Rotational Spectra and Conformational Analysis of Diethylsilane and Diethyldifluorosilane

Sean A. Peebles,* Michal M. Serafin, and Rebecca A. Peebles

Department of Chemistry, Eastern Illinois University, 600 Lincoln Avenue, Charleston, Illinois 61920

Gamil A. Guirgis

Department of Chemistry and Biochemistry, The College of Charleston, 66 George Street,
Charleston, South Carolina 29424

Howard D. Stidham

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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The rotational spectra belonging to the ^{28}Si isotopologue for three conformers of diethyldifluorosilane (Et_2SiF_2) and three conformers of diethylsilane (Et_2SiH_2) have been measured between 4 and 17 GHz by using pulsed-jet Fourier-transform microwave spectroscopy. Rotational spectra for the *gauche*−*gauche*, *trans*−*trans*, and *trans*−*gauche* conformers were identified for both molecules, while the significantly higher energy *gauche*−*gauche′* conformer was not observed. Ab initio calculations at the MP2(Full)/6-311+G(2d,2p) and MP2(Full)/6-311+G(2df,2pd) levels for the fluorine and the hydrogen analogues, respectively, provided rotational constants, dipole moment components, and the relative energies of the conformers to assist in the spectral assignment. In both molecules, the *gauche*−*gauche* conformer was identified by the ab initio calculations as the most stable. Agreement of the ab initio rotational constants with those from experiment was at worst 5%, with most rotational constants being predicted to within 2%.

Introduction

Ethylated silanes have important applications in the semiconductor industry as reagents for chemical vapor deposition to provide a source for SiO_2 and so a desire for detailed knowledge of their properties and reactivity has led to a significant amount of effort having been invested in their study. From a chemical point of view, such molecules allow for interesting comparisons of structural properties such as the relative stabilities of their conformational isomers, electronic properties like dipole moments, or energetic properties like barriers to internal rotation of CH_3 groups. Spectroscopic studies of simple silanes such as ethylsilane[1,2] and ethylmethylsilane[3] may be found in the chemical literature going back several decades, although microwave spectroscopic measurements of the relatively simple molecule diethylsilane, $(C_2H_5)_2SiH_2$ (and its fluorinated derivative, $(C_2H_5)_2SiF_2$), have not yet been made; microwave studies of the corresponding methyl derivatives dimethylsilane[4,5] and difluorodimethylsilane[6] do, however, exist.

Just as is the case for pentane (the carbon analogue of diethylsilane), four conformers are possible for the silicon-containing species diethylsilane and diethyldifluorosilane: namely *trans*−*trans* (*tt*), *trans*−*gauche* (*tg*), *gauche*−*gauche* (*gg*), and *gauche*−*gauche′* (*gg′*) (see Figure 1), where these labels describe the relative orientation about the C−C−Si−C dihedral angles; the *trans* label refers to a dihedral close to 180° while *gauche* refers to an angle of 55−60° (the exception being the angle in the *gg′* conformer where steric crowding forces one of the angles to increase to something closer to 80−90°)—this will be discussed later in more detail in connection with our ab initio optimizations which suggest a different order of stability in the silicon analogue from that suggested in previous microwave work[7] for pentane. Note also that the *tt* conformer has a conformational degeneracy of 1, while the other three conformers have a degeneracy of 2.

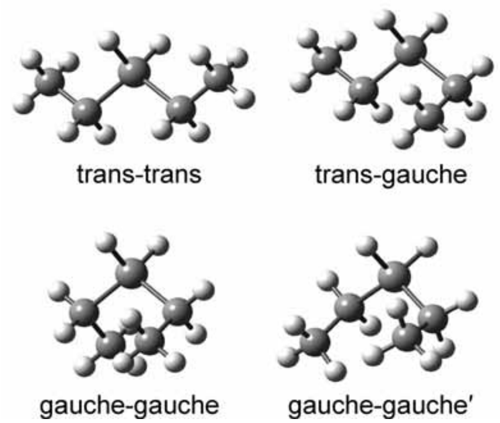

Figure 1. The four most stable conformers (*tt*, *tg*, *gg*, *gg′*) of the Et_2SiX_2 molecule (where X = H or F on the central silicon atom)—see text and Tables 1 and 2 for further discussion of relative stabilities. The symmetries of these conformers are C_{2v}, C_1, C_2, and C_1, respectively. The C−C−Si−C dihedral angles for the optimized structures are as follows: *tt* (both 180°); *tg* (180° and −59°); *gg* (both ~56°); *gg′* (~80°, ~−55°).

