Chapter 2

The Homocyclotrisilenylium Ion

-A Free Silyl Cation in the Condensed Phase-

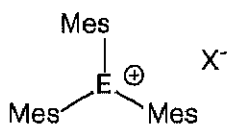
Summary

Cyclotetrasilenylium ion **11**$^+$ was obtained by treatment of tetrakis[di-*tert*-butyl-(methyl)silyl]cyclotrisilene **3** with $[Et_3Si(benzene)]^+$ in benzene via a methyl group abstraction followed by skeletal rearrangement. The structural analysis of **11**$^+$ showed that **11**$^+$ is a free silyl cation lacking any significant interaction with both counter anion and solvent molecules. Experimental and theoretical studies indicate that **11**$^+$ is the first homoaromatic compound consisting of silicon atom with 2π electron system.

Introduction

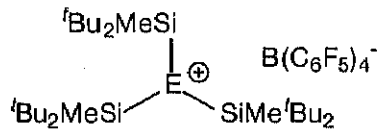
The chemistry of three-coordinated cations of heavier Group 14 elements (Si, Ge, Sn) in the condensed phase, that is free cations without any covalent interaction with both counteranion and solvent molecules, has developed in the last decade.[1-3] Report on the X-ray crystal structure of $[Et_3Si(toluene)]^+\bullet[(C_6F_5)_4B]^-$ by Lambert[4] and $^iPr_3Si^+\bullet CB_{11}H_6Br_6$ by Reed[5] in 1993 have raised the problem of the free silyl cation (R_3Si^+) in the condensed phase. Silyl cations are much more reactive than carbocations (R_3C^+) and are usually coordinated in the condensed phase by the counteranion and solvent.

In 1997, Lambert and Zhao synthesized $Mes_3Si^+\bullet B(C_6F_5)_4^-$ (Mes = 2,4,6-timethyl-phenyl) by the reaction of the corresponding allylsilane with appropriate electrophiles.[6] The germanium and tin analogue of Mes_3Si^+ were also synthesized in the same condition.[6c] Mes_3Si^+ was characterized a free cation by its ^{29}Si NMR chemical shift in aromatic solvent such as benzene and toluene which was in good agreement with the calculated δ_{Si} value. Quite recently, Lambert et al. reported the crystallographic analysis of Mes_3Si^+ by using $CB_{11}H_6Br_6^-$ as counteranion at last.[7] Later, Sekiguchi et al. reported the synthesis of $^tBu_2MeSi$-substituted germyl and stannyl cations by the one-electron oxidation of the corresponding germanium and tin radicals.[8]



Mes = 2,4,6-trimethylphenyl
E = Si, Ge. Sn

J. B. Lambert (1999, 2002)

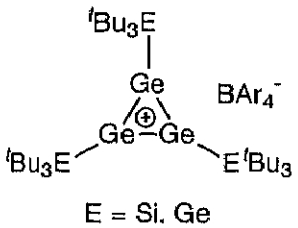


E = Ge. Sn

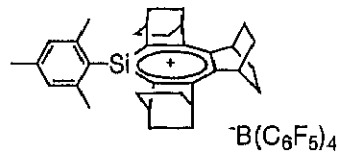
A. Sekiguchi (2003)

The study on chemistry of π conjugated cations of heavier Group 14 elements are also active area. In 1997, Sekiguchi et al. successfully synthesized and characterized a free

germyl cations, $[(^tBu_3E)_3Ge_3]^+$ (E = Si, Ge) which are germanium analogue of cyclopropenylium ions, by the reaction of $^tBu_3E$-substituted cyclotrigermenes with trityl tetraarylborates (trityl = triphenylmethyl).[9] The evidence for aromaticity of cyclotrigermenylium ion was demonstrated by X-ray analyses. In 2000, Komatsu et al. succeeded in the observation of the silatropilyium ion with rigid bicyclo[2.2.2]octane units by NMR spectra at low temperature.[10] The free state and aromaticity of the silatropilyium ion were supported by theoretical calculations.



A. Sekiguchi (1997)



K. Komatsu (2000)

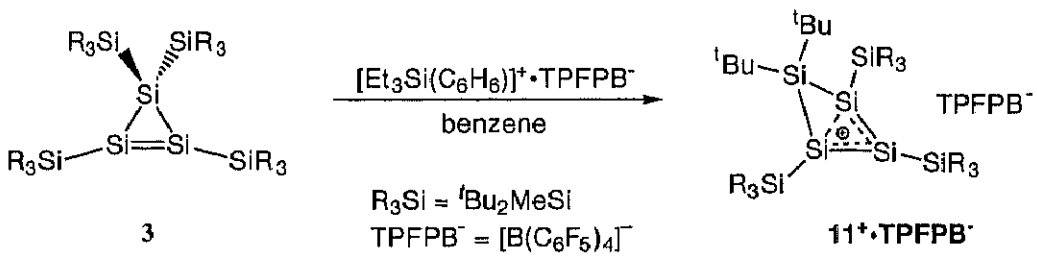
Cyclotrisilenes that may be good precursor for the cyclotrisilenylium ion were independently synthesized by Kira et al.[11] and this work as shown in Chapter 1. However, all of attempts to prepare the cyclotrisilenylium ion by the reaction of cyclotrisilene **3** with trityl tetraarylborate were failed. However, the author has unexpectedly found that the reaction of **3** with $[Et_3Si(benzene)]^+\cdot[(C_6F_5)_4B]^-$ afforded a cyclotetrasilenylium ion $[(^tBu_2MeSiSi)_3Si^tBu_2]^+$ (**11**$^+$) which is a free silyl cation in the condensed phase. Both structural and spectroscopic characteristics are similar to those of the cyclobutenylium ion that is homocyclopropenylium ion, which is well-established by both experimental and theoretical studies.

In this chapter, synthesis and X-ray structure of cyclotetrasilenylium ion are reported. The theoretical investigation of the nature of homoaromaticity in the cyclotetrasilenylium ion is also discussed.

