond length at the MP2/6-31+G\* level is 2.251 Å, the shortest distance in this work, but still in reasonable agreement with experiment. It is clear that the electron correlation is essential for the right structure. The hybrid DFT calculations with the B1LYP and B3LYP functionals produce longer Si-N distances than the experimental value by 0.07-0.15 Å. The Si-N distance is 2.285-2.355 Å in the B3PW91 calculations. Using the mPW1PW91 functional, the calculated Si-N distances are 2.271-2.364 Å which are shorter than those in other hybrid DFT methods. The Si-N distance agrees well with the gas phase experimental value in the case of PW91 correlation functional while the calculations with the LYP correlation functional always result in longer Si-N distances than the experiment. It appears that the PW91 correlation functional describes the N→Si interaction better than the LYP ones. The nitrogen atom of 1-fluorosilatrane has a lone pair which interacts with the silicon atom. When the diffuse basis functions are included as in 6-31+G\* and 6-311+G\* basis

**Table 2.** Calculated bond lengths (in Å) of the silatranyl cation

Basis set	Method	R(Si-N)	R(Si-O)
6-31G*	HF	1.857	1.605
	MP2	1.881	1.637
	B1LYP	1.879	1.628
	B3LYP	1.882	1.630
	B3PW91	1.875	1.629
	<i>m</i> PW1PW91	1.871	1.626
6-31+G*	HF	1.856	1.604
	MP2	1.877	1.639
	B1LYP	1.879	1.630
	B3LYP	1.881	1.632
	B3PW91	1.873	1.630
	<i>m</i> PW1PW91	1.869	1.626
6-311G*	HF	1.855	1.599
	MP2	1.872	1.627
	B1LYP	1.879	1.625
	B3LYP	1.881	1.627
	B3PW91	1.873	1.625
	<i>m</i> PW1PW91	1.869	1.622
6-311+G*	HF	1.855	1.600
	B1LYP	1.881	1.626
	B3LYP	1.882	1.628
	B3PW91	1.874	1.626
	<i>m</i> PW1PW91	1.870	1.622

sets, the Si-N distance becomes shorter by 0.03-0.07 Å than the results of 6-31G\* and 6-311G\* basis sets. The N→Si

interaction is well described by the correlation effects or PW91 correlation functional and the diffuse basis sets.

Table 2 shows the optimized structure of the silatranyl cation. This cation is stable and may play an important role as an intermediate in the reaction of silatranes. This cation exhibit different bonding characteristics compared with the 1-fluorosilatrane. As the Si atom has four coordinations, there is a substantial increase of covalent bonding between Si and N atoms. The Si-N bond length about 1.88 Å is substantially shorter than that of 1-fluorosilatrane. While the Si-N distance of silatrane is contracted by the correlation effects, the Si-N distance of the silatranyl cation is elongated by about 0.02 Å. There is little difference between the results of the LYP correlation functional and those of PW91 correlation functional. The effects of the diffuse basis functions are negligible since the Si-N bond is not a dative bond any more. The bond angle around the Si atom ( $\angle$ O-Si-N) in the silatranyl cation is about 97° which means that the Si atom lies below the plane made by three oxygen atoms (Figure 2). On the contrary, the  $\angle$ O-Si-N of 1-fluorosilatrane is about 82° (Figure 1). The Si atom lies above the plane of three oxygen atoms. The silatranyl cation is a local minimum on the potential energy surface with a definite Si-N bond.

