Gas Phase Structure of Ruppert's Reagent, CF_3SiMe_3

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CF_3SiMe_3 (Ruppert's reagent) has been investigated by gas phase electron diffraction, microwave spectroscopy and quantum chemical methods, deriving structural parameters and the barrier height for the methyl torsion. The bond length of the Si−CF_3 bond, 1.941(3) Å, is the longest Si−C bond observed so far in the gas phase. The V_3 barrier for the methyl group torsion (V_3 = 5.71 kJ/mol) is only slightly lower than barriers determined for other trimethylsilane compounds.

Introduction

Trifluoromethylated organic compounds exhibit interesting physical, chemical, and biological properties that make them attractive for new applications in the areas of materials science, agrochemistry, and biomedical chemistry.[1−3] Though several methods have been developed for introducing trifluoromethyl groups in organic substances, the use of (trifluoromethyl)-trimethylsilane, CF_3SiMe_3, as a nucleophilic trifluoromethylating reagent has become the method of choice. This silane was first synthesized by Ruppert in 1984 by condensing CF_3Br and $ClSiMe_3$ with $(Et_2N)_3P$ and is now commonly called Ruppert's reagent.[4] Several modifications of this synthesis and other methods for the synthesis of this reagent have since been proposed.[5] In the past 10 years a large number of publications involving Ruppert's reagent have appeared, many of which are summarized in three review articles.[5−7] The high tendency for CF_3 transfer to many organic compounds has been rationalized by the weak Si−CF_3 bond in Ruppert's reagent.

Previous structural studies have demonstrated that CH_3/CF_3 substitution in silanes causes strong lengthening of the Si−C bond. The Si−C bond in CF_3−SiH_3 (1.923(3) Å)[8] is considerably longer than that in CH_3−SiH_3 (1.864(1) Å).[9] This lengthening has been attributed to the electron withdrawing nature of fluorine, resulting in a high positive net charge for carbon as well as for silicon, Si^+−C^+. This weakening of the bond upon fluorination is also indicated by the force constants of 2.63 and 3.07 N cm^{-1} for the Si−CF_3 and Si−CH_3 bonds in CF_3SiMe_3, respectively.[10] In the present study we report the determination of the geometric structure of gaseous (trifluoromethyl)trimethylsilane and of the barrier hindering internal rotation of the methyl groups. The principal interest lies in the difference between the Si−CF_3 and Si−CH_3 bond lengths in this compound. The most accurate method to derive geometric structures of gaseous molecules, especially in the case of closely spaced bond distances, is a joint analysis of gas electron diffraction intensities (GED) and rotational constants derived from microwave spectra (MW). The experimental investigations are supplemented by quantum chemical calculations.

Quantum Chemical Calculations

The geometry of CF_3SiMe_3 was optimized with the MP2 approximation (6-31G*, 6-31+G(2df), cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets) and with the DFT method B3LYP/6-311++G(2df,pd). The calculated geometric parameters are listed together with the experimental values in Table 3. It can be seen from the MP2 structures derived with basis sets of different quality that even the best basis set is not sufficient for the determination of a reliable ab initio structure. The influence of the diffuse functions on the Si−CF_3 bond length is much more pronounced than the influence of the size (quality) of the set. This trend is reversed in the case of the Si−CH_3 bond lengths. Vibrational frequencies were derived with the MP2/6-31G* method. From this force field vibrational amplitudes and vibrational corrections for interatomic distances ($\Delta r = r_a - r_{h1}$) and for rotational constants (ΔB) were derived using the method of Sipachev.[11] This method that is based on the use of curvilinear coordinates in a harmonic force field takes better account of large amplitude motions than the conventional concept of rectilinear (perpendicular) vibrations. All quantum chemical calculations were performed with the Gaussian98 program set.[12] To obtain the V_3 potential of the methyl groups, we determined the potential energy surface (PES) by calculating the electronic energies at the MP2 level. In $CF_3Si(CH_3)_3$, all three CH_3 groups and the CF_3 group perform internal rotation. To restrict the problem to three dimensions, we decided to treat the motion of the CF_3 group separately.