Pentane itself has been studied quite extensively and its conformational stability has long been of interest, being the subject of theoretical studies ranging from more recent low level molecular mechanics and molecular dynamics simulations[8] to much higher level ab initio investigations[9,10] as well as to a

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* Address correspondence to this author: e-mail sapeebles@eiu.edu, phone (217) 581-2679, and fax (217) 581-6613.

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TABLE 1: Ab Initio Predictions (MP2(Full)/6-311+G(2d,2p)) of Rotational Constants and Dipole Moment Components for Et_2SiF_2

parameter	*tt* (C_{2v})	*tg* (C_1)	*gg* (C_2)[a]	*gg′* (C_1)[b]
A/MHz	3625	2757	2083	1997
B/MHz	1295	1493	1877	1984
C/MHz	1284	1316	1381	1368
P_{aa}/u Å^2	322.1	269.6	196.3	185.6
P_{bb}/u Å^2	71.37	114.5	169.7	183.9
P_{cc}/u Å^2	68.05	68.82	72.92	69.19
μ_a/D	0.00	0.88	0.00	1.12
μ_b/D	2.38	1.95	2.52	1.80
μ_c/D	0.00	1.19	0.00	1.31
μ_{total}/D	2.38	2.45	2.52	2.49
rel energy/cm^{-1}	61	79	0	285
rel energy (ZPE corrected)/cm^{-1}	76	81	0	299

[a] Me groups on opposite sides of the C−Si−C heavy atom plane. [b] Me groups on the same side of the C−Si−C heavy atom plane.

TABLE 2: Ab Initio Predictions (MP2(Full)/6-311+G(2df,2pd)) of Rotational Constants and Dipole Moment Components for Et_2SiH_2

parameter	*tt* (C_{2v})	*tg* (C_1)	*gg* (C_2)[a]	*gg′* (C_1)[b]
A/MHz	13455	7798	4900	4843
B/MHz	1524	1854	2501	2561
C/MHz	1439	1640	2015	1890
P_{aa}/u Å^2	322.6	258.0	174.9	180.2
P_{bb}/u Å^2	28.53	50.22	75.97	87.22
P_{cc}/u Å^2	9.031	14.59	27.18	17.13
μ_a/D	0.00	0.26	0.00	0.06
μ_b/D	0.82	0.63	0.73	0.57
μ_c/D	0.00	0.39	0.00	0.48
μ_{total}/D	0.82	0.78	0.73	0.75
rel energy/cm^{-1}	158	135	0	390
rel energy (ZPE corrected)/cm^{-1}	111	101	0	388

[a] Me groups on opposite sides of the C−Si−C heavy atom plane. [b] Me groups on the same side of the C−Si−C heavy atom plane.

number of experimental studies dating back to the 1960s, including far-IR measurements[11] and electron diffraction.[12,13] The rotational spectra of the *trans*−*trans* and *trans*−*gauche* conformers of pentane were only recently measured in the 7−19 GHz region by Fourier-transform microwave spectroscopy[7] and those results were consistent with the *trans*−*trans* form being the most stable, with the *trans*−*gauche* form being predicted to lie ~0.55 kcal mol^{-1} higher in energy.[7]

A previous normal coordinate analysis of diethylsilane[15] identified the *tt* form to be the only form observed in the crystal state; all four forms were observed in the liquid and all but the *gg′* conformer were seen in the vapor phase. An ab initio study of diethylsilane[14] identified the *tt* form as the lowest energy closely followed by the *tg* and *gg* (being respectively 0.07 and 0.03 kcal mol^{-1} (~24 cm^{-1} and ~10 cm^{-1}) higher in energy than the *tt* conformer), although it should be noted that these studies used structures optimized only at the HF/6-31G* levels, with single-point energies then computed at the MP2/6-31G* level.

In the present paper we report on the identification and characterization of (by means of their rotational spectra and dipole moments) the conformers that are present in a jet-cooled expansion for the most abundant ^{28}Si isotopologue of both diethylsilane and diethyldifluorosilane. A normal coordinate analysis for diethylsilane has previously been carried out[15,16] while a similar analysis for diethyldifluorosilane will be presented separately,[17] along with detailed structural analysis and comparison using combined ab initio and microwave data. The present paper will focus on the analysis and assignment of rotational spectra for the different conformers of these two molecules and will discuss the predicted stability of the conformers based on an analysis and comparison of ab initio and microwave data. Results for diethylsilane and diethyldifluorosilane will also be compared to those for similar chemical species.