Results and Discussion

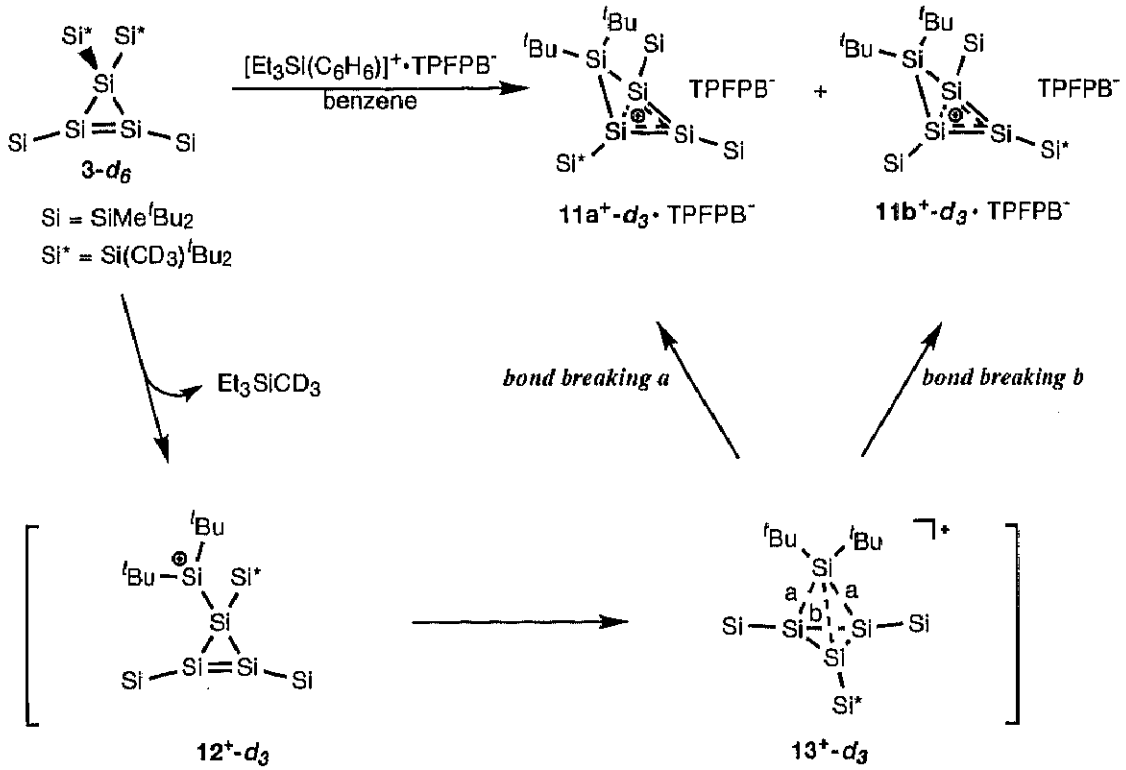
Synthesis of Cyclotetrasilenylium Ion

A benzene solution of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene **3** was added to $[Et_3Si(benzene)]^+ \bullet TPFPB^-$ prepared by the reaction of Et_3SiH and $Ph_3C^+ \bullet TPFPB^-$ in benzene. The red-orange color immediately disappeared to afford two layers, the top phase contains triethyl(methyl)silane. The lower one consisting of dark red viscous oil was washed with hexane to give yellow crystals of 1,2,3-tris[di-*tert*-butyl(methyl)silyl]-4,4-di-*tert*-butylcyclotetrasilenylium ion ($\mathbf{11}^+ \bullet TPFPB^-$) in 91% yield (Scheme 2-1).



Scheme 2–1

The formation of the cyclotetrasilenylium ion $\mathbf{11}^+$ from three-membered cyclotrisilene **3** is quite interesting, and prompted the author to investigate its formation mechanism. The reaction of $[Et_3Si(benzene)]^+ \bullet TPFPB^-$ with deuterium-labeled cyclotrisilene **3-d_6** in which CH_3 groups in the di-*tert*-butyl(methyl)silyl groups on saturated silicon atom were replaced by CD_3 groups, gave $\mathbf{11a}^+$-d_3 and $\mathbf{11b}^+$-d_3 in a 2:1 molar ratio. This result indicates that the methyl group in $^tBu_2MeSi$ group on the saturated silicon atom initially abstracted by $[Et_3Si(benzene)]^+$ to form Et_3SiCD_3 and a silyl cation intermediate $\mathbf{12}^+$, followed by isomerization to $\mathbf{11}^+$ via an intermediate or transition state $\mathbf{13}^+$ (Scheme 2-2).



Scheme 2–2

Solid-State Structure of Cyclotetrasilenylium ion 11+TPFPB-

The structure of **11**$^+$•TPFPB$^-$ was determined by X-ray analysis of a single-crystal obtained by recrystallization from benzene. There are two crystallographically independent **11**$^+$•TPFPB$^-$ in the unit cell, and both structures are similar except for the orientation of the ^{t}Bu$_2$MeSi group on Si2 atom. The crystal structure reveals that a four-membered silicon ring system exists as a 1:1 salt with TPFPB$^-$ as counteranion and 1.5 benzene molecules are contained as solvent of crystallization (Figure 2-1). However, the distances between the cationic silicon atoms (Si1, Si2, Si3) and the carbon atoms in benzene range from 6.71(2) to 7.70(2) Å, showing that there is no interaction between them, unlike the case of [Et$_3$Si (toluene)]$^+$•TPFPB$^-$. The closest distance between the cationic silicon atoms and fluorine atoms on TPFPB$^-$ is 4.861(8) Å, which is longer than the sum of the van der Waals radii for

silicon and fluorine atoms.[12] These results indicate that the cyclotetrasilenylium ion **11**$^+$ is a free silyl cation in the solid state.

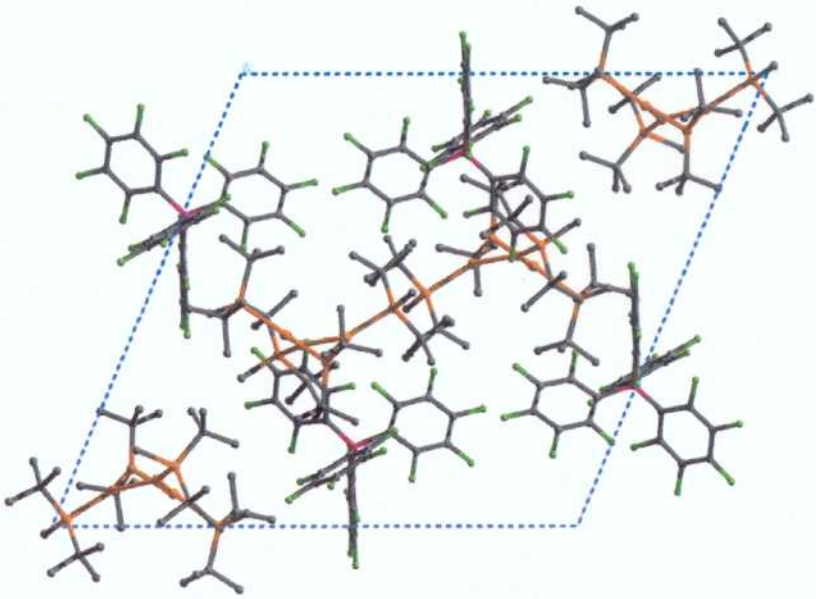


Figure 2-1. Crystal packing of **11**$^+$**•TPFPB**$^-$ (benzene molecules are omitted).

The four-membered ring is folded as shown Figure 2-2, the dihedral angle between the positively charged part, Si1-Si2-Si3 and Si1-Si4-Si3 being 46.6°. The angles at the silicon atoms in the four-membered ring suggest that the cationic part (Si1, Si2,and Si3) has a completely planar sp^2 geometry and Si4 has a distorted sp^3 environment. The Si-Si bonds of the cationic part, Si1-Si2 and Si2-Si3, have lengths of 2.240(2) and 2.244(2) Å, respectively, which are intermediate between the Si=Si double bond [2.138 (2) Å] and the Si-Si single bond [2.364(3) and 2.352(3) Å] of the precursor **3**. The bond lengths of Si1-Si4 [2.336(2) Å] and Si3-Si4 [2.325(2) Å] range in the normal region. The interatomic distance between Si1 and Si3 is 2.692(2) Å, which is only 15% longer than a normal Si-Si single bond, indicating a possibly 1,3-orbital interaction to give the homoaromaticity of **11**$^+$, as the precedent for all carbon system.[13]