To determine the potential energy curve of the rotation of the CF_3 group, the energies were calculated at the MP2/6-311G** and MP2/6-311++G** levels. The CF_3 group was rotated in steps of 15°. During this rotation the torsional angle of one F in the CF_3 group was fixed, all other parameters were optimized. According to the ab initio results for similar molecules[13] the staggered positions for the methyl groups were chosen as the starting geometry for optimization. As expected, also the CF_3 group is in a staggered position at the energy minimum. The resulting V_3 barrier is 8.27 kJ/mol at the MP2/6-311G** level and 9.29 kJ/mol at the MP2/6-311++G** level.

In the next step the potential energy surfaces of the rotation of the methyl groups were calculated on the same levels of theory. The methyl groups were rotated in steps of 15°, choosing the all staggered conformation as the starting geometries. During this rotation the torsional angle of one H in each CH_3 group

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TABLE 1: Fourier Coefficients of the PES Calculated on MP2/6-311G and MP2/6-311G** Level**

coefficient	MP2/6-311G**	MP2/6-311++G**
$a_{100}^{000} = a_{010}^{000} = a_{001}^{000}$	3.5340(12)	3.3321(11)
$a_{110}^{000} = a_{101}^{000} = a_{011}^{000}$	0.2253(16)	0.2614(15)
$a_{110}^{110} = a_{101}^{101} = a_{011}^{011}$	−0.1875(16)	−0.2198(15)
$a_{200}^{000} = a_{020}^{000} = a_{002}^{000}$	0.0545(12)	0.0415(11)
$a_{110}^{100} = a_{011}^{010} = a_{101}^{001} = - a_{101}^{100} = - a_{011}^{001} = - a_{110}^{010}$	0.0256(16)	0.0316(15)
$a_{120}^{000} = a_{012}^{000} = a_{102}^{000} = a_{210}^{000} = a_{021}^{000} = a_{201}^{000}$	−0.0152(16)	−0.0143(15)

was fixed, all other parameters were optimized. As in the analysis of the internal motions of $(CH_3)_3SiCl$,[13] the three-dimensional PES is expressed as a Fourier series.

$$V(\alpha_1,\alpha_2,\alpha_3) = \sum_{w=0}^{1}\sum_{v=0}^{1}\sum_{u=0}^{1}\sum_{m=0}^{\infty}\sum_{l=0}^{\infty}\sum_{k=0}^{\infty} a_{klm}^{uvw} f^{\,u}(3k\alpha_1)\, f^{\,v}(3l\alpha_2)\, f^{\,w}(3m\alpha_3)$$

with $f^{\,0}(x) = \cos x$ and $f^{\,1}(x) = \sin x$. The dihedral angle FCSiC was determined to be 60°. Therefore the same set of conditions and relations between the Fourier coefficients as in the case of $(CH_3)_3SiCl$ apply.

$$a_{n00}^{100} = a_{0n0}^{010} = a_{00n}^{001} = 0$$

$$a_{n00}^{000} = a_{0n0}^{000} = a_{00n}^{000}$$

Identical coefficients and such coefficients differing only in

$$a_{nm0}^{000} = a_{0nm}^{000} = a_{m0n}^{000} = a_{mn0}^{000} = a_{0mn}^{000} = a_{n0n}^{000}$$

$$a_{nm0}^{100} = a_{0nm}^{010} = a_{m0n}^{001} = - a_{n0m}^{100} = - a_{0mn}^{001} = - \mathrm{a}_{\mathrm{mno}}^{010}$$

sign were fitted together. The resulting parameters with values larger than 10 J mol^{-1} are shown in Table 1. The errors indicate how well the parameters could be least-squares fitted to the model function. They do not tell anything about the quality of the calculations; i.e., they cannot be used for the discussion of experimental results. The V_3 barrier to internal rotation of the methyl groups was calculated to be 7.07 kJ mol^{-1} at the MP2/6-311G** level and 6.66 kJ mol^{-1} at the MP2/6-311++G** level, respectively.