Table 3 and Table 4 show the atomic charge analyses for 1-fluorosilatrane and the silatranyl cation, respectively. In both Tables the atomic charges from the Mulliken population analysis (MPA) depend strongly on the method and the basis set. The MPA atomic charge on the Si atom of 1-

**Table 3.** Calculated atomic charges of 1-fluorosilatrane from Mulliken population analysis (MPA) and natural population analysis (NPA)

Basis set	Method	MPA			NPA		
		Q(Si)	Q(N)	Q(F)	Q(Si)	Q(N)	Q(F)
6-31G*	HF	1.704	-0.716	-0.477	2.678	-0.646	-0.693
	MP2	1.392	-0.568	-0.409	2.429	-0.593	-0.645
	B1LYP	1.254	-0.491	-0.364	2.460	-0.586	-0.642
	B3LYP	1.222	-0.476	-0.355	2.440	-0.581	-0.638
	B3PW91	1.238	-0.499	-0.363	2.424	-0.586	-0.639
	<i>m</i> PW1PW91	1.256	-0.521	-0.370	2.435	-0.549	-0.644
6-31+G*	HF	2.755	-0.642	-0.476	2.700	-0.682	-0.708
	MP2	2.303	-0.916	-0.433	2.468	-0.618	-0.671
	B1LYP	2.136	-0.690	-0.335	2.513	-0.615	-0.674
	B3LYP	2.075	-0.687	-0.327	2.495	-0.610	-0.671
	B3PW91	1.962	-0.700	-0.320	2.467	-0.613	-0.668
	<i>m</i> PW1PW91	2.000	-0.704	-0.319	2.479	-0.619	-0.671
6-311G*	HF	1.831	-0.596	-0.513	2.591	-0.642	-0.679
	MP2	1.496	-0.480	-0.488	2.318	-0.584	-0.628
	B1LYP	1.454	-0.444	-0.419	2.388	-0.589	-0.635
	B3LYP	1.428	-0.437	-0.414	2.369	-0.585	-0.631
	B3PW91	1.421	-0.457	-0.420	2.338	-0.584	-0.630
	<i>m</i> PW1PW91	1.432	-0.466	-0.421	2.354	-0.587	-0.633
6-311+G*	HF	1.721	0.292	-0.275	2.588	-0.677	-0.680
	B1LYP	1.323	0.058	-0.245	2.400	-0.621	-0.646
	B3LYP	1.285	0.053	-0.240	2.381	-0.616	-0.642
	B3PW91	1.152	0.164	-0.216	2.340	-0.611	-0.638
	<i>m</i> PW1PW91	1.156	0.204	-0.209	2.350	-0.615	-0.641

**Table 4.** Calculated atomic charges of the silatranyl cation from Mulliken population analysis (MPA) and natural population analysis (NPA)

Basis set	Method	MPA		NPA	
		Q(Si)	Q(N)	Q(Si)	Q(N)
6-31G*	HF	1.627	-0.791	2.671	-0.745
	MP2	1.353	-0.606	2.452	-0.661
	B1LYP	1.243	-0.547	2.481	-0.674
	B3LYP	1.216	-0.530	2.464	-0.668
	B3PW91	1.240	-0.544	2.454	-0.665
	<i>m</i> PW1PW91	1.258	-0.562	2.468	-0.669
6-31+G*	HF	2.917	-1.238	2.689	-0.774
	MP2	2.258	-1.209	2.482	-0.685
	B1LYP	2.282	-1.107	2.521	-0.697
	B3LYP	2.217	-1.086	2.505	-0.691
	B3PW91	2.034	-0.999	2.489	-0.686
	<i>m</i> PW1PW91	2.085	-1.006	2.502	-0.691
6-311G*	HF	1.756	-0.720	2.576	-0.723
	MP2	1.458	-0.556	2.352	-0.643
	B1LYP	1.438	-0.549	2.401	-0.663
	B3LYP	1.416	-0.539	2.385	-0.658
	B3PW91	1.415	-0.548	2.370	-0.651
	<i>m</i> PW1PW91	1.426	-0.558	2.382	-0.654
6-311+G*	HF	1.461	-0.029	2.578	-0.751
	B1LYP	1.101	-0.163	2.416	-0.687
	B3LYP	1.069	-0.160	2.400	-0.681
	B3PW91	0.964	-0.018	2.381	-0.673
		<i>m</i> PW1PW91	0.981	0.015	2.393