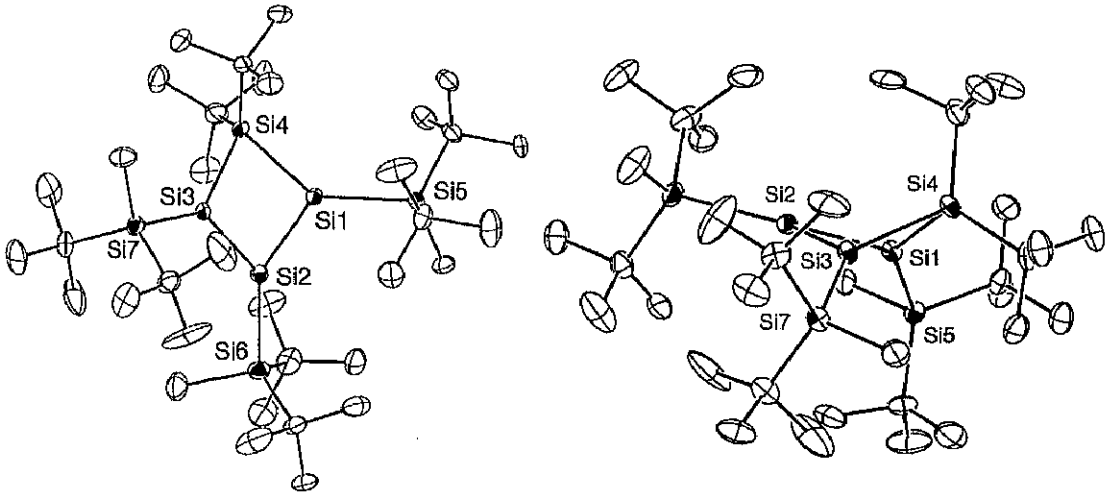


Figure 2-2. ORTEP drawings of 11^+ (hydrogen atoms are omitted).

Structure of Cyclotetrasilenylium Ion 11^+•TPFPB$^-$ in Solution

The free silyl cation in solution of 11^+ was demonstrated by ^{29}Si NMR spectroscopy. ^{1}H and ^{13}C NMR spectra of **11^+•TPFPB$^-$** in CD_2Cl_2 at 298K showed the existence of two sets of signals from different methyl groups and three resonances for the nonequivalent *tert*-butyl groups. The signals arising from two *tert*-butyl groups in the silyl substituents on Si4 and the signal which is assigned to four *tert*-butyl groups in the silyl substituents on Si1 and Si3 are equivalent, respectively, indicating that ring inversion of four-membered ring skeleton in **11^+** is very fast at 298 K. The ring inversion of four-membered ring is occurred even at 210 K. The ^{29}Si NMR resonances appear at δ = 15.7 (^{t}Bu$_2$*Si*), 34.4 (2 ^{t}Bu$_2$Me*Si*), 44.0 (^{t}Bu$_2$Me*Si*), 77.3 (2 *Si*), and 315.7 (*Si*). These chemical shifts are independent of the solvent (dichloromethane-d_2, benzene-d_6, and toluene-d_8), implying the lack of any covalent interaction with solvent molecules (Figure 2-3). However, more polar and nucleophilic solvent such as THF-d_8 can readily react with **11^+** to produce rubbery polymer resulting by ring opening polymerization of THF catalyzed by **11^+** in a moment.

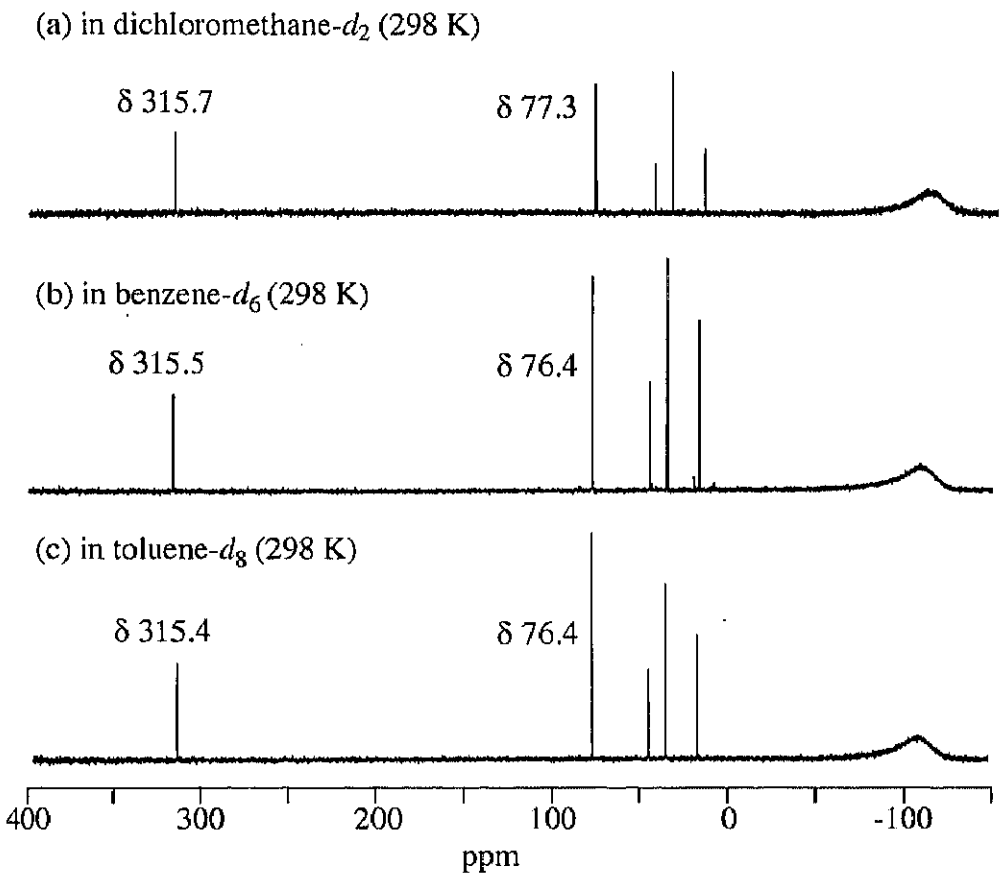


Figure2-3. ^{29}Si NMR spectra of **11**$^+$ • TPFPB$^-$ in (a) dichloromethane-d_2, (b) benzene-d_6, (c) toluene-d_8, at 298K.

If the usual allylic structure will be predominant, the positive charge is expected to reside mainly on Si1 and Si3 atoms. However, the central silicon atom in the cation part (Si2; δ 315.7) is more deshielded than the terminal silicons (Si1 and Si3; δ 77.3). The downfield shift of ^{29}Si resonance for Si2 relative to Si1 and Si3 is also reproduced by GIAO calculation method (GIAO/B3LYP/6-31G(2df,p)//B3LYP/6-31G(d)) for model compound $[(H_3SiSi)_3SiMe_2]^+$. The calculated δ_{Si} values for the model compound are 335.2 (Si2) and 175.0 (Si1 and Si3). The delocalization of the positive charge at the Si1, Si2, and Si3 atoms is due to the homoconjugation between Si1 and Si3 to give the homoaromatic character of **11**$^+$.