Experimental Section

A commercial sample of CF_3SiMe_3 (Aldrich, 99%) was used. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[14] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was cooled to −30 °C and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with an Agfa Duoscan HiD scanner and total scattering intensity curves were obtained from the TIFF-file using the program SCAN3.[15] Averaged experimental molecular intensities in the ranges $s = 2-18$ and $8-35$ Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} ($s = (4\pi/\lambda)\sin\theta/2$, where λ is the electron wavelength and θ is the scattering angle) are shown in Figure 1.

The microwave spectra were recorded in Aachen with the molecular beam Fourier transform microwave spectrometer (MB−FTMW)[16] in the range 2.5−25.5 GHz and in Tübingen with a conventional 50 kHz modulated Stark spectrometer in the range 23−36 GHz. Lists of all recorded transitions for the main isotopomer as well as for the isotopomers ^{29}Si, ^{30}Si, $^{13}CF_3$, and the asymmetrically substituted species, $CF_3Si(^{13}CH_3)(^{12}CH_3)_2$ are given in Tables S1−S5 as Supporting Information.

Analysis of the MW Spectra. In case of a rigid structure (high barrier to internal rotation) CF_3SiMe_3 is a symmetric top with the conventional selection rules $\Delta J = \pm1$, $\Delta K = 0$. However, in the case of a relatively low barrier to internal rotation of the three methyl groups, a complex torsional fine structure can be observed. Because the CF_3 group is situated on the axis of symmetry in the symmetric isotopomers, it is clear from the theory of internal rotation that it will not cause any splittings in the spectrum. $CF_3Si(^{13}CH_3)(CH_3)_2$ is a slightly asymmetric rotor and the barriers to internal rotation of the CF_3 group and the methyl groups are calculated to be in the same order of magnitude. Nevertheless, no further splittings due to an internal rotation of the CF_3 group were detected. This appears reasonable because not only is the angle between the internal rotor axis and the a-axis very small but the moment of inertia of a CF_3 group is also much bigger compared to a methyl group.

In the case of low temperature (−30 °C) conventional spectroscopy the rotational transitions are complicated by the presence of many vibrationally (torsionally) excited states, but with the molecular beam technique at an effective rotational temperature of a few Kelvin, practically only molecules in the vibrational ground state are populated. For this work, where the structure of Ruppert's reagent and the barriers to internal rotation of the methyl groups are focused upon, only these transitions will be discussed.

Thus, the Hamiltonian used for the description of the microwave spectra of the symmetric top species as well as the ^{13}C substituted asymmetric top species will consist of six partial Hamiltonians describing the different types of movement and interactions:

$$\mathbf{H} = H_{\mathrm{rot.}} + H_{\mathrm{tors}} + H_{\mathrm{rr}} + H_{\mathrm{tt}} + H_{\mathrm{rt}} + H_{\mathrm{cd}}$$

$H_{\mathrm{rot.}}$ represents the Hamiltonian for a rigid asymmetric top consisting of a rigid frame and three internal rotors. H_{tors} represents the Hamiltonian of a Mathieu oscillator and describes the contribution of hindered internal rotation of the three methyl rotors. H_{rr} can be interpreted as the contribution from a change of the location of the principal axes system due to the angular momentum created by internal rotation (Coriolis coupling). H_{tt} describes the kinetic interaction between the internal rotors. H_{rt} represents the interaction between internal and overall rotation of the whole molecule and finally H_{cd} contains the quartic centrifugal distortion terms for an asymmetric rotor.

