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(Trimethylsilyl)trifluoroethene, a Floppy Molecule[†]

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Introduction

The structure of vinylsilane, $H_3SiCH=CH_2$, has been studied extensively by microwave spectroscopy.[1,2] This compound possesses an eclipsed conformation, i.e., one Si−H bond is synperiplanar to the C═C double bond, with a 3-fold potential for internal rotation around the C−Si bond and a barrier of ca. 1.50 kcal mol^{-1}. *Ab initio* calculations[3,4] demonstrate that (p−d)π-bonding between silicon and the π system of the vinyl group ("hyperconjugation") is negligible in contrast to the interpretation of spectral effects.[5] Gas phase structures are also reported for some substituted derivatives, where the silyl hydrogen atoms are replaced by methyl or chlorine: $MeH_2SiCH=CH_2$,[6] $Me_3SiCH=CH_2$,[7] $Me_2ClSiCH=CH_2$,[8] and $Cl_3SiCH=CH_2$.[9] All compounds possess eclipsed structures with one Si−R bond (R = H, Me or Cl) synperiplanar to the C═C double bond. The C(sp^2)−Si bond length depends on the substituents in the silyl group. In the present study, we are interested in the effects of fluorination of the vinyl group and report the structure investigation of $Me_3SiCF=CF_2$ by using gas electron diffraction (GED) and *ab initio* calculations. We and others have studied the chemistry of fluorinated silanes in detail. They are generally highly useful reagents for the introduction of fluoroalkyl (CF_3, C_3F_7) and fluoroaryl (C_6F_5) groups into a variety of substrates.[10] However, we find the trifluorovinyl silane $Me_3SiCF=CF_2$ to be quite unreactive under reaction condititions useful for the introduction of CF_3 and C_6F_5 moieties with $CF_3Si(Me)_3$ or $C_6F_5Si(Me)_3$.

Experimental Section

The silane $C_2F_3Si(Me)_3$ is prepared by procedures reported in the literature.[10] The GED intensities are obtained with a gas diffractograph, KD-G2,[11] at nozzle-to-plate distances of 25 and 50 cm and with an accelerating voltage of ca. 60 kV. The electron wavelength is determined from ZnO powder diffraction patterns. The sample reservoir is cooled to −28 °C and the inlet system and gas nozzle are at room temperature. The camera pressure never exceeds 2×10^{-5} Torr during the experiment. The photographic plates (Kodak Electron Image, 13 × 8 cm) are analyzed with the usual procedures.[12] Averaged molecular intensities for both camera distances in the *s*-ranges 20−180 and 80−135 nm^{-1} are shown in Figure 1.

Ab Initio Calculations

The geometry of $Me_3SiCF=CF_2$ is optimized for various torsional orientations of the $SiMe_3$ group with the HF/3-21G* method by using the Gaussian 92 program system.[13] The potential function for internal rotation around the C(sp^2)−Si bond is presented in Figure 2. The global minimum occurs at ϕ(C═C−Si−C) = 60°, where the methyl groups on silica stagger the C═C double bond. A second and very flat minimum, 0.42 kcal mol^{-1} higher in energy, occurs for the eclipsed conformation (ϕ(C═C−Si−C) = 0°). This calculated potential function can be approximated by a superposition of V_3 and V_6 terms

$$V(\phi) = (V_3/2)(1 + \cos 3\phi) + (V_6/2)(1 - \cos 6\phi)$$

with $V_3 = 0.42$ and $V_6 = 0.34$ kcal mol^{-1}. The geometric parameters for the staggered conformation are given in Table 1 together with the experimental values.

Structure Analysis

The experimental radial distribution function (RDF) is derived by Fourier transform of the modified molecular intensities and is shown in Figure 3. Model calculations demonstrate that the staggered conformation with ϕ(C═C−Si−C) = 60° leads to better agreement with the experimental curve than the eclipsed conformation. In the least-squares analysis, the molecular intensities are multiplied with a diagonal weight matrix and known scattering amplitudes and phases are used.[14] The choice of the molecular model is supported by the results of the *ab initio* calculations. (1) The C═C bond length, which is very similar to the C−F bond lengths, could not be refined and was set to 131 pm with an estimated uncertainty of ±2 pm. This length corresponds to the value reported for $F_2C=CF_2$ (131.1(7)) pm.[15] (2) The C−F bond lengths in the CF_2 group were assumed to be equal (C2−F2 = C2−F2′). If the calculated difference between these two bond lengths (1.5 pm) is used in the GED analysis, the C═C−F bond angles change by less than their error limits. The difference between C2−F bond lengths and the C−F bond adjacent to the $SiMe_3$ group (C1−F1) was set to the *ab initio* value ((ΔCF = C1−F1 − C2−F) = 4.1 pm). (3) All three C═C−F bond angles are allowed to be different. These angles are well determined by the strong contributions of the nonbonded Si−F distances. (4) C_{3v} symmetry is assumed for the $SiMe_3$ group. Attempts to refine a tilt angle between the C_3 axis and the C−Si bond direction results in a small value with a large error limit (1.1(18)°). Therefore, the tilt angle is set to zero for subsequent analyses. The *ab initio* calculations predict a tilt angle of 1.5°. (5) The CH_3 groups are assumed to possess C_{3v} symmetry and to stagger the opposite Si−C bonds. Vibrational amplitudes were collected in groups according to length and type of distance. The

