Density functional theory (DFT)/IGLO ^{29}Si NMR study of trialkylsilylated arenium, bromonium, oxonium and nitrilium ions, comparison with experimental data and the question of persistent trialkylsilicenium ions in solution [1]

George A. Olah *, Golam Rasul, G.K. Surya Prakash *

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, CA 90089-1661, USA

Abstract

Density functional theory (DFT)/IGLO ^{29}Si NMR studies show that there is no significant silicenium ion nature in trialkylsilyl substituted arenium, bromonium, oxonium and nitrilium ions. High electrophilicity of trivalent silicon and its affinity for π-donor arene solvents, as well as for oxygen, halogen and nitrogen heteroatoms of solvents or counter ions, is responsible for the inability to observe long-lived trisubstituted silyl cations.

Keywords: Silicon; Silicenium ions; MO calculations; Density functional theory; NMR

1. Introduction

Trialkylsilicenium ions are thermodynamically more stable than their carbon counterparts and are readily observed in the gas phase as high-abundance fragments in the mass spectra of organosilicon compounds [2a]. However, these ions have remained elusive as long-lived species in solution or in the solid state [2b]. In contrast, long-lived carbocations can be readily prepared and studied as stable entities in solution and even in solids. Their kinetic instability (i.e. reactivity) against n- or π- (or even σ-) electron donors (in counter ions or solvents) has prevented observation of trialkylsilicenium ions under long-lived ion conditions [3]. Recently, Lambert et al. [4] claimed to have obtained the crystal structure of a stable trialkylsilicenium cation, Et$_3$Si$^+$B(C$_6$F$_5$)$_4^-$, from toluene solution with only distant coordination to solvent (toluene) remaining in the crystal lattice. The reported crystal structure was, however,

shown to be that of the arenium ion, a σ complex, [Et$_3$Si-C$_6$H$_5$CH$_3$]$^+$, with a relatively long Si-C$_{para}$ bond (2.195 Å), instead of stable triethylsilicenium cation (Olah et al. [3], Pauling [5], Schleyer et al. [6], and Olsson and Cremer [7]). Previously, Lambert and Zhang had already claimed [8] the preparation of trisubstituted silicenium cations using tetrakis(pentafluorophenyl)borate as a weakly nucleophilic anion [9] in solvents such as benzene and toluene. However, the reported ^{29}Si NMR chemical shifts were in the range δ ^{29}Si 82 to 112 ppm, indicating the absence of any significant trivalent, tricoordinate silicenium cation character. Kira et al. [10] showed that n-donor solvents such as ethers, ketones and nitriles readily form silylated onium ions with trialkylsilyl tetrakis(3,5-bistrifluoromethylphenyl)borates. Bahr and Boudjouk [11] also showed the formation of stable trialkylsilylated nitrilium ions with tetrakis(3,5-bistrifluoromethylphenyl)borate anion. Cacace et al. [12] gave compelling evidence for the existence of [R$_3$Si-arene]$^+$ σ complexes by the actual isolation of the silylated neutral products from gas phase radiolytic ion-molecule reactions and from the mechanistic insight from FT-ICR mass spectrometry.

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* Corresponding authors.
[1] Dedicated to Professor Robert Corriu. See Ref. [1].

Reed and coworkers [13a] reported the X-ray structure of $R_3Si(Br_6CB_{11}H_6)$ with Si–Br bond distances of 2.43–2.48 Å and claimed that the complex is essentially close to a free trigonal silicenium ion. The average C–Si–C bond angles were found to be 115–117°. However, the Si–Br distances are only about 0.2 Å longer than usual; the Si–Br single bonds are clearly not those of trivalent silicenium ions and very strongly indicate only a silylated bromocarborane. The ^{29}Si NMR chemical shift of 105–115 ppm also reaffirms the bromonium ion character. A similar study has recently been reported with tris(isopropyl)silyl–$X_6CB_{11}H_6$ complexes whose ^{29}Si NMR chemical shifts were observed at $\delta\,^{29}Si$ 115, 110 and 97 for chloro, bromo and iodo derivatives respectively, clearly indicating halonium zwitter ionic characters [13b]. Reed and coworkers [14a] isolated a stable salt of $^{t}Bu_3Si(OH_2)^+$. The CP-MAS ^{29}Si NMR resonance of $^{t}Bu_3Si(OH_2)^+$ was at δ 46.7, in accordance with the onium ion character of the ion. The Si–O distance (1.779 Å) in the crystal structure of $^{t}B_3Si(OH_2)^+$ is only 0.1 Å longer than a typical Si–OH bond, again in good accord with the onium ion character. Olah et al. [14b] recently reported the observation of tris-trimethylsilyloxonium ion by NMR spectroscopy.

