Trimesitylsilylium cation verification of a free silylium cation in solution by NMR chemical shift calculations

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Abstract

NMR chemical shift calculations at the SOS–DFPT/PW91/[7s6p2d/5s4p1d/3s]//B3LYP/6-31G(d) level of theory were used to describe the trimesitylsilylium cation **1**, recently synthesized in benzene solution and investigated by NMR spectroscopy. The conformation of cation **1** is characterized by mesityl rings rotated by 47° in a propeller-like form. Contrary to other silylium cations investigated, cation **1** forms a weak Van der Waals complex **3** with benzene rather than a Wheland σ-complex. The calculated ^{29}Si NMR chemical shifts for **1** and **3** are 226 and 227 ppm, compared to the experimental value of 225.5 ppm. The agreement between calculated and measured NMR chemical shifts provides evidence that cation **1** presents the first free silylium cation synthesized. © 1997 Elsevier Science B.V.

1. Introduction

Until recently all attempts to generate silylium cations, R_3Si^+ (R: alkyl or aryl), in solution have failed because of the strong electrophilic character of the R_3Si^+ ions, which in solution react with either solvent molecules or the counterion thus forming tetra-, penta- or even higher coordinated Si compounds [1–3]. Attempts to generate R_3Si^+ in weakly nucleophilic solvents such as benzene or toluene in the presence of specially designed counterions such as tetrakis(pentafluorophenyl)borate, $(C_6F_5)_4B^-$ (TPFPB), where the negative charge is largely delocalized and in addition sterically shielded, Lambert et al. [4] gave lead to Wheland σ-complexes $R_3Si-C_6H_6^+$ with a largely developed C–Si bond, which indicates that the silylium cation character is completely lost in this situation [1,2,5]. Calculations predicted that R_3Si^+ reacts even with noble gas atoms

[2] and alkanes [6] so that a completely free silylium cation seemed to be an illusion.

Experimentally the nature of a silylium cation in solution is tested by measuring its NMR chemical shifts. Suitable reference values, which reveal whether the cation in question has changed its nature by solvent and/or counterion coordination are available from quantum chemical calculations [1–3,5,6]. Quantum chemical calculations on the stability, structure and magnetic properties of silylium cations in connection with NMR measurements in solution provide the most detailed and reliable account of the true nature of these species [1,2].
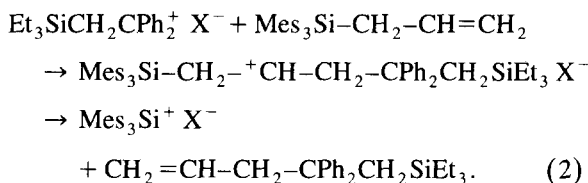
Recently, Kraka et al. [7] have investigated dimesitylcarbonyl oxide, which Sander et al. [8] had synthesized as the first carbonyl oxide that could be generated in solution at -78°C and investigated by NMR spectroscopy. Calculation of the geometry, conformation and the NMR chemical shifts of this

molecule using density functional theory (DFT) fully confirmed the results of the experimentalists and in addition, showed that the two mesityl groups effectively stabilize the labile R_2COO molecule and protect it against the attack of the nucleophilic solvent molecules. It is obvious that mesityl groups should also be used to stabilize a silylium cation, however the generation of the trimesitylsilylium cation, Mes_3Si^+ (1), via

$$Ph_3C^+ X^- + R_3Si{-}H \rightarrow Ph_3C{-}H$$

$$+ R_3Si^+ X^- \qquad (1)$$
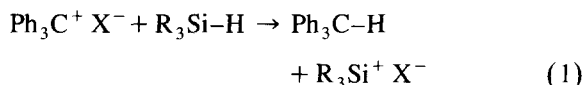
(X = TPFPB) in benzene solution does not work for Mes_3SiH because the bulky mesityl groups prevent a trityl cation in coming close enough to abstract a hydride ion from the silane.