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[†] This paper is dedicated to Professor Dr. mult. Dr. h. c. Alois Haas on the occasion of his 65th birthday.

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(1) O'Reilly, J. M.; Pierce, L. *J. Chem. Phys.* **1991**, *34*, 1176.
(2) Shike, Y.; Hasagawe, A.; Hayashi, M. *J. Mol. Struct.* **1982**, *78*, 185.
(3) Zeek, E. *Theor. Chim. Acta* **1974**, *35*, 301.
(4) Oberhammer, H.; Boggs, J. E. *J. Mol. Struct.* **1979**, *57*, 175.
(5) Ebsworth, E. A. V. *Volatile Silicon Compounds*; Permagon Press: Oxford, England, 1963.
(6) Imachi, M.; Nagayama, A.; Nakagawa, J.; Hayashi, M. *J. Mol. Struct.* **1981**, *77*, 81.
(7) Page, E. M.; Rice, A. A.; Walsh, R.; Hagen, K. *J. Mol. Struct.*, in press.
(8) Shen, Q. *J. Mol. Struct.* **1982**, *95*, 215.
(9) Vilkov, L. V.; Mastryukov, V. S.; Akishin, P. A. *J. Struct. Chem. USSR (Engl. Transl.)* **1964**, *5*, 168.
(10) Patel, N. R.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1993**, *32*, 4802. Patel, N. R.; Kirchmeier, R. L. *Inorg. Chem.* **1992**, *31*, 2537 and references therein. Prakash, S.; Krashnamarti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393.
(11) Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: London, **1976**; Vol. 4, p 24.
(12) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.
(13) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robbs, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92, Revision C. Gaussian Inc., Pittsburgh, PA, 1992.
(14) Haase, J. *Z. Naturforsch.* **1970**, *25A*, 936.
(15) Carlos, J. L.; Karl, R. R.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 177.

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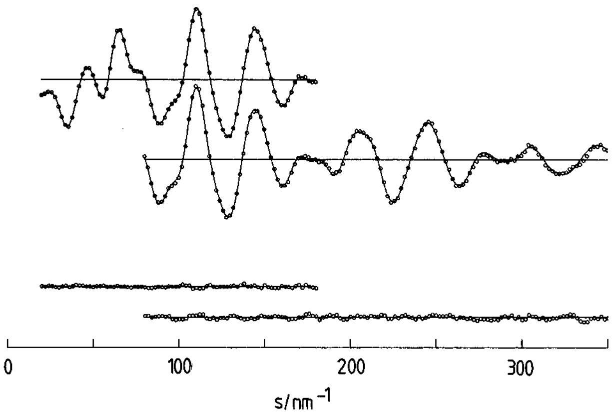

Figure 1. Experimental (dots) and calculated (full line) molecular intensities for 50 cm (above) and 25 cm nozzle-to-plate distances (below) and differences.

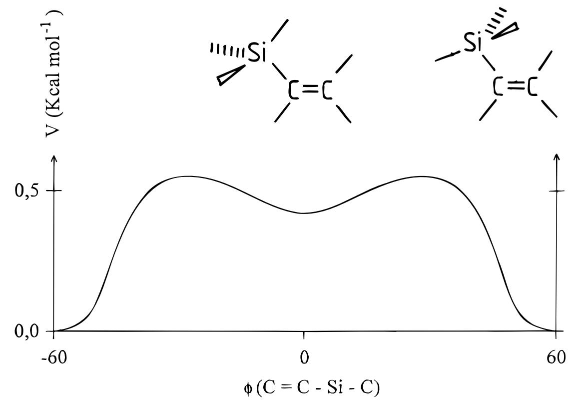

Figure 2. Calculated (HF/3-21G*) potential curve for internal rotation around the C(sp^2)—Si bond.