Homoaromaticity of Cyclotetrasilenylium Ion

Although the experimental and theoretical studies for homoaromaticity in cyclobutenylium ion that is homocyclopropenylium ion which is a carbon analogue of cyclotetrasilenylium ion are well-established,[13] the chemistry of homoaromatic compound consisting of heavier Group 14 elements is less studied. In order to establish the homoaromaticity of cyclotetrasilenylium ion, theoretical investigation of cyclobutenylium analogues of C and Si was performed.[14]

The 1,2,3-tris(trihydrosilyl)-4,4-dimethylcyclotetrasilenylium ion $[(H_3SiSi)_3SiMe_2]^+$ in which the three ^{t}Bu$_2$MeSi groups and two ^{t}Bu groups on Si4 in **11**$^+$ have been replaced by H_3Si and Me groups, respectively, serves as a close model for **11**$^+$. The optimized geometry of $[(H_3SiSi)_3SiMe_2]^+$ is shown in Figure 2-4. At the B3LYP/6-31G(d) level, the symmetric C_s structure of $[(H_3SiSi)_3SiMe_2]^+$ is a minimum. This clearly shows that the slight distortions of **11**$^+$•**TPFPB**$^-$ in the crystal structure (Si1-Si2; 2.240(2), Si2-Si3; 2.244(2) Å) are due to the electrostatic influence of the counteranion, lattice effect, and/or orientation of anisotropic ^{t}Bu$_2$MeSi substituents. The calculated Si-Si bond length of the cation part in the four-membered ring of $[(H_3SiSi)_3SiMe_2]^+$ (2.2359 Å) is in excellent agreement with the average value found in the X-ray structure of **11**$^+$•TPFPB$^-$ (2.2420 Å). However, the folding angle of the four-membered ring skeleton in the model compound (36.5°) is significantly smaller than the experimental value (46.6°). This difference may be due to the steric hindrance of ^{t}Bu$_2$MeSi groups of **11**$^+$•TPFPB$^-$. The interatomic distance between the 1,3-position in cation part is calculated to be 2.807 Å, which is longer than the corresponding distance in the X-ray structure of **11**$^+$•TPFPB$^-$ (2.692(2) Å), indicating that 1,3-orbital interaction is effectively appeared in the **11**$^+$ compared to the model compound $[(H_3SiSi)_3SiMe_2]^+$.

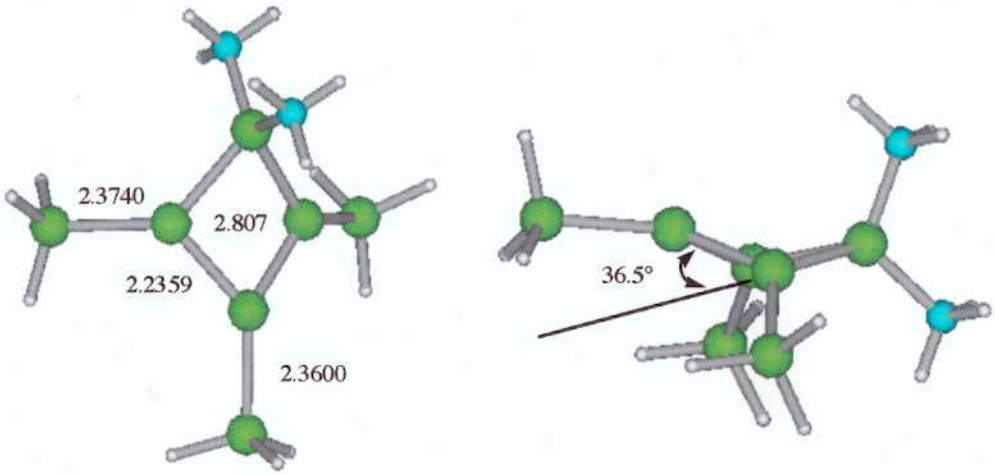


Figure 2-4. Optimized geometries and selected structural parameters (Å and deg) of $[(H_3SiSi)_3SiMe_2]^+$ (C_s) at B3LYP/6-31G(d) level.

The existence of 1,3-orbital interaction can be established in the molecular orbital of $[(H_3SiSi)_3SiMe_2]^+$. The molecular orbitals (HOMO, LUMO, and LUMO+1) of $[(H_3Si\text{-}Si)_3SiMe_2]^+$ calculated at B3LYP/6-31G(d)//B3LYP/6-31G(d) level are shown in Figure 2-5. The picture of the HOMO for $[(H_3SiSi)_3SiMe_2]^+$ reveals the presence of a bonding interaction between the silicon atoms at 1,3-positions. The positive charge can be equally distributed over these three silicon atoms to form three-center two-electron (3c-2e) bond by charge delocalization inside the three coordinated silicon atoms, giving rise to the homocyclotisilenylium system. It is also interesting that the overlap between orbitals at 1,3-positions lead to rise the LUMO level and to reduce the level of LUMO+1 of acyclic trisilaally cation $[(H_3Si)_5Si_3]^+$ as shown Figure 2-5. To characterize the nature of the bonding in $[(H_3SiSi)_3SiMe_2]^+$, a natural bond orbital (NBO) analysis[15] was performed at the NBO-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory. The Wiberg bond indexes (WBI) (Si1-Si3; 0.425, Si1-Si2; 1.368) and the overlap-weighted natural atomic orbital (NAO) bond order (Si1-Si3; 0.249, Si1-Si2; 1.034) for the bonds in the cation part suggest the formation of a 3c-2e bond. The homoaromatic conjugation is supported by the nucleus-independent chemical shift (NICS)[16] value for $[(H_3SiSi)_3SiMe_2]^+$. The NICS value at the

center of the triangle composed of homoconjugative atoms calculated to be -17.7.

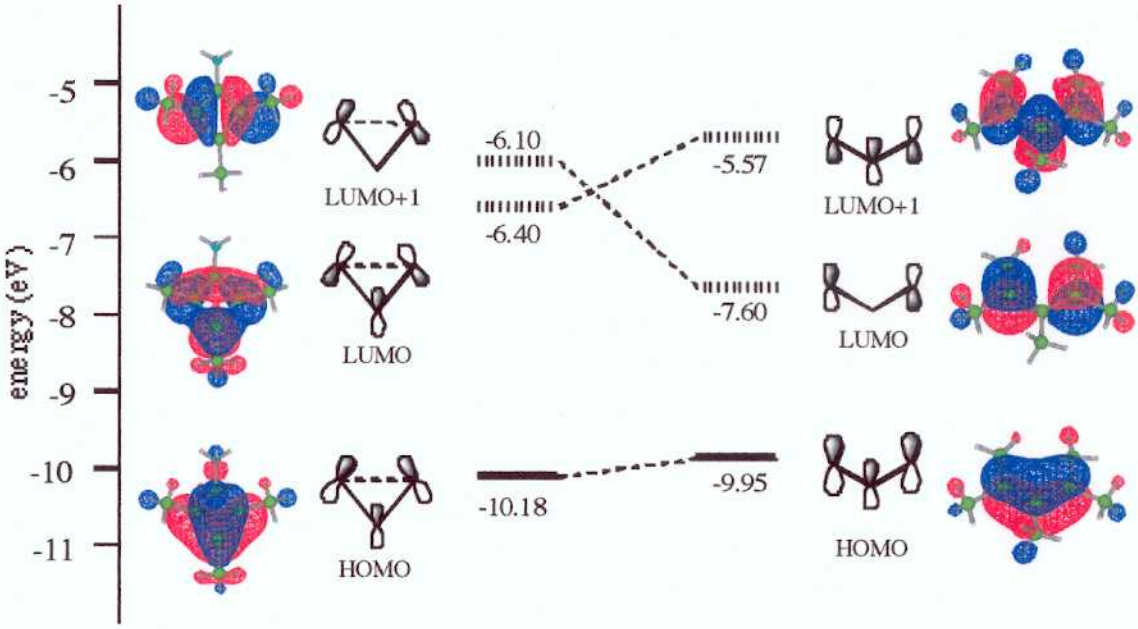
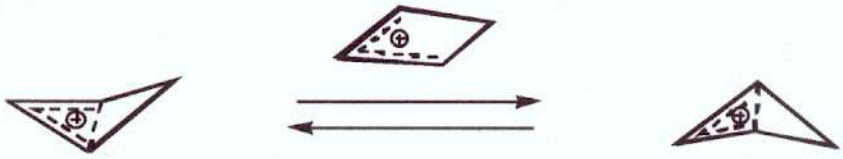


Figure 2-5. Representation of the molecular orbitals and energy diagram for $[(H_3SiSi)_3SiMe_2]^+$ and $[(H_3Si)_5Si_3]^+$.