Lambert and Zhao [9] solved this problem by: (a) moving the reaction center of the silane away from the mesityl groups with the help of an allyl group; and (b) using the weakness of the Si–C bond in a ß-silyl carbenium ion to generate 1 in benzene solution by the decomposition of an intermediately formed carbocation (see reaction 2):

$$Et_3SiCH_2CPh_2^+ X^- + Mes_3Si{-}CH_2{-}CH{=}CH_2$$

$$\rightarrow Mes_3Si{-}CH_2{-}^+CH{-}CH_2{-}CPh_2CH_2SiEt_3 \ X^-$$

$$\rightarrow Mes_3Si^+ X^-$$

$$+ CH_2{=}CH{-}CH_2{-}CPh_2CH_2SiEt_3. \qquad (2)$$

The ^{29}Si NMR chemical shift of 1 in benzene solution was measured to be 225.5 ppm, which suggests that Si possesses a considerable positive charge. The $\delta^{29}Si$ value hardly changed ($\Delta < 1$ ppm) when other aromatic solvents were used, causing the authors to conclude that the interactions between 1 and the solvent are weak and a free silylium cation had been generated [9].

In this Letter, we determine the geometry and conformation of cation 1 using DFT. In particular, we calculate the NMR chemical shifts of 1 to compare them with the shifts reported by Lambert and Zhao [9]. As found in the case of dimesitylcarbonyl oxide [7], the mesityl groups of 1 may rotate, which could lead to rotationally averaged NMR chemical shifts. The barrier for a synchronous rotation of the three mesityl groups was therefore determined by calculating the relative energy of form 2, in which
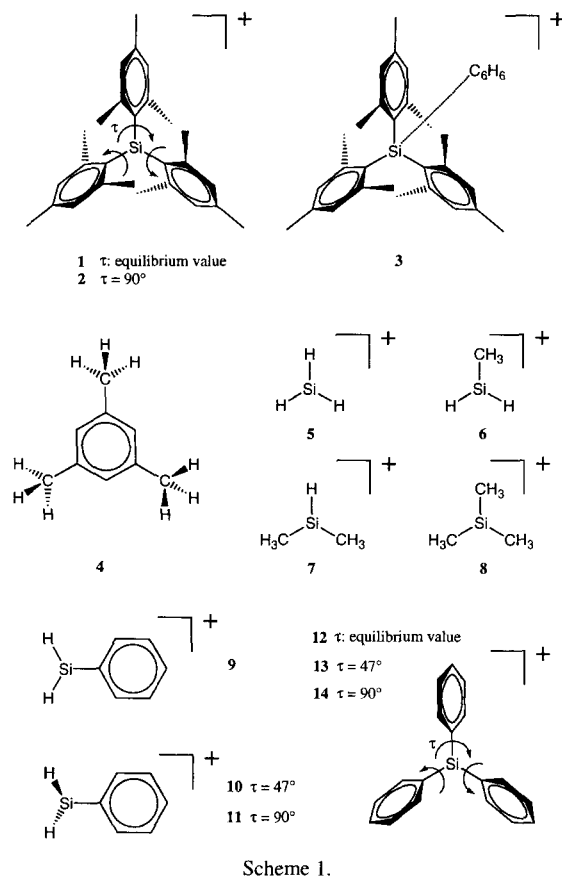
Scheme 1.

the three mesityl groups are rotated by $\tau = 90°$ relative to the SiC_3 reference plane of cation 1 (compare with Scheme 1).

DFT calculations lead to the NMR chemical shifts of 1 in the gas phase, which are experimentally not known. Agreement between the calculated NMR chemical shifts and the measured shifts does not necessarily imply that the properties of 1 in the gas phase are identical with those in benzene solution since errors in the calculation could lead to an accidental agreement between the corresponding values. To exclude this possibility we have investigated a possible Wheland σ-complex between cation 1 and benzene (3, Scheme 1). In addition, we have compared the NMR chemical shifts of both 1, 2, and 3 with those of mesitylene (4) and the silylium cations 5–14 shown in Scheme 1 in order to relate the

calculated NMR chemical shifts to the electronic structure of a silylium cation.