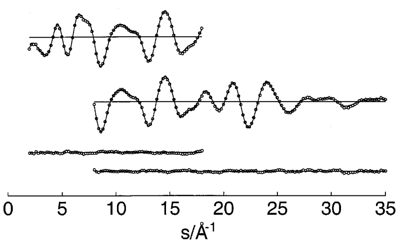

Figure 1. Experimental (dots) and calculated molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

TABLE 2: Molecular Constants of $(CH_3)_3SiCF_3$[a]

	$(^{13}CH_3)(CH_3)_2SiCF_3$	main isotopomer	$(CH_3)_3{}^{29}SiCF_3$	$(CH_3)_3{}^{30}SiCF_3$	$(CH_3)_3Si^{13}CF_3$
B_J/GHz[b]	1.266363196(28)	1.278599447(39)	1.275565007(20)	1.272592603(24)	1.275755171(20)
B_K/GHz[c]	0.717069(22)	0.732984973[h]	0.736019433[h]	0.738991837[h]	0.735829269[h]
$B\_$/GHz[d]	0.004966216(26)	0.0	0.0	0.0	0.0
D_J/kHz	0.11162(21)	0.11343(29)	0.11343[j]	0.11343[j]	0.11343[j]
D_{JK}/kHz	0.1052(51)	0.1052[i]	0.1052[i]	0.1052[i]	0.1052[i]
V_3/GHz	14315.0(54)	14315.0[i]	14315.0[i]	14315.0[i]	14315.0[i]
V_3/kJ mol^{-1}	5.7121(22)	5.7121[i]	5.7121[i]	5.7121[i]	5.7121[i]
N[e]	180	94	31	38	33
σ/kHz[f]	2.2	2.6	3.2	3.7	3.2
I_α/uA^2	3.259[g]	3.259[g]	3.259[g]	3.259[g]	3.259[g]
F_0/GHz	155.07[g]	155.07[g]	155.07[g]	155.07[g]	155.07[g]
$\vartheta_{i,a}(^{12}C)$/deg	107.2578[g]	106.2[g]	106.2[g]	106.2[g]	106.2[g]
$\vartheta_{i,a}(^{13}C)$deg°	105.6690[g]				
A/GHz	1.983433(22)	2.011584420[g]	2.011584440[g]	2.011584440[g]	2.011584440[g]
B/GHz	1.271329411(34)	1.278599447(39)	1.275565007(20)	1.272592603(24)	1.275755171(20)
C/GHz	1.261396980(42)	1.278599447(39)	1.275565007(20)	1.272592603(24)	1.275755171(20)

[a] Only transitions up to $J = 10-9$ were used, torsional hyperfine structure analyzed with I_α and angle between internal axes and *a*-axis as well as rotational constant *A* fixed to GED/MW structure. [b] $B_J = 0.5(B + C)$. [c] $B_K = A - 0.5(B + C)$. [d] $B\_ = 0.5(B - C)$. [e] *N*: number of torsional components in the fit. [f] σ: standard deviation of the fit. [g] Fixed to experimental structure. [h] *A* fixed to experimental structure. [i] Fixed to $^{13}CH_3$ isotopomer. [j] Fixed to main isotopomer.

Usually barriers to internal rotation are determined by investigating the torsional fine structure of the main isotopomer. $CF_3Si(CH_3)_3$ is a symmetric top molecule showing centrifugal distortion effects on the usual order of magnitude. During the analysis of the spectra it turned out that the splittings due to internal rotation were of the same order of magnitude as the frequency differences of transitions with the same *J* but different *K* values. This results in patterns of many lines partly superimposed, which were found to be quite difficult to analyze. Therefore we decided to analyze the isotopomer with a ^{13}C substitution on one methyl group first. Due to this substitution we were dealing with a slightly asymmetric top molecule, which removed the problem of overlapping *K* patterns.