In view of our continuing interest in silylated onium ions and the silicenium ion problems, we report now density functional theory (DFT) [15]/IGLO [16] ^{29}Si NMR studies of silylated arenium, bromonium, oxonium and nitrilium ions and comparisons with the experimental data. DFT has recently become a successful alternative to traditional ab initio methods as it requires less computational effort but still includes some degree of correlation. All results indicate that the reported crystal structures are not those of "free" or "closely approaching" silicenium cations.

2. Results and discussion

2.1. p-Triethylsilyltoluenium ion [p-Et₃Si–C₆H₅CH₃]⁺ and triethylsilicenium ions Et₃Si⁺

The reported X-ray data [17] show two distinct isomers of [p-Et₃Si–C₆H₅CH₃]⁺, 1 and 2, depending on the conformation of the ethyl groups. We have fully optimized the structures at the B3LYP/6-31G* level

[18]. Isomer 1 is only 0.02 kcal mol⁻¹ more stable than isomer 2. Selected optimized parameters along with experimental data are given in Fig. 1 and Table 1. The calculated critical Si1–C8 bond distance in 1, 2.208 Å, agrees very well with the experimental value of 2.195 Å. This is also in good agreement with the reported ab initio (HF/6-31G* level) calculated [1,3] value of 2.197 Å. This longer Si–C8-bond length in 1 compared with the normal covalent bond distance of 1.85 Å is due to β-silicon hyperconjugation as shown in Scheme 1. The calculated average C–Si–C angle in 1, 114.1°, is also close to the experimental value of 113.9°. This good correlation between calculated and experimental parameters for 1 and 2 further indicates their true arenium ion nature.

We have also calculated the ^{29}Si NMR chemical shifts of 1, 2 and the triethylsilicenium ion 3 by IGLO II′ [19] using B3LYP/6-31G* optimized geometries (denoted as IGLO II′//B3LYP/6-31G*). The IGLO method was shown to be accurate for the ^{29}Si NMR chemical shift calculations [1,3,6,7,16,20,21] using ab initio HF/6-31G* and MP2/6-31G* geometries, but was not tested before for the DFT geometries (i.e. B3LYP/6-31G*). The calculated ^{29}Si NMR chemical shifts of 1 and 2 are $\delta\,^{29}Si$ 79.7 and 79.8 ppm respectively. These values are very close to the experimental $\delta\,^{29}Si$ value of 81.8 ppm for [p-Et₃Si–C₆H₅CH₃]⁺. However, the calculated ^{29}Si NMR chemical shift of 3 is 371.3 ppm, extremely far from the experimentally observed value of 81.8 ppm. The almost 290 ppm difference between the experimentally observed and calculated values excludes the presence of any claimed "free" or "closely approaching" triethylsilicenium ion 3. The optimized geometry of 3 is given in Fig. 2.