Olah suggested that the barrier for ring inversion of four-membered ring of cyclobutenylium ion was a measure of homoaromatic stabilization.[17] The barrier to the ring inversion of parent cyclobutenylium ion ($C_4H_5^+$) was found to be 8.4 kcal/mol determined by VT-NMR method (Scheme 2-3). However, the flipping of the four-membered ring in **11**$^+$ can be easily occurred even at low temperature as mentioned above, indicating that homoaromatic stabilization of the cyclotetrasilenylium ion may be smaller than its carbon system.



$\Delta G^{\ddagger} = 8.4$ kcalmol^{-1} (VT-NMR)

Scheme 2-3

To better understand this difference, theoretical caluculation of the ring inversion barriers of the model compounds ($Si_4H_5^+$ and $C_4H_5^+$) were carried out at B3LYP/6-31G(d) level of theory. The *Cs* structure of $Si_4H_5^+$ and $C_4H_5^+$ are found as minimum structures, and the highly symmetrical C_{2v} geometries which have planar four-membered ring were transition state of the ring inversion system. The ring inversion barrier of $Si_4H_5^+$ is calculated to be 0.34 kcal/mol which is much smaller than the corresponding value (6.9 kcal/mol) of $C_4H_5^+$ (Figure 2-6). This results indicating that the existence of the homoaromaticity in the cyclotrisilenylium ion is definite, but its effect is smaller than the homocyclopropenylium system.

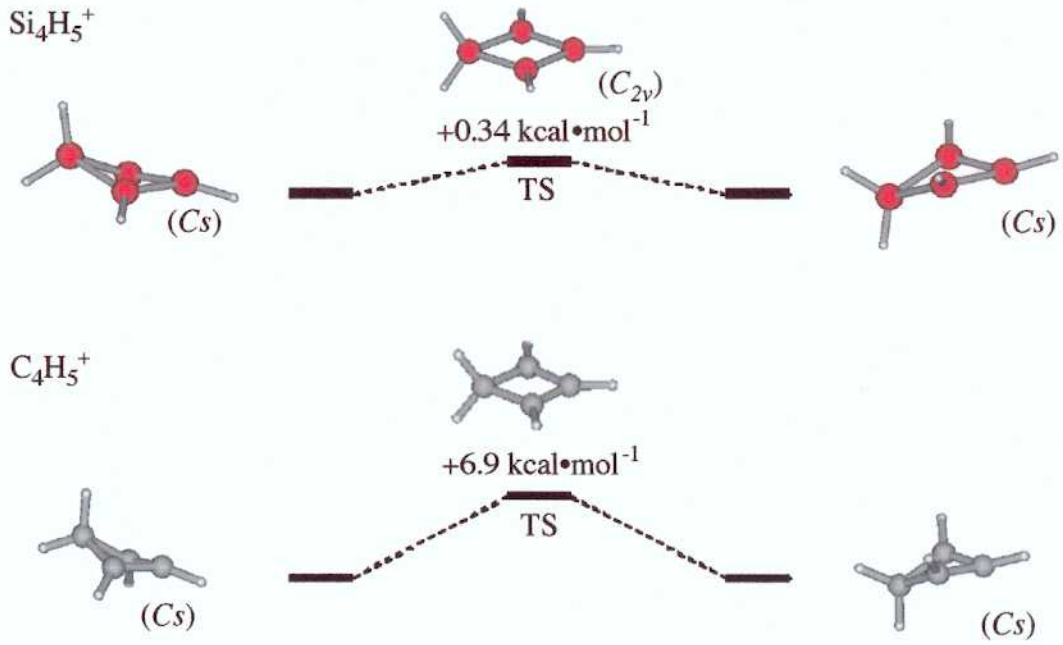


Figure 2-6. Calculated Ring Inversion Barriar of $Si_4H_5^+$ and $C_4H_5^+$(B3LYP/6-31G(d)).

Conclusion

Cyclotetrasilenylium ion **1 1**$^+$, that is homocyclotrisilenylium ion was obtained by the methyl abstraction of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene with $[Et_3Si(benzene)]^+$. The X-ray analysis and NMR spectroscopy show that the cyclotetrasilenylium ion **11**$^+$ is a free silyl cation in the condensed phase, with lacks any coordination to the counteranion as well as to the solvent molecules. The characteristics of X-ray structure and ^{29}Si NMR data are also indicate that there is a 1,3-orbital interaction in the for-membered ring to give the homoaromaticity of **11**$^+$.

The isolation of stable cyclotetrasilenylium ion has given the break through of the chemistry of silyl radical, as shown in the next chapter.

Experimental Section

General procedure

All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques and dry, oxygen-free solvents. NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer (^{1}H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz). Mass spectra were obtained on a JEOL JMS SX-102 instrument (EI, 70 eV). UV spectra were recorded on a Shimadzu UV-3150 UV-visible spectrophotometer in hexane. Elemental analyses were performed at the Analytical Centers of Tsukuba University (Tsukuba, Japan) and Tohoku University (Sendai, Japan). Et_3SiH and Ph_3C^+•TPFPB$^-$[18] (TPFPB$^-$ = tetrakis(pentafluorophenyl)borate were prepared according to the literature procedure.

Synthesis of 1,2,3-tris[di-*tert*-butyl(methyl)silyl]-4,4-di-*tert*-butylcyclotetrasilenylium tetrakis(pentafluorophenyl)borate

[Et_3Si(benzene)]$^+$•TPFPB$^-$ was prepared by treatment of Et_3SiH (30 mg, 0.25 mmol) with Ph_3C^+•TPFPB$^-$ (160 mg, 0.17 mmol) in benzene (1 mL). A benzene solution of **3** (130 mg, 0.18 mmol) was added to the resulting triethylsilylcation/benzene complex. The mixture was stirred at room temperature, and the color immediately turned from red-orange due to **3** to dark red to give two layers, the lower one consisting of a dark red viscous oil. The top phase was removed, and the lower oily substance was washed with benzene and hexane in a glove-box to afford air- and moisture-sensitive yellow crystals of **11**$^+$•TPFPB$^-$ (217 mg, 91%); ^{1}H NMR (CD_2Cl_2, δ) 0.65 (s, 6 H, ^{t}Bu$_2$MeSi), 0.78 (s, 3 H, ^{t}Bu$_2$MeSi), 1.20 (s, 36 H, ^{t}Bu$_2$MeSi), 1.25 (s, 18 H, ^{t}Bu$_2$MeSi), 1.30 (s, 18 H, ^{t}Bu$_2$Si); ^{13}C NMR (CD_2Cl_2, δ) -4.4, -4.3, 22.2, 22.7, 23.5, 29.0, 29.1, 32.3, 123.8 (broad, *ipso*-C), 136.0 (d, $^1J_{13C\text{-}19F}$ = 240.3 Hz), 137.9 (d, $^1J_{13C\text{-}19F}$ = 245.3 Hz), 147.9 (d,$^1J_{13C\text{-}19F}$ = 241.3

Hz); ^{29}Si NMR (CD_2Cl_2, δ) 15.7, 34.3, 44.0, 77.3, 315.7. The assignment of ^{29}Si signals was confirmed by ^{1}H-^{29}Si two-dimensional NMR techniques.