fluorosilatrane varies from 1.152 to 2.755 as the method and the basis set vary. The MPA atomic charge on the N atom of 1-fluorosilatrane is also sensitive to the method and the basis set. One extreme is the positive charge of 0.292 for the N atom with 6-311+G\* basis set. The atomic charges from the natural population analysis (NPA), on the contrary, have little dependence on the method and the basis set. The NPA atomic charges of the Si atom of 1-fluorosilatrane are 2.3~2.5, and those of the N atom -0.58~-0.62. While the charge of the Si atom differs very little between 1-fluorosilatrane and the silatranyl cation, the NPA charges on the N atom of the silatranyl cation are -0.65~-0.69 which are more negative (about -0.07) than that of 1-fluorosilatrane.

Table 5 shows the bond characteristics of 1-fluorosilatrane. In the NBO analysis from the MP2//MP2/6-31+G\*, there is a bond between the Si and the N atom. The occupation is 1.862. This bond is mainly the N atom (96%) with a small contribution from the Si atom (4%). The Si atom has 12% s character, 42% p character, and 42% d character in the Si-N bond. The N atom has 13% s character, and 87% p character. The Si-N NBO is formed from the  $sp^{3.86}d^{3.48}$  hybrid on the Si atom interacting with the  $sp^{6.60}$  hybrid on the N atom. The d character of Si atom plays an important role in this bond. The d character of the Si atom also contributes to the Si-O and Si-F bonds. The Si atom has 13% d character in the Si-O bond and 25% d character in the Si-F bond. There is no bond between the Si and the N atoms

**Table 5.** Natural bond orbital analysis for bond characters of 1-fluorosilatrane calculated with the 6-31+G\* basis set

Method	Bond	Occupation	Atom	Ratio of Bonding (%)	hybrids (%)		
					s	p	d
MP2//MP2							
	Si-N	1.862	Si	4.01	11.99	46.23	41.77
			N	95.99	13.17	86.83	0.00
	Si-O	1.912	Si	11.43	22.26	65.49	12.25
			O	88.57	31.01	68.79	0.20
	Si-F	1.940	Si	9.67	23.67	51.51	24.92
			F	90.33	39.08	60.71	0.21
MP2//B3PW91							
	Si-N	1.857	Si	3.83	11.93	45.93	42.13
			N	96.17	11.33	88.67	0.00
	Si-O	1.921	Si	11.42	22.30	65.56	12.13
			O	88.58	31.39	68.41	0.20
	Si-F	1.940	Si	9.73	23.83	51.65	24.52
			F	90.27	39.60	60.18	0.21
B3PW91//B3PW91							
			N	100.0	10.84	89.16	0.00
	Si-O	1.971	Si	13.58	26.98	70.71	2.31
			O	86.42	32.63	67.20	0.17
	Si-F	1.983	Si	11.69	19.56	78.24	2.19
			F	88.31	40.94	58.83	0.23
B3PW91//MP2							
			N	100.0	12.65	87.35	0.00
	Si-O	1.971	Si	13.60	27.10	70.60	2.30
			O	86.40	32.22	67.61	0.17
	Si-F	1.982	Si	11.63	19.18	78.56	2.26
			F	88.37	40.42	59.35	0.23

in the B3PW91//B3PW91/6-31+G\* result. In any other hybrid DFT methods, there is no bond between the Si and the N atoms. In addition, the d character of the Si atom does not contribute to the Si-O or the Si-F bond. While there is a dative bond between Si and N atoms in the MP2//B3PW91 calculations, the N atom has a lone pair in the B3PW91//MP2 calculation. The present analysis implies that the Si-N bonding is not evident in the DFT calculations, and the variation of the Si-N distance is not due to the Si-N bonding. The Si atom in 1-fluorosilatrane has a large positive charge, about 2.6, and there remains about 1.4 valence electrons. These electrons must be responsible for 5 bonds around Si atom, three Si-O bonds, one Si-F bond and one Si-N bond. Major contributions are from other atoms. The Si-O bond is 89% O atom, and the Si-F bond 90% F atom.