The rather large calculated binding energy of −34.2 kcal mol⁻¹ [p-Me₃Si–C₆H₅CH₃]⁺ relative to the separated Me₃Si⁺ and toluene, found by Schleyer et al. [6] at the MP2/6-31G*//HF/6-31G* + ZPE level, can be compared with the gas-phase high-pressure spectroscopically measured value of −28.4 kcal mol⁻¹ [22]. We have now calculated the binding energy of [p-Et₃Si–C₆H₅CH₃]⁺ 1 relative to the separated Et₃Si⁺ and toluene at the DFT B3LYP/6-31G*//B3LYP/6-31G* level to be −26.0 kcal mol⁻¹, again in good agreement with the experimental binding energy of [p-Me₃Si–C₆H₅CH₃]⁺.
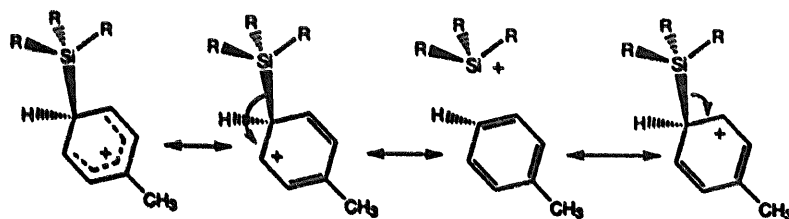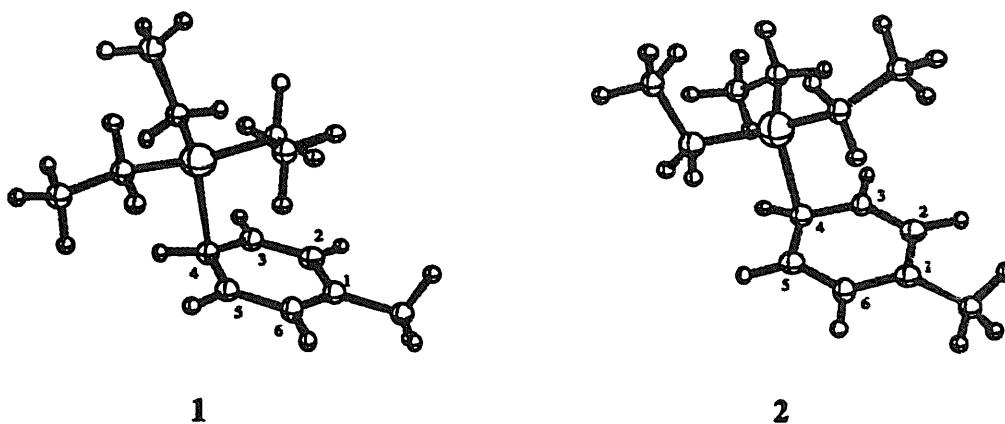

Scheme 1.

Fig. 1. B3LYP/6-31G* optimized structures of 1 and 2 (see Table 1 for parameters).

2.2. p-Trimethylsilylbenzenium ion $[p\text{-}Me_3Si\text{-}C_6H_5]^+$ and trimethylsilicenium ions Me_3Si^+

In order to understand the bonding and ^{29}Si NMR chemical shifts in silicenium ions in more detail we have also investigated the $[p\text{-}Me_3Si\text{-}C_6H_6]^+$ σ complex 4. 4 is closely related to the experimentally determined X-ray structure of 1. Ion 4, however, was only characterized in solution by ^{29}Si NMR spectroscopy [17].

We have systematically changed the crucial $Si\text{-}C_{para}$ bond distance of ion 4 from 1.85 to 4.85 Å. At each point we fully optimized the geometry at the B3LYP/3-21G level by keeping the $Si\text{-}C_{para}$ bond distance constant. For better energy comparison single point energies were computed at each point at the B3LYP/6-31G* level (i.e. B3LYP/6-31G*//B3LYP/3-21G). The resulting change of energy with respect to $Si\text{-}C_{para}$ bond distance is plotted in Fig. 3. The lowest energy structure of 4 at this level lies between $Si\text{-}C_{para}$ bond length. 2.1 and 2.4 Å, a distance similar to that of the experimental value for 1. The $Si\text{-}C_{para}$ bond distance with fully optimized geometry (no constraint) of 4 is 2.250 Å at the B3LYP/3-21G level. Changing the $Si\text{-}C_{para}$ bond distance of 4 beyond the optimized value of 2.250 Å sharply increases the energy. Even at a distance of 4 Å there is a considerable interaction between $(CH_3)_3Si^+$ and benzene. Increasing the $Si\text{-}C_{para}$ bond distance

from 4 to 5 Å results in a further decrease in interaction energy (by 5 kcal mol^{-1}). The ^{29}Si NMR chemical shifts of 4 were also calculated by IGLO (IGLO II'//B3LYP/3-21G) at each point, and are plotted against $Si\text{-}C_{para}$ bond distance in Fig. 4. The ^{29}Si NMR chemical shifts of 4 increase sharply with increasing $Si\text{-}C_{para}$ bond distance, and approach the value of free silicenium ion at about 4.5 Å. At the same level of calculation the ^{29}Si NMR chemical shift of the $(CH_3)_3Si^+$ ion is δ ^{29}Si 359.5 ppm. Thus it seems unlikely that any significant silicenium ion character can exist in complex 1 with $Si\text{-}C$ bond distance of 2.2 Å (i.e. with the para carbon).