Theoretical Calculation of Cyclotetrasilenylium ion

All calculations were performed with the Gaussian 98 series of program.[14] All structures were optimized in the given symmetry at B3LYP/6-31G(d) level. Vibrational frequencies were calculated at the same level to determined the nature of the stationary points as well as the zero-point energy correction. NICS value at the center of cationic silicon atoms was calculated at GIAO/B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level.

X-ray Crystal Structure Determination of $(\mathbf{11}^{+}\bullet\mathbf{TPFPB}^{-})_2(C_6H_6)_3$

A single crystal of $(\mathbf{11}^{+}\bullet TPFPB^{-})_2(C_6H_6)_3$ for X-ray diffraction was grown from a benzene solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromat ized Mo–Ka radiation (λ = 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 2-1a. The final atomic parameters, the bond length, and the bond angles of $(\mathbf{11}^{+}\bullet TPFPB^{-})_2(C_6H_6)_3$ are listed in Table 2-1b and Table 2-1c, respectively.

Table 2-1a. Crystal data and structure refinement for $(\mathbf{11}^{+}\bullet\mathbf{TPFPB}^{-})_2(C_6H_6)_3$.

Empirical formula	$C_{68}H_{90}BF_{20}Si_7$
Formula weight	1494.84
Temperature	120 K
Wavelength	0.71070 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 17.958(1) Å alpha = 112.202(5) deg. b = 21.086(1) Å beta = 90.688(4) deg. c = 22.148(2) Å gamma = 101.688(5) deg.
Volume	7578(1) Å^3
Z, Calculated density	4, 1.310 Mg/m^3
Absorption coefficient	0.214 mm^-1
F(000)	3124
Crystal size	0.3 x 0.3 x 0.2 mm
Theta range for data collection	2.25 to 28.03 deg.
Limiting indices	0<=h<=23, -27<=k<=27, -29<=l<=29
Reflections collected / unique	32425 / 32425 [R(int) = 0.0000]
Completeness to theta = 27.94	88.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	32425 / 0 / 1730
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0919, wR2 = 0.1848
R indices (all data)	R1 = 0.1973, wR2 = 0.2375
Extinction coefficient	0.00046(12)
Largest diff. peak and hole	0.562 and -0.408 e.Å^-3

Table 2-1b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $(\mathbf{11}^+\bullet\mathbf{TPFPB}^-)_2(C_6H_6)_3$.. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	Ueq
Si(1)	8053(1)	715(1)	-2059(1)	27(1)
Si(2)	6987(1)	1021(1)	-1640(1)	28(1)
Si(3)	7600(1)	790(1)	-884(1)	29(1)
Si(4)	8824(1)	1251(1)	-1066(1)	32(1)
Si(5)	8118(1)	-5(1)	-3183(1)	29(1)
Si(6)	5802(1)	1308(1)	-1862(1)	41(1)
Si(7)	7145(1)	151(1)	-220(1)	34(1)
Si(8)	8054(1)	5750(1)	2904(1)	31(1)
Si(9)	6958(1)	5983(1)	3304(1)	29(1)
Si(10)	7588(1)	5808(1)	4083(1)	29(1)
Si(11)	8779(1)	6358(1)	3913(1)	37(1)
Si(12)	8194(1)	5041(1)	1791(1)	33(1)
Si(13)	5803(1)	6212(1)	2942(1)	34(1)
Si(14)	7189(1)	5155(1)	4752(1)	32(1)
F(1)	3417(2)	3827(2)	1420(2)	46(1)
F(2)	2967(2)	3524(2)	2434(2)	54(1)
F(3)	1815(2)	2399(2)	2262(2)	54(1)
F(4)	1144(2)	1569(2)	1030(2)	53(1)
F(5)	1598(2)	1846(2)	7(2)	40(1)
F(6)	1923(2)	3235(2)	-1090(2)	49(1)
F(7)	1565(3)	2249(2)	-2267(2)	71(1)
F(8)	1950(3)	974(2)	-2580(2)	74(1)
F(9)	2727(3)	740(2)	-1644(2)	64(1)
F(10)	3098(2)	1730(2)	-450(2)	48(1)
F(11)	4086(2)	2714(2)	715(2)	43(1)
F(12)	5557(2)	3001(3)	594(2)	67(1)
F(13)	6119(2)	3736(3)	-138(2)	86(2)
F(14)	5122(2)	4144(3)	-797(2)	74(1)
F(15)	3624(2)	3843(2)	-694(2)	48(1)
F(16)	3662(2)	4688(2)	656(2)	48(1)
F(17)	2996(3)	5764(2)	1052(2)	64(1)
F(18)	1441(3)	5566(2)	901(2)	61(1)
F(19)	572(2)	4232(2)	365(2)	52(1)
F(20)	1236(2)	3138(2)	-13(2)	42(1)
F(21)	8357(2)	3106(2)	4977(2)	41(1)
F(22)	8776(2)	3424(2)	3967(2)	51(1)
F(23)	8157(2)	2588(2)	2729(2)	55(1)
F(24)	7092(2)	1385(2)	2521(2)	52(1)
F(25)	6676(2)	1032(2)	3514(2)	45(1)
F(26)	6481(2)	980(2)	5623(2)	38(1)
F(27)	4999(2)	575(2)	5698(2)	44(1)
F(28)	3949(2)	884(2)	5010(2)	50(1)
F(29)	4438(2)	1658(2)	4285(2)	50(1)
F(30)	5906(2)	2086(2)	4218(2)	42(1)
F(31)	8161(2)	1669(2)	6039(2)	40(1)

Table 2-1b (continued). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(\mathbf{11^+ \cdot TPFPB^-})_2(C_6H_6)_3$.. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

F(32)	8482(2)	2660(2)	7226(2)	58(1)
F(33)	7998(3)	3887(2)	7545(2)	63(1)
F(34)	7163(2)	4081(2)	6610(2)	57(1)
F(35)	6842(2)	3097(2)	5407(2)	43(1)
F(36)	6467(2)	155(2)	4254(2)	43(1)
F(37)	7203(2)	-874(2)	3906(2)	55(1)
F(38)	8756(2)	-607(2)	4099(2)	50(1)
F(39)	9554(2)	755(2)	4650(2)	45(1)
F(40)	8825(2)	1812(2)	4988(2)	36(1)
C(1)	7419(3)	275(3)	-3615(3)	41(1)
C(2)	7754(4)	-978(3)	-3339(3)	41(2)
C(3)	8222(4)	-1258(4)	-2962(5)	73(3)
C(4)	6945(4)	-1077(3)	-3144(4)	56(2)
C(5)	7725(6)	-1406(4)	-4079(4)	81(3)
C(6)	9119(3)	296(3)	-3398(3)	38(1)
C(7)	9709(4)	-65(4)	-3225(3)	50(2)
C(8)	9089(4)	128(4)	-4141(3)	49(2)
C(9)	9378(4)	1091(3)	-3027(3)	50(2)
C(10)	5466(5)	1666(5)	-1005(3)	74(3)
C(11)	5051(3)	534(3)	-2422(3)	43(2)
C(12)	4693(5)	81(5)	-2055(5)	90(3)
C(13)	4398(4)	804(4)	-2641(3)	56(2)
C(14)	5348(4)	67(4)	-3031(4)	60(2)
C(15)	6119(4)	2067(4)	-2131(4)	55(2)
C(16)	5506(5)	2524(4)	-1962(4)	75(3)
C(17)	6239(4)	1812(4)	-2837(3)	56(2)
C(18)	6881(5)	2540(4)	-1742(4)	79(3)
C(19)	7919(4)	-181(4)	75(4)	51(2)
C(20)	6859(4)	861(4)	526(3)	46(2)
C(21)	6524(5)	537(4)	1003(3)	71(2)
C(22)	7575(5)	1421(4)	869(4)	84(3)
C(23)	6304(6)	1216(6)	340(4)	105(4)
C(24)	6380(4)	-631(3)	-740(3)	45(2)
C(25)	5968(5)	-1031(4)	-349(4)	64(2)
C(26)	6763(6)	-1134(5)	-1270(5)	139(6)
C(27)	5792(5)	-454(5)	-1086(6)	126(5)
C(28)	9133(4)	2251(3)	-723(3)	45(2)
C(29)	9468(4)	2530(4)	-12(3)	56(2)
C(30)	9714(5)	2488(4)	-1137(4)	69(2)
C(31)	8459(5)	2585(3)	-734(4)	70(2)
C(32)	9569(3)	752(4)	-956(3)	41(2)
C(33)	9741(4)	886(4)	-226(3)	58(2)
C(34)	9246(4)	-34(3)	-1333(3)	50(2)
C(35)	10330(4)	961(4)	-1230(3)	56(2)
C(36)	7516(4)	5277(4)	1310(3)	48(2)
C(37)	7862(4)	4077(3)	1652(3)	39(1)
C(38)	8265(4)	3875(4)	2150(4)	58(2)