Experimental Section

The rotational spectra of three conformers for the most abundant ^{28}Si isotopologue of both molecules were measured on a Balle-Flygare Fourier-transform microwave spectrometer,[18] details of which have been described previously.[19,20] The samples were synthesized at the College of Charleston, South Carolina, using the procedure described in ref 17. Briefly, the sample of diethyldifluorosilane is prepared by fluorination of a commercial sample of dichlorodiethylsilane with freshly sublimed antimony trifluoride without solvent at 3 °C for 2 h. The diethylsilane is prepared by reduction of commercially available dichlorodiethylsilane by lithium aluminum hydride in dry dibutyl ether. In both cases, the volatile material is collected and purified by using trap-to-trap distillation. The purity of the samples is checked by infrared and NMR spectroscopy. The samples were then shipped to Eastern Illinois University for the microwave measurements as liquids in glass sample tubes. Vapor from each sample was condensed into a 1 L glass bulb and diluted to a total pressure of about 2 atm with first-run He/Ne carrier gas (17.5% He:82.5% Ne, BOC Gases), to yield a sample concentration of about 1%. The sample was expanded into the vacuum chamber of the spectrometer through a General Valve Series 9 solenoid valve with a 0.8 mm orifice at a 10 Hz repetition rate, using valve opening times of about 500−550 μs duration. Dipole moment measurements were made by the application of voltages ranging from ±700 V to ±5 kV to a pair of steel mesh plates located 31 cm apart within the Fabry-Pérot cavity and straddling the molecular jet expansion (corresponding to electric field strengths in the range ca. 45 to 320 V cm^{-1}). Electric field calibration was carried out using the $J = 1 \leftarrow 0$ transition of OCS, assuming a dipole moment of 0.71519(3) D.[21]

Results

I. Ab Initio Calculations. Ab initio optimizations were carried out at the MP2(Full)/6-311+G(2df,2pd) (diethylsilane) and MP2(Full)/6-311+G(2d,2p) (diethyldifluorosilane) levels with the Gaussian 03 suite of programs[22] (utilizing the OPT=TIGHT and SCF=TIGHT directives) and were used to provide initial estimates of the relative stabilities, rotational constants, and dipole moment components for each conformer to guide the spectral search and assignment. Harmonic vibrational frequency calculations were carried out to identify whether each of the conformers is a minimum on the potential energy surface and also to furnish the zero-point energy (ZPE) corrected energy.

There are four conformers that must be considered for each of these molecules: *trans*−*trans* (*tt*), *trans*−*gauche* (*tg*), *gauche*−*gauche* (*gg*), and *gauche*−*gauche′* (*gg′*), where the labels describe the C−C−Si−C dihedral angles (*trans*−*trans* = both angles 180°, *trans*−*gauche* = 180° and ~60°, and *gauche*−*gauche* = both ~60°). As mentioned in the Introduction, the *gauche*−*gauche′* conformer is particularly interesting since, due to steric crowding arising from both methyl groups being located on the same side of the C−Si−C plane, one of the dihedral angles is distorted quite significantly from the usual angle of ~60°, resulting in angles of ~+80° and −60°; these conformers are pictured in Figure 1, the caption of which also lists the value of the C−C−Si−C dihedral angle in each case. The principal axis coordinates resulting from the optimizations of all four conformers are included as Supporting Information.

For both the difluorodiethylsilane and the diethylsilane species the *gg* conformer (C_2 symmetry) was predicted to be the lowest in energy by 75 cm^{-1} (for the fluorinated species, Et_2SiF_2) or 101 cm^{-1} (for the hydrogen substituted species, Et_2SiH_2) relative to the next most stable conformer (see Tables 1 and 2 for the relative stabilities and predicted rotational constants and dipole moment components of all conformers). The *gg′* conformer was predicted to be the highest energy species for both compounds; these predictions are consistent with conventional chemical intuition making the most sterically hindered conformer (*gg′*) the least stable. The *tg* conformer (C_1 symmetry) and the *tt* conformer (C_{2v} symmetry) were close in energy in both species (<10 cm^{-1} separated them at the ZPE corrected level), with the *tt* form more stable for the fluorinated species while the *tg* form was slightly more stable for the hydrogen-substituted compound. The *tt*, *tg*, and *gg* species were all determined to possess no imaginary vibrational frequencies. For the *gg′* conformer, if constrained to C_s symmetry during the optimization, the resulting structure is found to possess one imaginary frequency; animation of this vibrational mode moves the two adjacent methyl groups apart in an up and down scissor motion. Slight distortion of the molecule along this coordinate (to break the C_s symmetry) followed by a reoptimization (with no symmetry constraints) results in the C_1 geometry shown in Figure 1 and this species is found to no longer possess any imaginary frequencies; this is consistent with results obtained for ab initio work on pentane which identify the existence of a similar C_1 symmetry species.[9] It should be mentioned that neither the rotational constants nor the derived planar moments are significantly affected in relaxing from a C_s symmetry to a C_1 symmetry form of the *gg′* conformer, so at the current level of calculation the predictive value of the rotational constants would not be diminished appreciably from assuming a symmetry plane. However, the dipole moment projections do change quite dramatically as a result of the different relative alignments of the methyl groups (and the consequent rotation of the principal axes). A C_s symmetry form of the diethyldifluorosilane possesses predicted dipole moment components of $\mu_a = 0.00$ D, $\mu_b = 2.07$ D, $\mu_c = 1.37$ D, with $\mu_{total} = 2.48$ D (to be compared with the values of $\mu_a = 1.12$ D, $\mu_b = 1.80$ D, $\mu_c = 1.31$ D, and $\mu_{total} = 2.49$ D obtained for the C_1 form), while the C_s form of the less polar diethylsilane shows much less pronounced differences ($\mu_a = 0.00$ D, $\mu_b = 0.56$ D, $\mu_c = 0.49$ D, with $\mu_{total} = 0.75$ D for the C_s form and $\mu_a = 0.06$ D, $\mu_b = 0.57$ D, $\mu_c = 0.48$ D, with $\mu_{total} = 0.75$ D for the C_1 form). The rotation of the principal inertial axes upon relaxation of the C_s symmetry clearly has profound effects on the dipole moment projections, particularly for the more polar fluorinated analogue.