We also optimized the structure 4 at the higher level, i.e. B3LYP/6-31G*. The calculated $Si\text{-}C_{para}$ bond distance in 4 is 2.228 Å (Table 1), again very close to the experimental value (2.195 Å) in 1 and the ab initio (HF/6-31G*) calculated value (2.214 Å) in 4. The IGLO calculated (IGLO II'//HF/6-31G*) ^{29}Si NMR
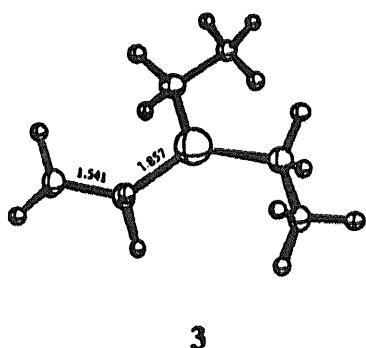

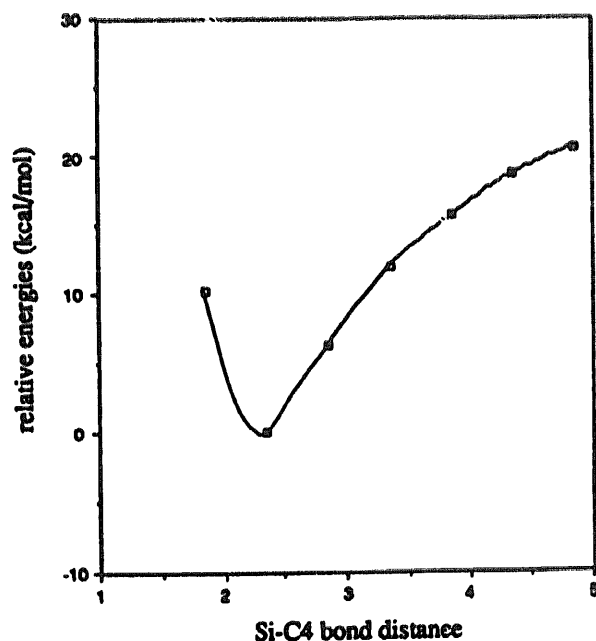Fig. 2. B3LYP/6-31G* optimized structure of 3.

Fig. 3. Energy vs. $Si\text{-}C_{para}$ bond distance (Å) in 4.

Table 1
Selected B3LYP/6-31G* optimized bond lengths (Å) and angles (°)

Parameters	1	1 (expt.) [a]	2	2 (expt.) [a]	4
Si–C4	2.208	2.195	2.207	2.174	2.228
R–Si–R [b]	114.1	113.8	114.2	114.1	114.3
Si–C4–C1	109.9	103.6	110.0	105.4	107.5
H–C4–C1	160.0	168.7	160.0	167.1	161.8

[a] X-ray data from Ref. [17]; [b] Average of three C–Si–C bond angles.

chemical shift of 4, 80.0 ppm (Table 2), is also in agreement with the experimentally determined value of 83.6 ppm in solution but far away from the calculated value of 354.2 ppm for free $(CH_3)_3Si^+$ ion at the same IGLO II'//B3LYP/6-31G* level.

2.3. Role of hyperconjugation

It was also argued [23] that weak π bonding of toluene to Si is responsible for the observed longer $Si-C_{para}$ bond distance in 1 rather than silicon hyperconjugation. We have now calculated as a model (lacking any π electrons), the β-trimethylsilyl-2-propyl cation 5, where the carbocationic centre can be stabilized only by β-Si hyperconjugation. Ion 5 was fully optimized at the B3LYP/6-31G* level. The calculated $Si-C_\beta$ bond distance in 5 is 2.197 Å, a distance similar to that in 1 (2.196 Å), indicating strong hyperconjugative stabilization of the carbocationic centre by the trialkylsilyl group. The average C–Si–C bond angle of 5 (114.7 Å) also agrees remarkably well with the average R–Si–R of 1 (114.2 Å). The calculated ^{29}Si NMR chemical shift (δ ^{29}Si 70.0) in 5 is also comparable with those of 1 (81.8) and 4 (83.6). Therefore in both triethylsilyl substituted arenium 1 and carbenium 5 ions, hyperconjugation is responsible for the lengthening of the Si=C bonds.