Table 2-1b (ccontinued). Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **(11^+•TPFPB$^-$)$_2$(C_6H_6)$_3$**.. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(39)	7008(4)	3923(3)	1714(3)	49(2)
C(40)	8000(5)	3621(4)	969(4)	71(2)
C(41)	9205(4)	5353(3)	1614(3)	40(2)
C(42)	9804(4)	5033(4)	1839(3)	51(2)
C(43)	9218(4)	5166(4)	873(3)	58(2)
C(44)	9441(4)	6157(3)	1958(4)	54(2)
C(45)	6196(4)	6717(3)	2424(3)	50(2)
C(46)	5092(3)	5368(3)	2421(3)	36(1)
C(47)	4931(4)	4845(3)	2746(3)	54(2)
C(48)	4347(4)	5562(4)	2277(3)	50(2)
C(49)	5415(4)	5018(4)	1770(3)	54(2)
C(50)	5462(3)	6820(3)	3713(3)	40(1)
C(51)	4947(4)	7234(4)	3520(3)	58(2)
C(52)	5032(4)	6433(4)	4099(3)	59(2)
C(53)	6155(4)	7356(3)	4157(3)	54(2)
C(54)	7985(4)	4817(4)	4988(4)	55(2)
C(55)	6935(4)	5843(3)	5528(3)	41(2)
C(56)	6543(4)	5483(4)	5962(3)	52(2)
C(57)	7670(5)	6361(4)	5912(4)	67(2)
C(58)	6415(4)	6262(4)	5385(3)	59(2)
C(59)	6408(4)	4365(3)	4242(3)	42(2)
C(60)	6244(5)	3842(4)	4568(4)	70(3)
C(61)	6674(5)	4003(3)	3564(3)	65(2)
C(62)	5669(4)	4585(4)	4151(4)	61(2)
C(63)	8957(4)	7363(3)	4208(3)	47(2)
C(64)	9265(5)	7692(4)	4935(4)	71(2)
C(65)	9563(5)	7631(4)	3822(4)	78(3)
C(66)	8241(5)	7617(3)	4163(4)	74(3)
C(67)	9595(4)	5971(4)	4093(3)	47(2)
C(68)	9749(4)	6156(5)	4839(3)	67(2)
C(69)	9352(4)	5170(4)	3757(3)	50(2)
C(70)	10344(4)	6215(4)	3830(4)	63(2)
C(71)	232(5)	3289(4)	1949(5)	76(3)
C(72)	784(6)	3589(6)	1684(5)	76(3)
C(73)	1326(6)	4119(6)	2045(7)	91(3)
C(74)	1354(6)	4372(5)	2715(7)	98(4)
C(75)	795(7)	4080(7)	3008(5)	93(4)
C(76)	226(6)	3531(6)	2628(5)	81(3)
C(77)	5679(4)	2250(4)	2236(4)	62(2)
C(78)	5426(5)	2113(4)	2764(4)	58(2)
C(79)	4812(5)	2336(4)	3032(4)	62(2)
C(80)	4429(4)	2706(4)	2782(4)	64(2)
C(81)	4686(5)	2841(4)	2249(4)	62(2)
C(82)	5312(5)	2607(4)	1981(4)	66(2)
C(83)	8785(6)	772(5)	2308(6)	92(3)
C(84)	8825(6)	964(6)	2970(6)	82(3)
C(85)	9353(6)	1499(5)	3356(5)	74(3)

Table 2-1b (continued). Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **(11^+•TPFPB$^-$)$_2$(C_6H_6)$_3$**.. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(86)	9860(5)	1869(5)	3107(5)	74(2)
C(87)	9848(6)	1682(5)	2445(6)	80(3)
C(88)	9307(7)	1132(6)	2038(5)	85(3)
C(89)	2554(3)	2846(3)	648(3)	32(1)
C(90)	2859(4)	3243(3)	1290(3)	38(1)
C(91)	2634(4)	3109(3)	1825(3)	38(1)
C(92)	2056(4)	2539(4)	1746(3)	42(2)
C(93)	1717(4)	2132(3)	1124(3)	38(1)
C(94)	1968(3)	2280(3)	596(3)	36(1)
C(95)	2521(3)	2541(3)	-681(3)	32(1)
C(96)	2131(3)	2621(3)	-1188(3)	36(1)
C(97)	1942(4)	2113(3)	-1816(3)	46(2)
C(98)	2131(4)	1474(3)	-1979(3)	49(2)
C(99)	2527(4)	1363(3)	-1504(3)	44(2)
C(100)	2711(4)	1887(3)	-889(3)	38(1)
C(101)	3762(3)	3284(3)	38(3)	33(1)
C(102)	4300(3)	3085(3)	340(3)	39(1)
C(103)	5071(4)	3219(4)	288(3)	49(2)
C(104)	5359(4)	3589(4)	-85(3)	54(2)
C(105)	4861(4)	3795(4)	-413(3)	50(2)
C(106)	4086(4)	3631(3)	-353(3)	42(2)
C(107)	2491(3)	3843(3)	269(3)	32(1)
C(108)	2892(4)	4531(3)	555(3)	38(1)
C(109)	2556(4)	5105(3)	768(3)	45(2)
C(110)	1787(4)	5020(3)	704(3)	47(2)
C(111)	1341(4)	4339(3)	432(3)	41(2)
C(112)	1705(4)	3792(3)	238(3)	35(1)
C(113)	7473(3)	2050(3)	4309(3)	30(1)
C(114)	8006(3)	2651(3)	4380(3)	33(1)
C(115)	8236(4)	2833(3)	3858(3)	40(1)
C(116)	7938(4)	2420(3)	3239(3)	38(1)
C(117)	7398(4)	1811(3)	3133(3)	38(1)
C(118)	7194(3)	1647(3)	3661(3)	32(1)
C(119)	6284(3)	1531(3)	4898(3)	30(1)
C(120)	5987(3)	1161(3)	5281(3)	29(1)
C(121)	5232(3)	944(3)	5325(3)	33(1)
C(122)	4693(3)	1086(3)	4981(3)	35(1)
C(123)	4950(3)	1484(3)	4618(3)	33(1)
C(124)	5723(3)	1699(3)	4591(3)	36(1)
C(125)	7497(3)	2331(3)	5639(3)	30(1)
C(126)	7903(3)	2258(3)	6139(3)	32(1)
C(127)	8081(4)	2767(3)	6767(3)	41(1)
C(128)	7839(4)	3381(3)	6930(3)	42(2)
C(129)	7412(4)	3478(3)	6459(3)	43(2)
C(130)	7260(3)	2964(3)	5843(3)	35(1)
C(131)	7605(3)	1049(3)	4671(3)	32(1)
C(132)	7239(3)	345(3)	4380(3)	32(1)