The torsional barrier V_3 was determined by least-squares fitting using the program XIAM.[17] During the fit of the barrier to internal rotation we had to fix the rotational constant of the methyl group as well as the angle between the internal rotor axis and the inertial *a* axis. In the first fit (I) we fixed these values to the ab initio structure calculated at MP2/cc-pVTZ level. In a second fit (II) these values were fixed to the experimental structure. Both fits lead to very similar results (V_3(ab initio) = 5.86 kJ/mol, V_3(exp) = 5.71 kJ/mol). The complete result of the latter fit is given in Table 2.

For the analysis of the symmetric top species we fixed the barrier to internal rotation to the value obtained in the analysis of the asymmetric top isotopomer. Because the inertial *a* axis of the $^{13}CH_3$ isotopomer is rotated by less than 1° with respect to the main isotopomer, we decided to fix the centrifugal distortion constants for the symmetric top species, where insufficient data were available, to the values obtained for the $^{13}CH_3$ species. The weight of the measured transitions used in the fit (Tables S1−S5 in Supporting Information) was chosen according to their experimental uncertainty. To derive the rotational constants, the fine structure of the transitions must first be elucidated. The spectrum of the off-axis substituted isotopomer $CF_3Si(^{13}CH_3)(^{12}CH_3)_2$ plays a particular role in the analysis of the rotational spectra. For this species it was possible to determine the rotational constants B_J, B_K and B_-, as well as the centrifugal distortion constants D_J and D_{JK}. Furthermore, V_3, the barrier to internal rotation of the CH_3 groups, was determined by a least-squares fit[17] using the Hamiltonian described above. Due to numerous superposition of lines and due to the weakness of transitions with $K \geq 1$, only the strongest transitions were used in the fit. For the rotational constant F_0 of the methyl group, the moments of inertia I_α were fixed to the structure. In the analysis of the spectrum for the parent isotopomer the values of D_{JK} and V_3 were fixed to those derived above. For the rare symmetric isotopic species D_J was also fixed. The results of the analysis of the MW spectra are included in Table 2.

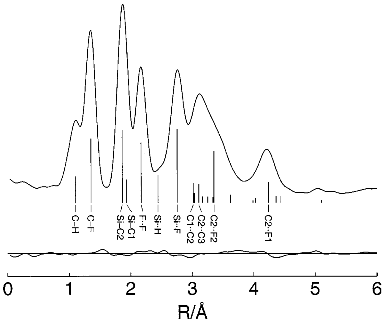

Figure 2. Experimental radial distribution function and difference curve. Important interatomic distances are indicated by vertical bars.

Structure Determination. The experimental radial distribution function (Figure 2) was calculated by Fourier transformation of the molecular electron diffraction intensities which were modified with an artificial damping function $\exp(-\gamma s^2)$, $\gamma = 0.0019$ Å^2. The geometric parameters were derived by least-squares fitting of the intensities, assuming C_{3v} overall symmetry as well as C_{3v} local symmetry for the CF_3 and CH_3 groups. These assumptions are justified by the results of quantum chemical calculations. For the two different Si−C bond lengths the average value and the difference were refined. Vibrational amplitudes for non bonded C···H, F···H, and H···H distances were fixed to calculated values. With these assumptions seven geometric parameters and nine vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.6|: $(Si-C)_{mean}/FCF = -0.64$, $C-F/FCF = 0.77$, $\Delta SiC/FCF = -0.80$ and $\Delta SiC/l(Si-C) = -0.77$. The geometric parameters derived in this analysis are listed in Table 3. A molecular model with atom numbering is shown in Figure 3.