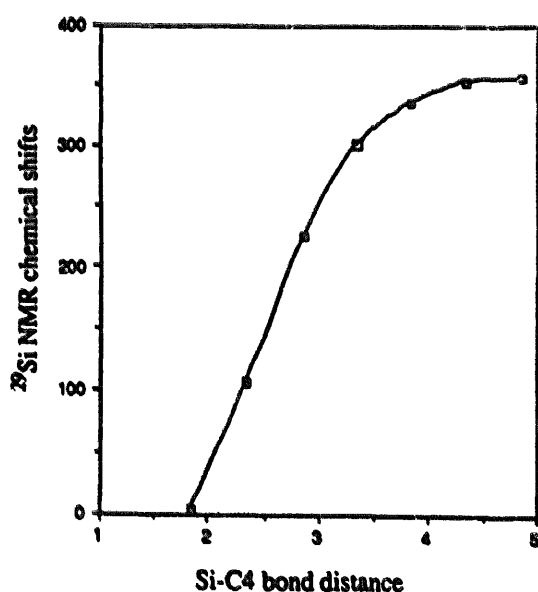Fig. 4. ^{29}Si NMR chemical shifts of 4 with respect to $Si-C_{para}$ bond distance (Å).

2.4. Silabromonium ions

The X-ray structure of $Et_3Si(Br_6-CB_{11}H_6)$ 6 has also been reported [13a] and the species was claimed to be of close to triethylsilicenium ion nature. The Si–Br bond distance of 2.444 Å seems however, to support a zwitterion with bromonium nature. However, the authors [13a] characterized it as a closely approaching silicenium ion. We have now calculated (at the B3LYP/6-311 + G* level) the methylsilabromonium ion $Me_3SiBrCH_3^+$ 7 and the protiosilabromonium ion Me_3SiBrH^+ 8 as models for the $Et_3Si(Br_6-CB_{11}H_6)$ 6. We have also calculated the geometry of the parent Me_3SiBr 9 at the same level and compared it with 7 and 8. The calculated Si–Br bond distance and C–Si–C bond angle in 9 are 2.284 Å and 111.6° respectively. They agree well with the experimental values [24] of 2.235 Å and 111.3° respectively (Fig. 6). However, the Si–Br bond in methylated trimethylsilyl bromide 8 is 2.523 Å, 0.239 Å longer than that in trimethylsilyl bromide 9 and very close to the observed Si–Br bond (2.430 Å) in 6. In the protonated analogue 7 the Si–Br bond (2.619 Å) is even longer. The average C–Si–C angle of 8, 116.4°, also agrees very well with the average C–Si–C angle 116.3° observed in 6. We also calculated the ^{29}Si NMR chemical shifts of 7, 8 and 9 at the IGLO II'' [25]//B3LYP/6-311 + G* level and these are listed in Table 2. Again the calculated ^{29}Si

Table 2
^{29}Si NMR chemical shifts of 1–13 (in ppm from TMS)

Compound	IGLO II'//B3LYP/6-31G*	Expected
TMS (T_d)	0.0	0.0
1 $Et_3Si C_6H_5CH_3$	79.7	81.8 [a]
2 $Et_3Si C_6H_5CH_3$	79.8	
3 Et_3Si^+	371.3	
4 $Me_3Si C_6H_6$	80.0	83.6 [a]
5 $Et_3Si C_3H_6$	70.0	
7 Me_3SiBrH^+	154.4 [b]	
8 $Me_3SiBrCH_3^+$	117.5 [b]	
9 Me_3SiBr	33.9 [b]	26.4 [c]
10 Me_3SiOH	15.1	
11 $Me_3SiOH_2^+$	101.9	
12 $(Me_3Si)_2OH^+$	67.6	
13 $Me_3SiNCCH_3^+$	51.5	
Me_3Si^+	354.2	