Table 6 shows the bonding characteristics of the silatranyl cation. There is a bonding between Si and N atoms and, furthermore, the hybrids are quite similar among MP2 and different DFT methods. The Si atom has 19% s character, 78% p character, and 3% d character in the Si-N bond. The N atom has 18% s character and 82% p character. This bond is formed from the  $sp^{4.11}$  hybrid on the Si atom interacting with the  $sp^{4.44}$  hybrid on the N atom according to the MP2 calculations. The d character of the Si atom also contributes

**Table 6.** Natural bond orbital analysis for bond characters of 1-fluorosilatrane calculated with the 6-31+G\* basis set

Method	Bond	Occupation	Atom	Ratio of Bonding (%)	hybrids (%)		
					s	p	d
MP2//MP2							
	Si-N	1.913	Si	10.39	18.95	77.81	3.24
			N	89.61	18.38	81.55	0.06
	Si-O	1.940	Si	13.92	27.35	70.27	2.38
			O	86.08	30.56	69.14	0.31
B3PW91//B3PW91							
	Si-O	1.944	Si	11.19	19.25	77.61	3.14
			N	88.81	18.55	81.41	0.04
	Si-F	1.968	Si	14.71	27.22	70.54	2.24
			O	85.29	32.03	67.70	0.28

to the Si-O bond. The Si-O bond is formed from the  $sp^{2.57}$  hybrid on the Si atom and the  $sp^{2.26}$  hybrid on the N atom. In the DFT method, there is no concept about the multi-configuration induced by the electron excitations. The electron correlations are only expressed by the correlation functional. If the atom has only s and p valence electrons and the d character of the atom contained in the hybrids are all due to electron correlations, as in this 1-fluorosilatrane, the NBO cannot show any d character in DFT methods. In other words only the molecular orbital methods can express the  $sp^a d^f$  hybrids by the NBO analysis. The silatranyl cation is not hypervalent. The hybrids need only the valence s and p characters. In this case, the bonding characters in DFT and *ab initio* methods by NBO analysis are similar.

### Conclusions

The structures of 1-fluorosilatrane and the silatranyl cation are optimized with HF, MP2, and various hybrid DFT methods using various basis sets. The correlation effects are very important in the 1-fluorosilatrane. The Si-N distance in MP2 calculations is shorter than the gas phase experimental value but longer than that of the crystal. Among the hybrid DFT methods, the B3PW91 and mPW1PW91 functionals describe the Si-N distance well while the Si-N distance is quite longer than the experimental one in B1LYP and B3LYP calculations. In 1-fluorosilatrane, the diffuse basis functions are important, accounting for the decrease of the Si-N distance by about 0.03 Å-0.07 Å. In the silatranyl cation the Si atom is on the side of the N atom with respect to the plane of the three O atoms while the Si atom in 1-fluorosilatrane is on the other side of the plane. The Si-N distance in the silatranyl cation is about 1.87 Å.

The NBO analysis of 1-fluorosilatrane shows that the d character in the Si atom plays an important role. The Si-N bond is formed by a  $sp^{3.86} d^{3.48}$  hybrid on the Si atom and a  $sp^{4.44}$  hybrid on the N atom in the MP2 calculation. The DFT methods allow only a small portion of the d character in the Si atom to participate for the hybrids resulting in a lone pair of the N atom and no Si-N bond in the NBO analysis of 1-

fluorosilatrane. In the silatranyl cation the Si atom has four coordinations and is weakly hypervalent. The d character of the Si atom is almost absent in the hybrids and the Si-N bond is formed by a  $sp^{4.11}$  hybrid on the Si atom interacting with a  $sp^{4.44}$  hybrid on the N atom even in MP2 calculations. In this study, the difference in the nature of Si-N bond between 1-fluorosilatrane and the silatranyl cation is clearly demonstrated. In addition, the silatranyl cation appears to be quite stable and could be a good candidate for a future experimental study.

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