Investigations of **1–14** should also provide a basis to answer the question as to whether cation **1**, synthesized by Lambert and Zhao [9], represents the first free silylium cation in solution.

2. Computational methods

DFT using Becke's three-parameter functional B3LYP [10,11] and the 6-31G(d) basis set [12] to determine geometry and conformation of cation **1**, its rotated form **2**, the possible complex **3** and the reference molecules **4–14** of Scheme 1 was used.

The DFT–IGLO (*DFT individual gauge for localized orbitals*) method described by Olsson and Cremer [13], which is based on the sum-over-states density functional perturbation theory (SOS–DFPT) of Malkin and co-workers [14] and the original Hartree–Fock IGLO method of Kutzelnigg and Schindler [15], was employed to calculate the ^{1}H, ^{13}C, ^{29}Si NMR chemical shifts of **1–14**. For the shift calculations, a combination of the Becke exchange [16] and the Perdew–Wang (PW91) correlation functionals [17], rather than B3LYP, was used as PW91 is known to lead to better shift values [13]. As appropriate basis sets both the (11s7p2d/9s5p1d/5s1p) [7s6p2d/5s4p1d/3s1p] and (12s8p3d/11s7p2d/6s2p) [8s7p3d/7s6p2d/4s2p] sets were employed, which are of VTZ + P and VQZ + 2P quality, designed by Kutzelnigg and co-workers [18] for NMR chemical shift calculations with the IGLO method. For cations **1–3** the VTZ + P basis without π-type polarization functions at H was used to reduce calculational cost. All the DFT calculations involved an accurate calculation of the Coulomb part and numerical integration of the exchange-correlation potential [13]. The well-known deficiencies of DFT methods which to lead to occupied orbitals with relatively high energies and accordingly, to an overestimation of the paramagnetic contributions to the chemical shifts [19] were compensated for by adding appropriate level shift factors to the orbital energy differences as was suggested by Malkin et al. [20] and studied in detail by Olsson and Cremer [13]. Chemical shift calculations were carried out with the COLOGNE96 [21] pro-

gram package while for the geometry optimizations the Gaussian 94 ab initio program package was used [22].

3. Results and discussion

In Figs. 1–3, the B3LYP/6-31G(d,p) geometry of **1**, **2** and **3** are shown, respectively. Cation **1** possesses C_3 symmetry and is characterized by a planar SiC_3 unit (C–Si–C angle: 120°) at its center. The mesityl groups are rotated by $\tau = 47.3°$ out of the SiC_3 reference plane, like a propeller, thus avoiding close contacts between the *o*-positioned methyl groups. Compared to the most stable conformation of mesitylene shown in Fig. 4 ($\tau(HC_{Me}C1C2)$: 90°, 210°, 330°, Fig. 4), the *o*-methyl groups are rotated by −40°, which also keeps steric repulsion between the three mesityl groups low. The closest H,H contact between two *o*-methyl groups of different mesityl substituents is 2.85 Å while the closest H,H contacts within a mesityl group are 2.38 and 2.28 Å (see Fig. 1), which is in the range of typical Van der Waals' distance between H atoms (2.2–2.4 Å) [23].

The barrier for a synchronous rotation of the three mesityl propeller blades of **1**, defined by the relative energy of **2** ($\tau = 90°$) is 32.1 kcal/mol, is significantly higher than the corresponding barrier of the triphenylsilylium cation (**12**) given by the energy difference between **12** ($\tau = 27°$) and **14** ($\tau = 90°$, $\Delta E = 26.2$ kcal/mol, Table 1). The relatively high barrier of **1** is caused by close H,H contacts of just 2.055 and 2.097 Å between the *o*-methyl groups (Fig. 2), which cannot be avoided if one or all mesityl groups rotate. Hence, rotation of the mesityl groups and averaging of its NMR chemical shifts can be excluded for **1** at room temperature.