Values tabulated in Tables 1 and 2 are equilibrium values of the rotational constants resulting from the ab initio optimizations and the energy differences between conformers are given both with and without the zero-point energy (ZPE) correction that was obtained from the harmonic frequency calculation. The order of stability in both cases (whether for the hydrogen or fluorine species) remains the same upon inclusion of ZPE corrections. An inspection of the relative energies for the conformers in Tables 1 and 2 shows that the three lowest energy conformers for each compound lie relatively close in energy (within about 110 cm^{-1} of each other at the ZPE corrected level), leading to the possibility of observing microwave spectra for more than one conformer, even in the vibrationally and rotationally cold environment of a supersonic jet.

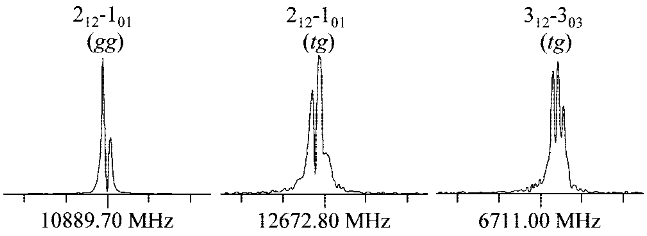

Figure 2. The $2_{12} \leftarrow 1_{01}$ transition for the *gg* and *tg* conformers of diethylsilane (average of 50 gas pulses each) and the $3_{12} \leftarrow 3_{03}$ transition for the *tg* conformer (200 gas pulses); the additional structure on the transitions arising from the *tg* conformer is clear. The divisions on the horizontal axis are 200 kHz apart and the given frequency corresponds to the center division of the displayed portion of the spectrum. The relative intensities of the three spectra (left to right) are approximately 1:0.056:0.009.

II. Rotational Spectra and Identification of Conformers. The ab initio predicted rotational constants were used to identify a search region for each of the conformers and an automatic scan of this spectral region was carried out. The ab initio calculations proved useful in providing reliable estimates of rotational constants and relative dipole moment components, helping the initial deconvolution of the spectra arising from different conformers. Both Stark effect measurements and careful consideration of the optimum microwave pulse length required to polarize a given transition based on the expected dipole moment components were helpful in determining the carriers of the spectra, and these factors assisted in the initial assignment of quantum numbers to the observed transitions. The full-width at half-maximum intensity of the observed transitions ranged from 20 to 35 kHz. Some of the transitions from the *trans*−*trans* and *trans*−*gauche* conformers of both molecules did exhibit some barely resolved fine structure that was spread over 100 kHz or so that is likely attributable to internal rotation of the terminal methyl groups, consistent with similar observations in previous high resolution studies of pentane.[7] Representative transitions for the *gg* and *tg* conformers are pictured in Figure 2 and illustrate the nature of the additional structure observed in some of the *tg* (and *tt*) transitions. Since most of these splittings were at the limit of our instrumental resolution no further attempts were made to analyze this structure; in the cases of broadened or split transitions the average transition frequencies were used for the fit.