Table 1. Geometric Parameters for $Me_3SiCF{=}CF_2$ from GED Analysis (Large Amplitude Model) and *ab Initio* Calculations (Staggered Conformer)

	GED[a]	HF/3-21G*
C—H	110.0 (5) (p_1)	108.8
C=C	131.0[20][b]	130.3
C2—F2	132.4 (5)[c] (p_2)	132.9
C2—F2′		134.4
C1—F1	136.5 (5)	137.8
C1—Si	187.7 (10) (p_3)	188.6
Si—C_m[d]	186.5 (4) (p_4)	187.6
C1=C2—F2	127.7 (6) (p_5)	128.4
C1=C2—F2′	122.0 (6) (p_6)	120.8
C2=C1—F1	118.0 (8) (p_7)	117.2
C2=C1—Si	127.7 (13) (p_8)	124.5
C_m—Si—C_m	113.0 (10) (p_9)	111.6
H—C—H	109.2 (9) (p_{10})	107.7

[a] r_a distances in pm and $\angle_\alpha$ angles in degree. Error limits are 3σ values and include possible systematic errors (see text). For atom numbering see Figure 4. [b] Not refined, but varied within the given range. [c] The difference between C1—F1 and C2—F2 is fixed to the *ab initio* value. [d] C_m methyl carbon atom.

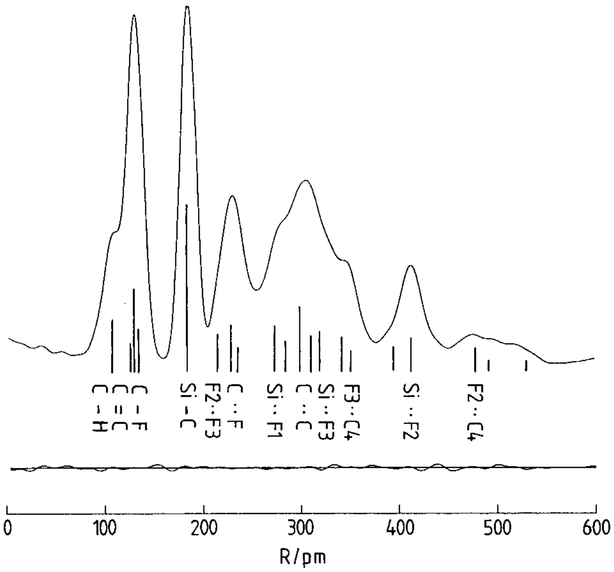

Figure 3. Experimental radial distribution function and difference curve. Important interatomic distances are indicated by vertical bars.

Table 2. Interatomic Distances (Without Nonbonded Distances Involving Hydrogen) for the Staggered Conformation and Vibrational Amplitudes for the Large Amplitude Model

	distance	amplitude		distance	amplitude
C=C	131	3.6[b]	Si···F3	318	223.7(76) a_5
C—F	132—136	4.7(2) a_1	F1···F3	353	6.0[b]
Si—C	187—188	5.0[5][c]	F3···C4	343	12.4(9) a_6
F2···F3	217	5.0(9) a_2	C2···C4	354	
C2···F1	229		F1···C4	396	
C1···F3	230		Si···F2	413	6.8(9) a_7
C1···F2	237		C2···C3	426	
Si···F1	274	13.6(29) a_3	F2···C4	477	15.0[b]
Si···C2	287		F3···C3	490	10.0[b]
F1···F2	276	7.5[b]	F2···C3	532	
C1···C3	298	11.7(10) a_4			
F1···F3	299				
C3···C4	311				

[a] Values in pm; error limits are 3σ values. Atom numbering is given in Figure 4. [b] Not defined. [c] Not refined but varied within the given range.

amplitude of the Si—C bonds was not refined, but its value was varied within ±0.5 pm. A possible systematic error due to this assumption is included in the error limit for the Si—C bond distances. Further constraints are evident from Table 2.