Table 2-1b (continued). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **($11^{+\bullet}TPFPB^-)_2(C_6H_6)_3$**.. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(133)	7607(4)	-203(3)	4181(3)	38(1)
C(134)	8387(3)	-72(3)	4270(3)	36(1)
C(135)	8785(3)	614(3)	4551(3)	36(1)
C(136)	8393(3)	1144(3)	4735(3)	30(1)
B(1)	2827(4)	3119(3)	60(3)	32(1)
B(2)	7214(4)	1740(3)	4886(3)	30(1)

Table 2-1c. Bond lengths [Å] and angles [deg] for $(\mathbf{11}^{+}\bullet\mathbf{TPFPB}^{-})_2(C_6H_6)_3$

Si(1)-Si(2)	2.2260(17)	Si(1)-Si(4)	2.3575(17)	Si(1)-Si(5)	2.3715(18)
Si(2)-Si(3)	2.2625(18)	Si(2)-Si(6)	2.3773(17)	Si(3)-Si(4)	2.3643(17)
Si(3)-Si(7)	2.3717(18)	Si(4)-C(28)	1.933(5)	Si(4)-C(32)	1.936(5)
Si(5)-C(1)	1.886(5)	Si(5)-C(6)	1.907(6)	Si(5)-C(2)	1.920(6)
Si(6)-C(10)	1.880(5)	Si(6)-C(11)	1.907(5)	Si(6)-C(15)	1.922(5)
Si(7)-C(19)	1.885(4)	Si(7)-C(20)	1.912(5)	Si(7)-C(24)	1.923(5)
C(2)-C(4)	1.519(7)	C(2)-C(5)	1.540(7)	C(2)-C(3)	1.545(8)
C(6)-C(8)	1.519(7)	C(6)-C(9)	1.531(8)	C(6)-C(7)	1.539(7)
C(11)-C(14)	1.535(7)	C(11)-C(13)	1.542(7)	C(11)-C(12)	1.544(7)
C(15)-C(16)	1.523(7)	C(15)-C(17)	1.545(7)	C(15)-C(18)	1.551(6)
C(20)-C(23)	1.524(7)	C(20)-C(21)	1.545(7)	C(20)-C(22)	1.547(7)
C(24)-C(26)	1.531(6)	C(24)-C(27)	1.538(7)	C(24)-C(25)	1.542(7)
C(28)-C(30)	1.530(7)	C(28)-C(29)	1.529(6)	C(28)-C(31)	1.536(7)
C(32)-C(35)	1.532(6)	C(32)-C(33)	1.535(6)	C(32)-C(34)	1.553(7)

Si(2)-Si(1)-Si(4)	91.41(6)	Si(2)-Si(1)-Si(5)	138.30(7)	Si(4)-Si(1)-Si(5)	130.29(7)
Si(1)-Si(2)-Si(3)	91.89(6)	Si(1)-Si(2)-Si(6)	130.82(7)	Si(3)-Si(2)-Si(6)	136.35(7)
Si(2)-Si(3)-Si(4)	90.33(6)	Si(2)-Si(3)-Si(7)	139.20(7)	Si(4)-Si(3)-Si(7)	126.67(7)
C(28)-Si(4)-C(32)	113.9(2)	C(28)-Si(4)-Si(1)	113.69(15)	C(32)-Si(4)-Si(1)	111.94(16)
C(28)-Si(4)-Si(3)	112.13(15)	C(32)-Si(4)-Si(3)	116.15(15)	Si(1)-Si(4)-Si(3)	86.18(6)
C(1)-Si(5)-C(6)	108.1(3)	C(1)-Si(5)-C(2)	105.5(3)	C(6)-Si(5)-C(2)	115.7(2)
C(1)-Si(5)-Si(1)	107.13(17)	C(6)-Si(5)-Si(1)	108.32(17)	C(2)-Si(5)-Si(1)	111.61(16)
C(10)-Si(6)-C(11)	106.2(2)	C(10)-Si(6)-C(15)	108.0(2)	C(11)-Si(6)-C(15)	116.4(2)
C(10)-Si(6)-Si(2)	108.02(17)	C(11)-Si(6)-Si(2)	108.78(16)	C(15)-Si(6)-Si(2)	109.13(15)
C(19)-Si(7)-C(20)	107.5(2)	C(19)-Si(7)-C(24)	106.4(2)	C(20)-Si(7)-C(24)	115.0(2)
C(19)-Si(7)-Si(3)	104.93(15)	C(20)-Si(7)-Si(3)	109.41(17)	C(24)-Si(7)-Si(3)	112.97(16)
C(4)-C(2)-C(5)	106.6(5)	C(4)-C(2)-C(3)	108.3(5)	C(5)-C(2)-C(3)	105.8(5)
C(4)-C(2)-Si(5)	112.2(4)	C(5)-C(2)-Si(5)	113.8(4)	C(3)-C(2)-Si(5)	109.7(4)
C(8)-C(6)-C(9)	108.2(5)	C(8)-C(6)-C(7)	108.3(5)	C(9)-C(6)-C(7)	107.0(5)
C(8)-C(6)-Si(5)	112.7(4)	C(9)-C(6)-Si(5)	108.8(4)	C(7)-C(6)-Si(5)	111.6(4)
C(14)-C(11)-C(13)	109.8(4)	C(14)-C(11)-C(12)	108.0(5)	C(13)-C(11)-C(12)	107.5(4)
C(14)-C(11)-Si(6)	110.8(4)	C(13)-C(11)-Si(6)	111.4(4)	C(12)-C(11)-Si(6)	109.2(3)
C(16)-C(15)-C(17)	107.8(4)	C(16)-C(15)-C(18)	108.9(4)	C(17)-C(15)-C(18)	108.0(4)
C(16)-C(15)-Si(6)	113.6(3)	C(17)-C(15)-Si(6)	107.7(4)	C(18)-C(15)-Si(6)	110.7(3)
C(23)-C(20)-C(21)	108.2(5)	C(23)-C(20)-C(22)	108.5(4)	C(21)-C(20)-C(22)	107.1(4)
C(23)-C(20)-Si(7)	114.3(4)	C(21)-C(20)-Si(7)	108.4(3)	C(22)-C(20)-Si(7)	110.1(4)
C(26)-C(24)-C(27)	108.7(4)	C(26)-C(24)-C(25)	108.6(4)	C(27)-C(24)-C(25)	107.2(4)
C(26)-C(24)-Si(7)	113.0(3)	C(27)-C(24)-Si(7)	107.9(3)	C(25)-C(24)-Si(7)	111.3(3)
C(30)-C(28)-C(29)	108.2(4)	C(30)-C(28)-C(31)	107.0(5)	C(29)-C(28)-C(31)	109.2(4)
C(30)-C(28)-Si(4)	108.8(4)	C(29)-C(28)-Si(4)	111.3(4)	C(31)-C(28)-Si(4)	112.1(4)
C(35)-C(32)-C(33)	108.4(4)	C(35)-C(32)-C(34)	108.2(4)	C(33)-C(32)-C(34)	107.1(4)
C(35)-C(32)-Si(4)	113.6(4)	C(33)-C(32)-Si(4)	110.6(3)	C(34)-C(32)-Si(4)	108.6(3)

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