The observed intensities were lower than is typical for monomer species on our instrument which is probably largely due to the distribution of intensity across several conformers, as well as some broadening of the lines (described above). The most intense transitions were observed for the *gg* conformers of both species (predicted to be the most stable in both molecules), with signal-to-noise measurements of up to 50 in 100 gas pulses, while most of the other conformers were observed at a signal-to-noise of 20 or lower. However, since many factors contribute to the observed intensity of transitions in an FTMW spectrometer, it is difficult to make reliable quantitative measurements of transition intensity with this technique. In particular, the location of the same transitions for different conformers in different frequency regions means that their intensities are greatly influenced by differences in the power of the polarizing radiation and also in the tuning of the microwave cavity at different frequencies. For this reason, it is

TABLE 3: Spectroscopic Constants of the Three Conformers Observed Experimentally for the $Et_2{}^{28}SiF_2$ Molecule

parameter	*trans−trans* (C_{2v})	*trans−gauche* (C_1)	*gauche−gauche* (C_2)
A/MHz	3632.6656(26)	2761.8531(9)	2119.6914(14)
B/MHz	1294.1180(6)	1492.8707(4)	1842.6802(12)
C/MHz	1278.1181(5)	1311.9727(4)	1373.6025(7)
Δ_J/kHz	0.089(10)	0.326(6)	1.559(38)
Δ_{JK}/kHz		−0.531(6)	−6.48(18)
Δ_K/kHz		3.69(12)	8.00(17)
δ_J/kHz		0.092(5)	0.692(18)
δ_K/kHz			−0.70(11)
N^a	9	41	18
$\Delta\nu_{rms}$/kHz^b	2.3	2.4	2.9
P_{aa}/u Å$^{2\,c}$	323.40403(22)	270.37415(14)	201.88216(27)
P_{bb}/u Å^2	72.00469(22)	114.83130(14)	166.04019(27)
P_{cc}/u Å^2	67.11603(22)	68.15419(14)	72.38086(27)

[a] N is the number of fitted transitions. [b] Root-mean-square deviation: $\Delta\nu_{rms} = [\sum(\nu_{obs} - \nu_{calc})^2/N]^{1/2}$. [c] Planar moments: $P_{aa} = 0.5(I_b + I_c - I_a) = \sum_i m_i a_i^2$ etc.

TABLE 4: Spectroscopic Constants of the Three Conformers Observed Experimentally for the $Et_2{}^{28}SiH_2$ Molecule

parameter	*trans−trans* (C_{2v})	*trans−gauche* (C_1)	*gauche−gauche* (C_2)
A/MHz	13297.8209(23)	7803.8028(13)	5010.0042(10)
B/MHz	1515.5923(25)	1826.1829(5)	2386.8613(7)
C/MHz	1431.8589(24)	1622.9829(5)	1959.8881(6)
Δ_J/kHz	0.15(4)	0.665(8)	3.887(27)
Δ_{JK}/kHz		−6.21(9)	−19.54(5)
Δ_K/kHz			37.30(9)
δ_J/kHz		0.178(8)	1.394(4)
δ_K/kHz			3.73(13)
N^a	9	29	23
$\Delta\nu_{rms}$/kHz^b	1.6	2.7	1.2
P_{aa}/u Å$^{2\,c}$	324.2008(6)	261.68453(10)	184.36047(10)
P_{bb}/u Å^2	28.7523(6)	49.70449(10)	73.50071(10)
P_{cc}/u Å^2	9.2523(6)	15.05612(10)	27.37326(10)

[a] N is the number of fitted transitions. [b] Root-mean-square deviation: $\Delta\nu_{rms} = [\sum(\nu_{obs} - \nu_{calc})^2/N]^{1/2}$. [c] Planar moments: $P_{aa} = 0.5(I_b + I_c - I_a) = \sum_i m_i a_i^2$ etc.

not possible to use the observed intensities to make any definitive statements as to the relative abundances of the conformers observed in our supersonic expansion.

For diethyldifluorosilane (Et_2SiF_2), rotational spectra for the three predicted lowest energy conformers (*tt*, *tg*, and *gg*) were assigned. The rotational spectra were fitted by using Pickett's SPFIT suite of programs[23] with a Watson *A*-reduction Hamiltonian in the I^r representation.[24] The fitted spectroscopic constants are given in Table 3; the rotational transition frequencies are available as Supporting Information. The *tt* and *gg* conformers, having C_{2v} and C_2 symmetry, respectively, both exhibit a pure *b*-type spectrum while the lower symmetry *tg* conformer (having C_1 symmetry) displays all three selection rules, and thus gives rise to a much richer rotational spectrum and provides a correspondingly larger data set of fitted transitions (Table 3).