SOS–DFPT NMR chemical shifts for ^{29}Si and ^{13}C atoms of **1–14** are given either in Figs. 1–4 or Table 1. The calculated δ^{29}Si value for **1** in the gas phase is 226.3 ppm, which is close to the experimental value of 225.5 ppm measured in a benzene solution of **1** [9]. This seems to suggest that there are no significant solvent–solute interactions in benzene solution, changing the silylium cation character of **1** and that Lambert and Zhao have indeed generated the first silylium cation in solution. However, one has to consider the question: to what extent the
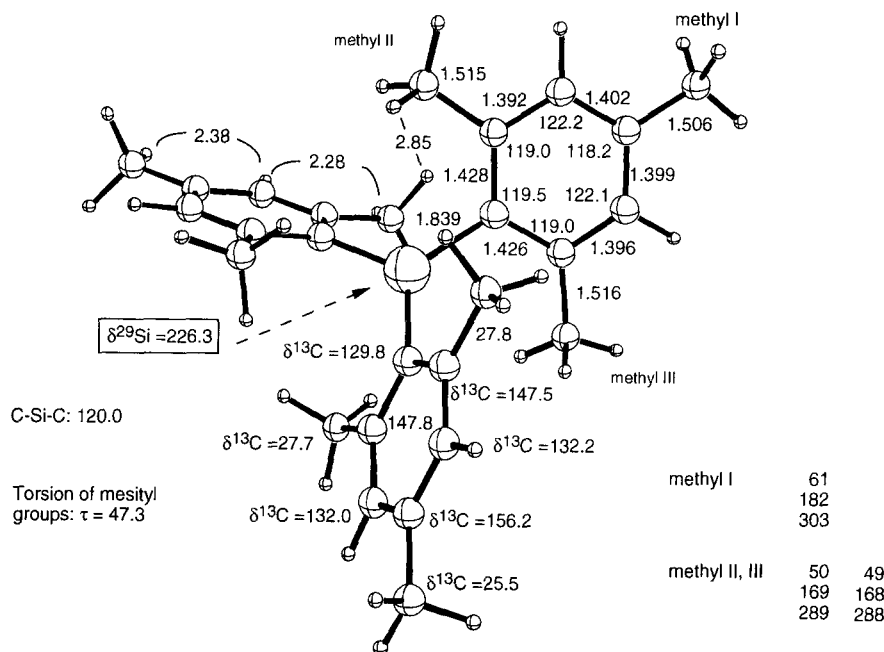
Fig. 1. B3LYP/6-31G(d) geometry and PW91/[7s6p2d/5s4p1d/3s] SOS–DFPT NMR chemical shifts of the trimesityl silylium cation (1). Geometrical parameters are given for the mesityl group in the upper right part. Calculated dihedral angles of methyl groups I–III are listed on the lower right side. Some non-bonded distance between H atoms are indicated for the mesityl group in the upper left part. ^{29}Si and ^{13}C NMR chemical shifts are given for the mesityl group at the bottom. Distances in Å, angles in deg, NMR chemical shifts relative to TMS in ppm (compare with Table 1).
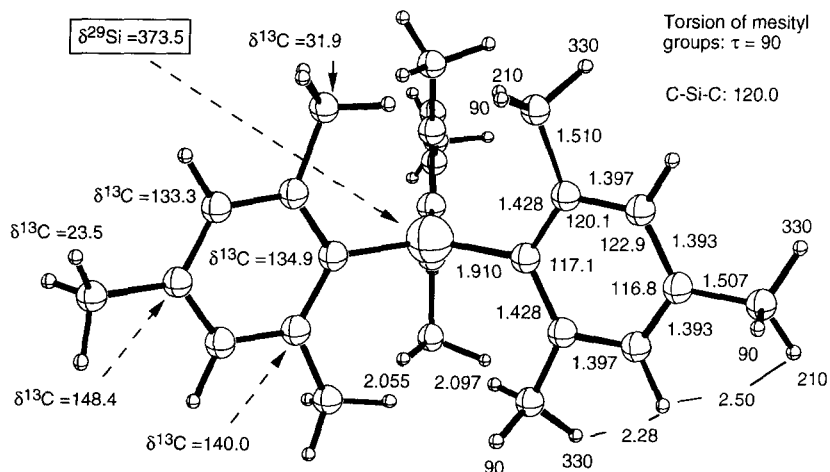
Fig. 2. B3LYP/6-31G(d) geometry and PW91/[7s6p2d/5s4p1d/3s] SOS–DFPT NMR chemical shifts of form 2, in which the three mesityl groups of 1 are rotated by 90° relative to the SiC$_3$ plane. Geometrical parameters are given for the mesityl group on the right side. Calculated dihedral angles H–C(methyl)–C(ipso)–C(ortho) (clockwise arrangement) of the methyl groups are also shown for each methyl hydrogen. Some non-bonded distance between H atoms are indicated in the lower part of the drawing. ^{29}Si and the ^{13}C NMR chemical shifts for the mesityl group on the left are also shown. Distances in Å, angles in deg, NMR chemical shifts relative to TMS in ppm (compare with Table 1).