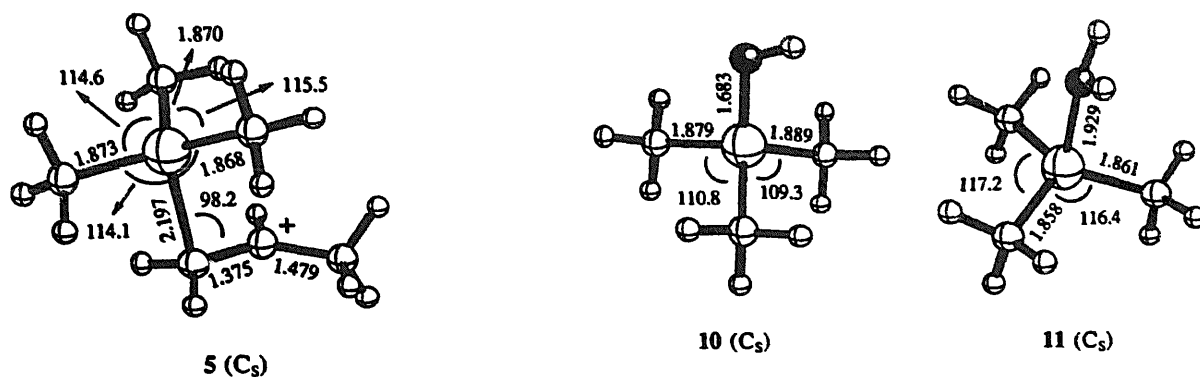[a] Ref. [17]; [b] at IGLO II''//B3LYP/6-311 + G*, see Ref. [25]; [c] Ref. [27].

Fig. 5. B3LYP/6-31G* optimized parameters of the β-trimethyl-silyl-2-propyl cation 5.

NMR chemical shift of **8** is 117.5 ppm, close to the experimental value of **6** (111.8 ppm) but completely outside the range of Et_3Si^+ (δ ^{29}Si 371.3). These comparisons clearly show that ion **6** has very little triethylsilicenium character and is de facto a bromonium zwitterion.

2.5. O-trialkyloxonium ions

We have calculated silanol Me_3SiOH **10** and silaoxonium ions $Me_3SiOH_2^+$ **11** and $(Me_3Si)_2OH^+$ **12** at the B3LYP/6-31G* level (Fig. 7). As expected, the calculated Si–O bond lengths in **11** (1.929 Å) and **12** (1.844

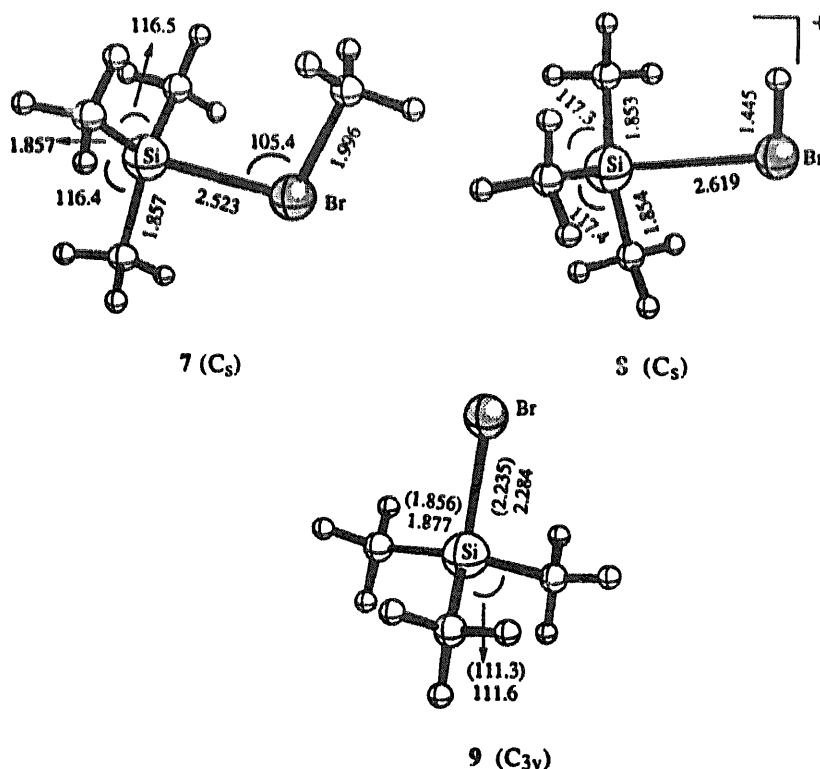Fig. 7. B3LYP/6-31G* optimized parameters of 10, 11 and 12.