Refinements based on a rigid model with a staggered $SiMe_3$ group and the above assumptions do not lead to a good fit of the experimental intensities. The fit improves if the $SiMe_3$ group is allowed to deviate from the exact staggered orientation with (ϕ(C=C—Si—C) = 32(3)°. This effective dihedral angle and the potential function obtained from the *ab initio* calculations (Figure 2) suggest that this molecule exhibits nonrigid behavior and the $SiMe_3$ group undergoes a large amplitude torsional motion. Therefore, a large amplitude model with internal rotation around the C—Si bond was used in the final refinements. Conformations with rotational angles ϕ from 0° (eclipsed orientation) to 60° (staggered orientation) in steps of $\Delta\phi = 10°$ are taken into account in the calculation of the molecular intensities. The individual conformations are weighted by exp($-V(\phi)/RT$), where $V(\phi)$ is the potential function for internal rotation. In addition to this rotation, a large amplitude bending motion of the C=C—Si angle was taken into account. According to the *ab initio* calculations, this angle increases from 124.5° in the staggered conformation to 130.6° in the eclipsed form. A linear increase of this angle upon internal rotation is assumed in the GED analysis. Refinements are performed with different potential functions for internal rotation, a V_3 potential, and a V_3/V_6 potential as predicted by *ab initio* calculation. It is not possible to refine any of these potential constants in the least-squares analysis. In the case of a V_3 potential the best fit is obtained for $V_3 = 0.25(20)$ kcal mol^{-1}. For the V_3/V_6 potential the ratio of the two potential constants is set to the *ab initio* value ($V_3/V_6 = 0.42/0.34 = 1.25$). The lowest agreement factors are obtained for $V_3 = 0.20(15)$ and $V_6 = 0.15(15)$ kcal mol^{-1}. The estimated uncertainties correspond to an increase of R_{50}

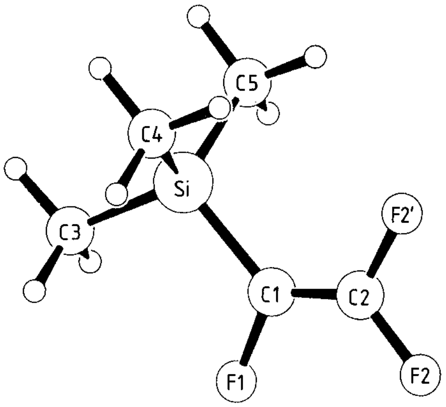

Figure 4. Molecular model with atom numbering.

by 10% (R_{50} is the agreement factor for the long camera distance intensities). The R factors for both analyses, V_3 or V_3/V_6 potential, are indistinguishable and the geometric parameters are identical. In these least-squares analyses, 10 geometric parameters p_i and seven vibrational amplitudes a_k are refined simultaneously. The following correlation coefficients have values larger than $|0.6|$: $p_3/p_4 = -0.94$, $p_3/p_8 = -0.66$, $p_4/p_8 = 0.62$, $p_5/p_6 = -0.72$, $p_8/a_3 = -0.67$, $p_8/a_5 = -0.75$, $a_3/a_4 = 0.68$. The final results are listed in Table 1 (geometric parameters) and Table 2 (vibrational amplitudes).

Table 3. C(sp^2)—Si Bond Lengths and C═C—Si Bond Angles in Vinylsilane and Substituted Derivatives

compound	C(sp^2)—Si	C═C—Si
$H_3SiCH{=}CH_2$[a]	185.3(3)	122.9(3)
$Me_2HSiCH{=}CH_2$[b]	185.0	124.5
$Me_3SiCH{=}CH_2$[c]	186.7(3)	124.6(18)
$Me_2ClSiCH{=}CH_2$[d]	183.8(6)	127.8(12)
$CH_3SiCH{=}CH_2$[e]	181(2)	121(3)
$Me_3SiCF{=}CF_2$[f]	187.7(10)	127.7(13)

[a] Reference 2. [b] Reference 6; no error limits given. [c] Reference 7. [d] Reference 8. [e] Reference 9. [f] This work.