Fig. 3. B3LYP/6-31G(d) geometry and PW91/[7s6p2d/5s4p1d/3s] SOS–DFPT NMR chemical shifts of complex 3. Geometrical parameters are given for the mesityl group on the right side and the benzene molecule. Some non-bonded distance between 1 and the benzene molecule are indicated by dashed lines. The ^{29}Si shift and the ^{13}C NMR chemical shifts for the mesityl group on the left are also shown. Distances in Å, angles in deg, NMR chemical shifts relative to TMS in ppm (compare with Table 1).

π-conjugation has reduced the silylium cation character of 1 and how much positive charge is spread over the C framework. It could be that 1 represents more a carbocation in the same way as the silaguanidinium ion represents more of an ammonium ion [1,24].

There is also the possibility that π-conjugation in 1 is strongly suppressed because of the steric strain between the mesityl groups and the rotation of these groups by 47°. The gas-phase chemical shift value of 1 could be in the region of 300 ppm (assuming an error of 80 ppm in the DFT–IGLO calculations, normally not observed (usual error: ±2 ppm) [1]); however, interactions between 1 and benzene molecules could cause an upfield shift to 225 ppm. Clearly, both situations (a silylium cation with strong delocalization of positive charge or a solvent complexed silylium cation) would not justify the definition of a free silylium cation in benzene solution in the case of 1. To consider the first situation we have to analyze the calculated NMR chemical shifts and the electron density distribution of 1 in more detail.

The ^{29}Si NMR chemical shift of 1 is much lower than the calculated gas-phase values of alkyl silylium cations as can be seen from Table 1. For SiH$_3^+$ (5), a δ^{29}Si value of 323 ppm is calculated, which increases to 352 (6), 366 (7) and 382 ppm (8) (VTZ + P

Fig. 4. B3LYP/6-31G(d) geometry and PW91/[5s4p1d/3s] SOS–DFPT NMR chemical shifts of mesitylene (4). Distances in Å, angles in deg, NMR chemical shifts relative to TMS in ppm.

basis) by successive replacement of H atoms with methyl groups. Improvement of the basis from VTZ + P to VQZ + 2P only leads to small changes in the calculated δ^{29}Si values (Table 1). A methyl group donates π-electronic charge to the Si($3p\pi$)-orbital (because of hyperconjugation), but in total withdraws more electronic charge from the Si than a H atom, deshielding the Si nucleus (Table 1), which is in line with its higher electronegativity χ(χ(CH$_3$): 2.472; χ(H): 2.176) [25]. A phenyl group donates electrons to Si$^+$ (Table 1) because of the conjugation of the empty $3p\pi$(Si) orbital with the π-system of the phenyl group. Delocalization of positive charge into the phenyl ring and the partial occupation of the $3p\pi$(Si) orbital leads to a δ^{29}Si shift of 217 ppm (9, Table 1). The ^{29}Si NMR signal is shifted by almost 100 ppm, to lower field, if the conjugation effect is suppressed by rotating the phenyl group by 90° (11, δ^{29}Si = 312 ppm, rotational barrier: 17.3 kcal/mol, Table 1). The δ^{29}Si chemical shift of 5 and 11 differ by just 11 ppm (Table 1), which suggests that the electron density distribution at the Si atom in 11 is similar to that in 5 (Table 1), probably because of a balance of inductive and hyperconjugative effects between SiH$_2^+$ and the phenyl substituent.