In the next step of the structural analysis the MW data were included. In this joint analysis of GED and MW data rotational constants of four C_{3v} isotopomers, $CF_3{}^{28}SiMe_3$, $CF_3{}^{29}SiMe_3$, $CF_3{}^{30}SiMe_3$, and $^{13}CF_3{}^{28}SiMe_3$ were used. These were corrected with the Sipachev method.[11] This correction $\Delta B = -3.59$ MHz

TABLE 3: Experimental and Calculated Geometric Parameters (Å and deg) for CF_3SiCH_3

	GED[a]	GED/MW[b]	MP2/ 6-31G*	MP2/ 6-31+G(2df)	MP2/ cc-pVDZ	MP2/ aug-ccpVDZ	MP2/ cc- pVTZ	B3LYP/ 6-31++G(2df,pd)
$(Si-C)_{mean}$	1.882(2)	1.882(1)	1.889	1.883	1.897	1.899	1.886	1.892
ΔSiC	0.080(7)	0.079(4)	0.051	0.065	0.054	0.063	0.065	0.076
$Si-CF_3$	1.942(5)	1.941(3)	1.927	1.932	1.937	1.946	1.935	1.949
$Si-CH_3$	1.862(3)	1.862(2)	1.876	1.867	1.883	1.883	1.870	1.872
$C-F$	1.355(2)	1.356(1)	1.366	1.355	1.363	1.375	1.355	1.360
$C-H_p$	1.102(5)	1.099(4)	1.094	1.095	1.104	1.103	1.090	1.092
$C-H_a$					1.103	1.102	1.089	
$F_3C-Si-CH_3$	106.0(5)	106.2(2)	106.5	105.6	106.5	105.9	106.1	106.1
$F-C-F$	106.5(2)	106.4(2)	106.4	106.1	106.6	106.1	106.4	106.1
$H-C-H$	110.3(8)	109.8(6)	107.9	108.1	108.2	108.1	108.1	107.9

[a] r_{h1} structure from GED intensities. Error limits are 2σ values and include a possible scale error of 0.1%. [b] r_{h1} structure from joint analysis of GED intensities and MW rotational constants. Error limits are 2σ values.

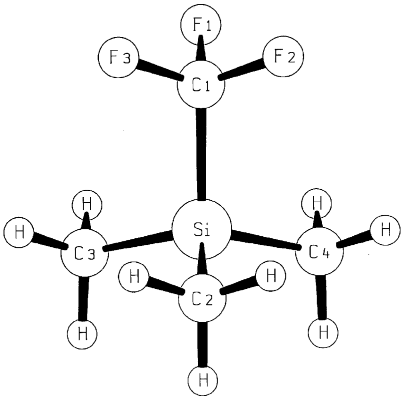

Figure 3. Molecular model with atom numbering.

TABLE 4: Interatomic Distances, Vibrational Amplitudes and Corrections (without C···H, F···H, and H···H Distances)[a]

	distance	ampl (GED)		ampl (MP2)	$\Delta r = r_a - r_{h1}$
C−H	1.10	0.077(5)	*l*1	0.077	0.0018
C−F	1.36	0.046(1)	*l*2	0.046	0.0006
Si−C	1.86−1.94	0.051(2)	*l*3	0.053	0.0003
F···F	2.17	0.057(2)	*l*4	0.058	0.0024
Si···H	2.44	0.112(9)	*l*5	0.122	0.0091
Si···F	2.75	0.080(3)	*l*6	0.084	0.0049
C1···C2	3.03	0.101(7)	*l*7	0.109	0.0073
C2···C3	3.09	0.101(7)	*l*7	0.106	0.0056
C2···F2	3.36	0.201(12)	*l*8	0.223	0.0133
C2···F1	4.22	0.097(9)	*l*9	0.095	0.0287

[a] Values in Å, error limits are 3σ values. For atom numbering see Figure 3.