Discussion

Two aspects of this structural study are of special interest: (1) the staggered orientation of the $SiMe_3$ group with respect to the C═C double bond with a very low barrier to internal rotation around the C—Si bond and (2) the strong distortion of the trifluorovinyl group. As pointed out in the Introduction, vinylsilane possesses an eclipsed conformation and internal rotation of the SiH_3 group can be described with a 3-fold potential with $V_3 = 1.488(24)$ kcal mol^{-1}. The staggered form corresponds to a maximum in this potential function. Eclipsed conformations are also observed for the substituted vinylsilanes $MeH_2SiCH{=}CH_2$,[6] $Me_3SiCH{=}CH_2$,[7] $Me_2ClSiCH{=}CH_2$,[8] and $Cl_3SiCH{=}CH_2$.[9] Mixtures of two conformers occur in compounds with unsymmetrically substituted silyl groups (MeH_2Si and Me_2ClSi), but in both conformers one Si—R bond (R = H, Me or Cl) is synperiplanar to the C═C double bond. Similarly, propene[16] and its fluorine-containing derivatives $CF_3CH{=}CH_2$[17] and $CF_3CF{=}CF_2$[18] exhibit eclipsed conformations, and the staggered forms correspond to maxima in the potential curve for internal rotation that are 1.5−2.0 kcal mol^{-1} higher in energy. In $Me_3SiCF{=}CF_2$ however, the staggered form is favored, which implies that one Si—Me bond is synperiplanar to the C1—F1 single bond. According to our *ab initio* calculations the eclipsed conformation corresponds to a flat minimum in the potential function for internal rotation (Figure 2). This conformation is predicted to be 0.42 kcal mol^{-1} higher in energy than the staggered form. The GED analysis results in a slightly lower energy of 0.20(15) kcal mol^{-1}. The barrier to internal rotation (0.55 kcal mol^{-1} from *ab initio* and 0.25(17) kcal mol^{-1} from GED) is lower than RT (ca. 0.6 kcal mol^{-1}) and nearly free rotation occurs at room temperature. The slight preference of the staggered orientation relative to the eclipsed orientation of the $SiMe_3$ group can be rationalized by interatomic contacts. In the eclipsed conformer the shortest nonbonded distance between a fluorine atom and methyl hydrogen atoms is 265 pm (F2′···H), and in the staggered form 290 pm (F1···H). Both contacts, however, are longer than the respective van der Waals distance of 255 pm.[19]

The *ab initio* calculations predict the C—F bond adjacent to the $SiMe_3$ group to be ca. 4 pm longer than those in the CF_2 group. This difference cannot be determined in the GED experiment. The C═C—F angles, however, are well detemined by the experiment and are strongly distorted from those in $F_2C{=}CF_2$ (123.8(2)°.[15] The angles in $Me_3SiCF{=}CF_2$ vary from 118.0(8)° for C2═C1—F1 to 127.7(6)° for C1═C2—F2. These angular distortions are well reproduced by the *ab initio* calculations.

Table 3 compares C(sp^2)—Si bond lengths and C═C—Si bond angles in vinylsilane and substituted derivatives. The C(sp^2)—Si bond in the parent compound is only ca. 1 pm longer than the C(sp^3)—Si bond in $H_3Si{-}CH_3$ (186.4(1) pm),[20] although the covalent single bond radius of sp^2-hybridized carbon is 3.6 pm smaller than that of sp^3-hybridized carbon (73.5 vs 77.1 pm).[21] Substitution of silyl hydrogens by methyl groups has a minor effect on the C—Si bond length. The bond lengthens by ca. 1 pm between $H_3SiCH{=}CH_2$ and $Me_3SiCH{=}CH_2$. Chlorination of the silyl group, however, leads to shortening of this bond by ca. 4 pm between $H_3SiCH{=}CH_2$ and $Cl_3SiCH{=}CH_2$. Fluorination of the vinyl group causes only a slight lengthening of the C—Si bond from 186.7(3) pm in $Me_3SiCH{=}CH_2$ to 187.7(10) pm in $Me_3SiCF{=}CF_2$, which is within the experimental uncertainties for these bond lengths. The small effect of fluorination of the vinyl group on the C(sp^2)—Si bond is in contrast to the very strong effect in the methyl compounds, where the C(sp^3)—Si bond lengthens from 186.4(1) pm in $H_3Si{-}CH_3$[20] to 192.3(3) pm in $H_3Si{-}CF_3$.[21] This observation is consistant with the lack of reactivity of the fluorinated vinyl compound as compared to CF_3 silanes.

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(16) Hirota, E.; Hirooka, T.; Morino, Y. *J. Mol. Spectrosc.* **1968**, *26*, 35.

(17) Christen, D.; Hoffmann, V.; Klaboe, P. *Z. Naturforsch.* **1979**, *34A*, 1320.

(18) Lowrey, A. H.; George, C.; D'Antonio, P.; Karle, J. *J. Mol. Struct.* **1979**, *53*, 189; Christen, D.; Hoffmann, V.; Klaboe, P. *J. Mol. Struct.* **1980**, *60*, 151.

(19) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(20) Wong, M.; Ozier, I.; Meerts, W. L. *J. Mol. Spectrosc.* **1983**, *102*, 83.

(21) Zeil, W. *Angew. Chem.* **1961**, *73*, 751.

(22) Beckers, H.; Bürger, H.; Rempfer, B.; Oberhammer, H. *J. Mol. Struct.* **1986**, *140*, 281.