The degree of electron delocalization in an aryl-substituted silylium cation can be assessed by the calculated electron population of the $3p\pi$(Si) orbital and the ^{13}C NMR chemical shift of the π-positioned C atom [26]. Appropriate values are listed in Table 1, where one has to use molecular forms with rotational angles $\tau = 90°$ as suitable reference systems. π-electron delocalization is reduced with the cosine of the rotational angle τ, i.e. at $\tau = 27°$ (12) there is only a 10% reduction while at $\tau = 47.3$ (1, 13) the reduction has increased to $\sim 30\%$. This is confirmed by the calculated $3p\pi$(Si) population values (populations calculated for 9–11 suggest a reduction of π-delocalization by 35% at $\tau = 47°$, Table 1) where there seems to be no difference between a phenyl and a mesityl substituent. Hence, the calculated δ^{29}Si value of 1 is in line with those of the model system 13, suggesting ~ 60–70% π-delocalization of a hypothetical triphenyl or trimesityl silylium cation with $\tau = 0°$ and no steric repulsion. Calculated population values also suggest hyperconjugative and inductive effects active in the 90° form 14, which leads to some shielding of the Si nucleus in 11 and 14 relative to that of 5. Paramagnetic effects seem to be similar for both 1 and 13. This will change only if

Table 1

B3LYP/6-31G(d) energies, PW91/[7s6p2d/5s4p1d/3s1p] and PW91/[8s7p3d/7s6p2d/4s2p] SOS/DFPT NMR chemical shifts, and Si charges of silylium cations 1–14 [a]

#	Molecule	Conf.	Sym.	Energy ΔE	δ^{29}Si	$3p\pi$(Si)	$+q$(Si)	δ^{13}C [c]
1	SiMes$_3^+$	$\tau = 47.3$	C$_3$	0	226.3 [b]	404	541	156.2
2	SiMes$_3^+$	$\tau = 90$	C$_3$	32.1	373.5 [b]	128	648	158.4
3	SiMes$_3^+ \cdot$ C$_6$H$_6$	$\tau = 45$–48	C$_1$	1.8	227.6 [b]	402	545	155.5
5	SiH$_3^+$		D$_{3h}$		322.8 (320.7)	0	760	
6	SiH$_2$CH$_3^+$		C$_s$		351.6 (350.3)	116	790	
7	SiH(CH$_3$)$_2^+$		C$_{2v}$		365.7 (365.3)	132	835	
8	Si(CH$_3$)$_3^+$		C$_{3h}$		381.8 (380.9)	196	885	
9	SiH$_2$Ph$^+$	$\tau = 0$	C$_{2v}$	0	217.2	320	551	154.5
10	SiH$_2$Ph$^+$	$\tau = 47.3$	C$_2$	8.0	250.9	211	598	151.5
11	SiH$_2$Ph$^+$	$\tau = 90$	C$_{2v}$	17.3	311.8	12	694	141.5
12	SiPh$_3^+$	$\tau = 27.2$	D$_3$	0	193.5 [b]	488	552	142.0
13	SiPh$_3^+$	$\tau = 47.3$	D$_3$	6.6	217.6 [b]	415	537	141.5
14	SiPh$_3^+$	$\tau = 90$	D$_{3h}$	26.2	279.9 [b]	123	614	136.5

[a] Dihedral angles τ in deg, energy differences in kcal/mol, NMR chemical shifts in ppm relative to TMS (magnetic shielding σ at PW91/[5s4p1d/3s]: 354.3 (^{29}Si) and 184.5 ppm (^{13}C); at PW91/[7s6p2d/5s4p1d/3s1p]: 351.0 (^{29}Si) and 186.7 ppm (^{13}C)). NMR chemical shifts in parentheses were calculated at PW91/[8s7p3d/7s6p2d/4s2p]. The electron population of the $3p\pi$(Si) orbital and the positive charge of the Si atom ($+q$) are given in melectron. B3LYP/6-31G(d) energies are: -1338.07015 (1), -1570.32205 (3), -290.93311 (5), -330.28762 (6), -369.63769 (7), -408.98328 (8), -522.05203 (9), -984.22284 hartree (12).