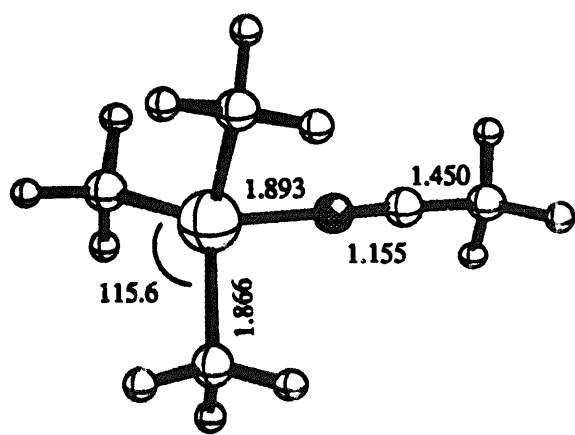Fig. 6. B3LYP/6-31G* optimized parameters (experimental) of 7, 8 and 9.

13 (C3v)

Fig. 8. B3LYP/6-31G* optimized parameters of 13.

3. Conclusion

In their work, both Lambert and Reed claimed to have isolated and characterized (by NMR and X-ray crystal structure) trialkylsilicenium salts or complexes closely approaching them. Our studies have, however, shown that these reported structures are not those of trialkylsilyl cations but of stable trialkylsilylated arenium, bromonium, oxonium and nitrilium ions. It is not thermodynamic but kinetic instability which prevents the observation of long-lived silicenium intermediates. In superacidic systems nucleophilic coordination with electron deficient species, such as carbocations, etc., is minimized. As stated before [1], silicenium ions, however, exert an even stronger attraction for fluorine, oxygen, etc. containing anions, as well as π or n-donor solvents, and thus do not exist as long-lived free species even in superacid solutions.

Å) are longer than that of neutral silanol precursor 10 (1.683 Å). However, the calculated Si–O bond length in 11 is only 0.1 Å longer than that found in the crystal structure of $^tBu_3Si(OH_2)^+$ (1.779 Å) [14], showing the silaoxonium ion nature of $^tBu_3Si(OH_2)^+$. The average C–Si–C angle in 11, 116.7°, is also close to that in $^tBu_3Si(OH_2)^+$ (116.0°). The IGLO II' calculated ^{29}Si NMR chemical shifts of 11 and 12 are 101.9 and 67.6 ppm respectively, considerably deshielded from that of the neutral precursor 10 (15.1 ppm). In contrast, the CP-MAS ^{29}Si NMR resonance of $^tBu_3Si(OH_2)^+$ at δ 46.7 ppm [14] is even shielded compared with those of 11 and 12. The geometries and ^{29}Si NMR chemical shifts of 11 and 12 were also calculated by Cremer and coworkers [7c] at the Hartree–Fock level (HF/6-31G*) and found similar to those in this study. Various trimethylsilylated oxonium ions were also calculated by Olah et al. [14b] at the Hartree–Fock level. The IGLO calculated ^{29}Si NMR chemical shifts (on HF/6-31G* geometries) of the ions are in good agreement with the experimental data obtained.

2.6. N-trimethylsilylacetonitrilium ion

We have optimized the trimethylsilylacetonitrilium ion $Me_3SiNCCH_3^+$ 13 at the B3LYP/6-31G* level (Fig. 8). The Si=N bond distance and C–Si–C bond angle in 13 are 1.893 Å and 115.6° respectively, matching the corresponding experimental values of 1.82 Å and 115.6° (in $^iPr_3SiNCCH_3^+$) [26]. The IGLO II' calculated ^{29}Si NMR chemical shift of 13 is 51.7 ppm, compared with the experimentally determined value of 37.0 ppm (in $Et_3SiNCPr_3^+$) [11]. Cremer and coworkers [7c] also calculated that of the ion 13 at the HF/6-31G* level.

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