For diethylsilane (Et_2SiH_2), the rotational spectra belonging to the same three lowest energy conformers (*tt*, *tg*, and *gg*) were assigned. Again, all observed transitions were fitted by using the Watson *A*-reduced Hamiltonian in the I^r representation;[24] the fitted spectroscopic constants are presented in Table 4. The *tt* and *gg* conformers possess C_{2v} and C_2 symmetry, respectively, and hence both exhibit pure *b*-type spectra. For the *tg* conformer (C_1 symmetry), all three components of the dipole moment are nonzero and so, as was the case with the fluorinated derivative, *a*-, *b*-, and *c*-type transitions were observed.

It should be noted that the predicted rotational constants from the ab initio calculation for the *gg* and *gg′* conformers of both the diethylsilane and diethyldifluorosilane molecules are similar enough to the experimental constants that some care needs to be exercised in assigning the spectra. Because the *gg* conformer is predicted to possess a pure *b*-type spectrum (while the *gg′* conformer might be expected to display all three selection rules), the observed spectrum quickly allows unambiguous determination of which conformer was assigned. The fact that only *b*-type transitions were observed seems to indicate that the *gg* conformer is the one identified experimentally. This is confirmed from the least-squares fits of the dipole moment components and will be further explored in the Dipole Moments section below. Finally, a comparison of the experimental planar moments (Tables 3 and 4) with the predicted values in Tables 1 and 2 also suggests a preference for the *gg* conformer—with the exception of slightly better agreement for the P_{aa} moment of the *gg′* conformer of diethylsilane, the second moments predicted for the *gg* conformer in both molecules are in far better agreement with the experimental data. Thus, the final assigned conformer can be confidently identified as the *gg* (C_2) structure. This is consistent with the ab initio calculations, which predict that the *gg′* structure should be considerably less stable than the next most stable conformer, equating to energy differences of 218 cm^{-1} for the diethyldifluorosilane and 277 cm^{-1} for the diethylsilane (using the ZPE corrected energies). Given the magnitude of this energy difference, we would not expect the *gg′* conformer to be significantly populated in our gas expansion and indeed no transitions that can be assigned to this species were observed.

III. Dipole Moments. Dipole moments for all observed conformers were obtained by least-squares fitting the calculated Stark coefficients ($\Delta\nu/E^2$) to measured values. The calculated Stark coefficients were computed by using second-order perturbation theory,[25] using the experimental rotational constants listed in Tables 3 and 4. A minimum of four M components (with $|M|$ values of 0 and 1 (with some $|M| = 2$)) selected from at least three low J ($J = 1 \leftarrow 0$, $2 \leftarrow 1$, and $3 \leftarrow 2$) rotational transitions were measured for each conformer and used to determine the dipole moment components; the selected components are tabulated as Supporting Information. The maximum observed frequency shift in an M component was ~790 kHz (for the *gg* conformer of the Et_2SiF_2), and no total frequency shift in any M component was less than 150 kHz.

The predicted dipole moments for all conformers of both molecules are included in Tables 1 and 2 while the measured dipole moments are listed in Table 5. The last row of this table lists the root-mean-square percentage differences between the observed and calculated Stark coefficients; these Stark coefficients are available as Supporting Information. It is expected that the C_2 symmetry *gg* conformer in both molecules would possess only a nonzero μ_b dipole moment component. Experimentally, a fit of only μ_b or combinations of (μ_a and μ_b) or of (μ_b and μ_c) or indeed of all three dipole moment components gives the same value of μ_b (to within the quoted uncertainty, Table 5) and zero values are obtained for the other components. This allows additional confirmation of the assignment of the spectra for the *gg* conformers rather than the *gg′* conformer of the two molecules.

Comparison of the variation of the dipole moments for the different conformers in going from the fluorine to the hydrogen

TABLE 5: Experimental Dipole Moment Data for Et_2SiF_2 and Et_2SiH_2

	Et_2SiF_2			Et_2SiH_2		
	tt (C_{2v})	*tg* (C_1)	*gg* (C_2)	*tt* (C_{2v})	*tg* (C_1)	*gg* (C_2)
μ_a/D		0.790(6)			0.2287(26)	
μ_b/D	2.166(5)	1.8151(25)	2.184(17)	0.8226(12)	0.643(10)	0.7443(9)
μ_c/D		1.0579(28)			0.408(16)	
μ_{total}/D	2.166(5)	2.2445(33)	2.184(17)	0.8226(12)	0.795(12)	0.7443(9)
N^a	5	7	5	4	8	5
rms^b	2.5	3.6	8.4	0.7	3.9	1.8

[a] *N* is the number of Stark (*M*) components included in the fit. [b] Root-mean-square percentage difference between the observed and calculated Stark coefficients; the transitions used in the fit, along with the Stark coefficients, are included in the Supporting Information.