[b] [7s6p2d/5s4p1d/3s] basis used.

[c] p-positioned C atom in an aryl group.

steric repulsion increases strongly, as is documented by the δ^{29}Si value of **2** (373 ppm, Table 1).

π-delocalization in **1** fills up the $3p\pi$(Si) orbital of **1** by just 40% (Table 1), which is twice as large as in the case of the hyperconjugative interactions of the three methyl groups (**8**, Table 1), but still small enough to guarantee silylium cation character for **1**. Since the LUMO of **1** is also dominated by the $3p\pi$(Si) orbital, both requirements for a silylium cation [1] are fulfilled and one can speak of a silylium cation in the case of **1**.

Previous quantum chemical investigations have shown that $(CH_3)_3Si^+$ (**8**), [5] $(CH_3CH_2)_3Si^+$, [1] $((CH_3)_3Si)_3Si^+$, [27] and the tris(9-borabicyclo[3.3.1]nonyl)silylium cation, $Si(9-BBN)_3^+$, [28] react with benzene to form a Wheland σ-complex. However, complex **3** (Fig. 3) represents a weak Van der Waals' complex rather than a Wheland σ-complex as is indicated by the calculated complexation energy of 1.8 kcal/mol and the calculated distance of 5.87 Å between the Si atom and the nearest benzene C, which is much larger than a Si,C Van der Waals' distance of 3.85 Å [23]. The closest H,H contacts between benzene and **1** are also well above the typical H,H Van der Waals' distances (Fig. 3).

Because of the large distance between the two molecules, the geometrical distortions of both benzene and cation **1** are moderate (Fig. 3). Noteworthy are the small changes in the SiC and CC bond lengths and in the rotation of the mesityl groups. Apart from this, the SiC_3 unit keeps its planarity, which indicates that the silylium cation character of **1** in the presence of the benzene molecule is preserved. Accordingly, charge distribution and NMR chemical shifts of **1** and **3** hardly differ. The calculated δ^{29}Si value of **3** is 227 ppm, again close to the measured value.

The calculated energies and geometries obtained could be affected by basis set superposition errors (BSSE), zero-point energy corrections and deficiencies of the B3LYP approach. BSSE corrections have not been considered in this work because of the large distance between the interacting molecules and the fact that DFT calculations are less sensitive to basis set completeness problems. Evaluation of zero-point energies at a lower level of theory suggests that there are no significant vibrational corrections to the com-

plexation energy of **3**. More serious, however, is the fact that DFT in general underestimates the stability of Van der Waals' complexes because it fails to correctly describe fluctuations in the electron density distribution at larger distances between interacting molecules. This deficiency is less obvious when electrostatic interactions dominate the stability of a Van der Waals' complex as in the case of H-bonded complexes, ion-dipole or dipole–dipole complexes.

In the case of **3**, induction, dispersion and exchange repulsion interactions determine the complex stability. Most likely, the complex stability is underestimated by 1–2 kcal/mol. The energy of the complex increases only slightly when the closest H,H contacts between the two molecules are reduced to 2.4 Å, but it increases by 6 kcal/mol on forcing the two molecules to a $Si,C_{benzene}$ contact distance of 4.5 Å, which is above the Si,C Van der Waals' distance of 3.85 Å. These data clearly indicate that a SiC contact that leads to any weak covalent interactions between the Si^+ center and the benzene molecule in the sense of a Wheland σ-complex is impossible.

The agreement of the calculated δ^{29}Si NMR chemical shift values of 226–227 ppm (**1** and **3**) with the measured value of 225.5 ppm [9], the low stability of complex **3** (1.8 kcal/mol) and the large $Si,C_{benzene}$ contact distance of 5.8 Å strongly suggest that **1** in benzene solution represents a free silylium cation synthesized in solution.

Acknowledgements

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