TABLE 5: Si−C Bond Lengths (Å) and Barriers to Internal Rotation in Some Silanes

silane	$Si-CH_3$	$Si-CF_3$	V_3 (kJ/mol)
H_3SiCH_3	1.8686(4)[a] (r_0)		6.9992(6)[b]
$Hsi(CH_3)_3$	1.868(2)[c] (r_s)		7.7[c] (17)
$CH_3Si(CH_3)_3$	1.875(2)[d] (r_a)		
$ClSi(CH_3)_3$	1.8606(1)[e] (r_0)		6.9012(107)[e]
$CF_3Si(CH_3)_3$	1.862(2)[f] (r_{h1})	1.941(3)[f] (r_{h1})	5.7121(22)[f]
$FSi(CH_3)_3$	1.848(2)[g] (r_g)		
$ISi(CH_3)_3$	1.8627(15)[k] (r_s)		7.4151(36)[k]
$F_2Si(CH_3)_2$	1.836(2)[g] (r_g)		
F_3SiCH_3	1.828(4)[g] (r_g)		3.89[h] (37)
	1.812(14)[h] (r_0)		
CF_3SiH_3		1.923(3)[i] (r_z)	
CF_3SiF_3		1.910(5)[j] (r_g)	

[a] Reference 20. [b] Reference 21. [c] Reference 22. [d] Reference 23. [e] Reference 13. [f] This work. [g] Reference 24. [h] Reference 25. [i] Reference 8. [j] Reference 26. [k] Reference 27.

for the main isotopic species. The uncertainties of the corrected constants were estimated to be 10% of the correction. In the joint analysis the relative weight of GED intensities and MW rotational constants was adjusted until the rotational constants were fitted within their estimated uncertainties. An increase of the weighting of the rotational constants beyond this point does not lead to a change of structural parameters. The results of this analysis are listed in Table 3 (geometric parameters) and in Table 4 (vibrational amplitudes).

The MW data alone are not sufficient for a complete structure determination of this molecule. However, it is possible to determine the geometric parameters of the SiC_4 skeleton using Kraitchman's method,[18] which involves differences of moments of inertia of the various isotopomers. This method results in $r_s(Si-CH_3) = 1.859$ Å, $r_s(Si-CF_3) = 1.913$ Å, and $F_3C-Si-CH_3 = 106.1°$. Whereas the values for the $Si-CH_3$ bond length and C−Si−C angles are in very close agreement with the r_{h1} results from the joint analysis, the r_s value for the $Si-CF_3$ bond is about 0.03 Å shorter than the r_{h1} value. This deviation can be attributed to the nonrigidity of the molecule, particularly involving the low-lying CF_3 torsion, which makes the application of the Kraitchman method questionable.

Discussion

Table 3 compares experimental structural parameters with the results of computational methods at various levels. Considering that equilibrium bond distances (r_e) derived from calculations are systematically shorter than r_{h1} distances derived from experiment by about 0.005 Å,[19] all calculated mean values of the Si−C distances are too long (by 0.006−0.022 Å). On the other hand, the predicted differences between the two kinds of Si−C bonds are too small (by 0.003−0.028 Å). Only the DFT method with a large basis set reproduces the experimental difference within its error limit.

Table 5 compares experimental $Si-CH_3$ and $Si-CF_3$ bond lengths in different silanes. Within the trimethylsilanes $X-Si(CH_3)_3$, the Si−C bond lengths shorten with increasing electronegativity of the substituents X from 1.872(2) Å in tetramethylsilane to 1.848(2) Å in fluorotrimethylsilane. In this bond a further shortening is observed upon increasing fluorination at the silicon atom. Also the $Si-CF_3$ bond shortens with increasing electronegativity of X (from 1.941(3) Å in CF_3SiMe_3 to 1.910(5) Å in CF_3SiF_3.

The longest Si−C bond distance observed so far for any gas phase structure is the $Si-CF_3$ bond in CF_3SiMe_3. Although no quantitative correlation between structural features and chemical reactivity is possible, this long bond together with its localized positive charges ($q(Si^+) \gg q(C^+)$) rationalizes qualitatively the observed high tendency of CF_3SiMe_3 for CF_3 donation.

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Supporting Information Available: Lists of all recorded transitions for the main species as well as for the isotopomers ^{29}Si, ^{30}Si, ^{13}CF$_3$ and ^{13}CH$_3$(^{12}CH$_3$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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