analogue reveals that the total dipole moment for the diethylsilane is about one-third that of the diethyldifluorosilane, being 34.1% (*gg*), 35.4% (*tg*), and 38.0% (*tt*) of the total dipole moment value for the diethyldifluorosilane. The ab initio results (Tables 1 and 2) for a given conformer parallel this behavior, although the decrease in the overall dipole moment on going from the fluorine to the hydrogen form is slightly overestimated, with the total dipole moment of the diethylsilane being predicted to be 29.0% (*gg*), 31.8% (*tg*), and 34.5% (*tt*) that of the diethyldifluorosilane. Nevertheless, the relative magnitudes of the changes—that is, the fact that the effect is most pronounced in the *tt* confirmer and least in the *gg* conformer—is reproduced. Unfortunately, no experimental measurements exist for the dipole moment of difluorodimethylsilane to further explore this trend in the dimethyl-substituted analogue, although a predicted theoretical dipole moment of 2.8 D is given in ref 6. From the value of μ_{total} for dimethylsilane of 0.75(1) D[4] and the trends observed in the present study, the theoretical value of 2.8 D can probably be considered an upper bound of the dipole moment. Since the ab initio calculation in ref 6 apparently computed the dipole moment by using the SCF density, this likely overestimates the charge separation; repeating the calculation with the MP2 density to obtain the properties of difluorodimethylsilane gives a considerably smaller value of 2.48 D, and this is probably a better estimate of the true dipole moment for this molecule.

Discussion

Comparison of the experimental rotational constants in Tables 3 and 4 with the ab initio estimates in Tables 1 and 2 reveals that the agreement for diethyldifluorosilane is reasonably good, with the largest difference being 1.8% (for the *B* rotational constant of the *gg* conformer). The quality of agreement for the diethylsilane is a little poorer, with the *gg* conformer being the worst, with a sizable 4.8% difference in the *B* rotational constant between theory and experiment. As mentioned earlier, the correct assignment of this conformer as the *gg* conformer has been confirmed based on observed selection rules, planar moment information, and dipole moment data. It is interesting to note that for both molecules, the experimental and theoretical results are in considerably worse agreement for the *gg* conformer than for the other two conformers.

The predicted dipole moment components (Tables 1 and 2) can also be compared to the experimental values (Table 5) and this reveals that the predictions for the more polar diethyldifluorosilane are in generally much poorer agreement with experimental values than the predictions for diethylsilane. The discrepancies between ab initio and experimental values are up to 15% for the difluoro analogue, with no difference less than 7%; in all cases the ab initio predictions overestimate the dipole moment. The behavior for the diethylsilane is perhaps less pronounced, with the highest difference being 14% (for the smallest value of $\mu_a = 0.2287(26)$ D for the *tg* conformer), with everything else agreeing to better than 5%. At the level of calculation used here, it is clear that the quality of agreement for properties such as dipole moments is sufficiently good to allow relative spectral intensities to be used for assignment of conformers. Nevertheless, from a theoretical point of view, there is still considerable room for improvement in the quality of agreement between the experimental and calculated values.

The variation of predicted structural parameters on going from the diethylsilane to the diethyldifluorosilane is worthy of mention. The C−Si−C bond angle is found to increase by 4.3−4.4° in going from a given diethylsilane conformer to the fluorinated version, while the Si−C bond distances in all conformers show decreases of 0.025 to 0.027 Å upon fluorination. This nicely parallels the experimental trend seen for the closely related molecule dimethylsilane[4,6] where the bond angle and distance change by 4.2° and 0.023 Å, respectively, upon fluorination.

Conclusions

The rotational spectra of three conformers of diethyldifluorosilane and three conformers of diethylsilane have been observed by using Fourier-transform microwave spectroscopy. Comparison of the measured rotational constants, planar moments, and dipole moment data with ab initio calculations have confirmed these assignments. Relative energy differences are consistent with our failure to observe spectra belonging to the *gg′* conformer, identified for both molecules to be the least stable, and considerably higher in energy than the other forms; it is therefore unlikely to be significantly populated in our supersonic jet expansion. For both the hydrogen and fluorine derivative, the *gg* form (having C_2 symmetry) is determined to be the most stable by our own ab initio optimizations although this result seems to be in conflict with previous theoretical studies (for diethylsilane)[14] which identify the *tt* form as the lowest energy conformer (although the three conformers were all predicted to lie very close in energy in that study (within less than 25 cm^{-1})). It is clear that an experimental determination of the relative abundances of the conformers in the gas expansion would be extremely valuable and this should be possible via broadband Fourier-transform microwave[26] spectroscopic studies of these molecules; such studies have already been initiated for the diethylsilane.[27] In the present resonant cavity-based microwave study described in this paper, a clear intensity preference was apparent for the *gg* conformer of both molecules, consistent with our ab initio predictions that it is the most stable form.

Given the relatively low intensity of the transitions in the present study, the paucity of unassigned lines, and limited quantities of sample, attempts to locate isotopically substituted species were not made. However, the significant improvement in signal-to-noise ratio afforded by the current generation of chirped-pulse Fourier-transform microwave spectrometers (which can record broadband (~11 GHz) spectra for each gas pulse)[26] should allow identification of the much isotopic weaker spectra belonging to the ^{29}Si and ^{30}Si isotopologues for all three conformers of the diethylsilane, as well as the ^{13}C substituted species for at least the most abundant ^{28}Si isotopic species. It is also hoped that, with all the transitions belonging to isotopically substituted species identified and removed from the measured spectra, the question of whether the *gg′* conformer is present in the gas expansion can be addressed. Finally, the quantitatively correct transition intensities obtained from such broadband measurements should allow deduction of the relative abundances of the conformers in the gas sample. Analysis of this broadband data is currently in progress and will appear in a future publication.[27]

Supporting Information Available: Tables giving principal axis coordinates from ab initio calculations, observed and calculated transition frequencies, and observed and calculated Stark coefficients for diethylsilane and diethyldifluorosilane. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Niide, Y.; Hayashi, M. *J. Mol. Spectrosc.* **2002**, *216*, 52.

(2) Niide, Y.; Hayashi, M. *J. Mol. Spectrosc.* **2002**, *216*, 61.

(3) Hayashi, K.; Matsumura, C. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 732.

(4) Pierce, L. *J. Chem. Phys.* **1961**, *34*, 498.

(5) Niide, Y.; Hayashi, M. *J. Mol. Spectrosc.* **2004**, *223*, 152.

(6) Schnell, M.; Grabow, J.-U.; Hartwig, H.; Heineking, N.; Meyer, M.; Stahl, W.; Caminati, W. *J. Mol. Spectrosc.* **2005**, *229*, 1.

(7) Churchill, G. B.; Bohn, R. K. *J. Phys. Chem. A* **2007**, *111*, 3513.

(8) Mencarelli, P. *J. Chem. Educ.* **1995**, *72*, 511.

(9) Salam, A.; Deleuze, M. S. *J. Chem. Phys.* **2002**, *116*, 1296.

(10) Knippenberg, S.; Huang, Y. R.; Hajgató, B.; François, J.-P.; Deng, J. K.; Deleuze, M. S. *J. Chem. Phys.* **2007**, *127*, 174306.

(11) Tomonaga, A.; Shimanouchi, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1446.

(12) Bonham, R. A.; Bartell, L. S.; Kohl, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4765.

(13) Bartell, L. S.; Kohl, D. A. *J. Chem. Phys.* **1963**, *39*, 3097.

(14) Fogarty, H. A.; Ottosson, C.-H.; Michl, J. *J. Mol. Struct. (THEOCHEM)* **2000**, *506*, 243.

(15) Ohno, K. *J. Sci. Hiroshima Univ. Ser. A: Phys. Chem.* **1973**, *37*, 429.

(16) Matsuura, H.; Murata, H. *J. Mol. Struct.* **1979**, *56*, 191.

(17) Peebles, S. A.; Peebles, R. A.; Guirgis, G. A.; Stidham, H. To be submitted for publication.

(18) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33.

(19) Hillig, K. W.; Matos, J.; Scioly, A.; Kuczkowski, R. L. *Chem. Phys. Lett.* **1987**, *133*, 359.

(20) Serafin, M. M.; Peebles, S. A. *J. Phys. Chem. A* **2008**, *112*, 12616.

(21) Reinartz, J. M. L. J.; Dymanus, A. *Chem. Phys. Lett.* **1974**, *24*, 346.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03* , Revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(23) Pickett, H. M. *J. Mol. Spectrosc.* **1991**, *148*, 371.

(24) Watson, J. K. G. *Vib. Spectra Struct.* **1977**, *6*, 1.

(25) Second-order Stark coefficients were computed with use of the University of Michigan modified version of the original ASYSPEC code, Beaudet, R. A., Ph.D. Thesis, Harvard University, 1961.

(26) Brown, G. G.; Dian, B. C.; Douglass, K. O.; Geyer, S. M.; Shipman, S. T.; Pate, B. H. *Rev. Sci. Instrum.* **2008**, *79*, 053103.

(27) Neill, J.; Muckle, M.; Steber, A. L.; Peebles, R. A.; Peebles, S. A.; Pate, B. H. Unpublished observations, 2008.

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