Infrared and Raman Spectra, Vibrational Assignment, and Barriers to Internal Rotation for Dimethylsilylamine

J. R. Durig* and P. J. Cooper[1]

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208 *(Received September 13, 1976)*

Publication costs assisted by the University of South Carolina

The infrared spectra of gaseous $(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$ have been recorded from 80 to 3800 cm^{-1}. The Raman spectra of $(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$ have been recorded to within 25 cm^{-1} of the exciting line in all three physical states. A vibrational assignment has been made, and the methyl and silyl torsional modes observed. A barrier to internal rotation of 3.23 kcal/mol has been calculated for the methyl groups, while a barrier of 1.51 kcal/mol was calculated for the silyl group. Upon consideration of all available data, it is concluded that an intramolecular d_π–p_π interaction in dimethylsilylamine is not very significant.

Introduction

Particular attention has been paid to the study of various silyl amines because of their tendency to form planar compounds. For example, previous studies of trisilylamine,[2–5] $(SiH_3)_3N$, have shown the vibrational spectra to be consistent with a planar heavy-atom skeleton. That trisilylamine adopts a planar configuration at the nitrogen atom has also been demonstrated by an electron diffraction investigation.[6] Vibrational[7,8] and electron diffraction[9] studies have both shown that methyldisilylamine, $CH_3N(SiH_3)_2$, also exhibits a planar heavy-atom configuration. In addition, a planar structure has also been indicated for disilylamine, $(SiH_3)_2NH$, in an electron diffraction study.[10] Of the silyl amine compounds studied to date, only dimethylsilylamine, $(CH_3)_2NSiH_3$, appears not to have a planar heavy-atom skeleton. Vibrational studies by Buttler and McKean[11] and by Goldfarb and Khare[8] have both implicated a nonplanar structure for dimethylsilylamine. A subsequent electron diffraction investigation[12] seemed to confirm this. However, discrepancies in certain vibrational assignments exist between the two vibrational studies, and the possibility that the molecule might be planar in the ground vibrational state is thought to exist.

In a continuing effort to elucidate the forces giving rise to the barriers to internal rotations, we are presently interested in the torsional barriers in compounds containing group 4A and group 5A elements. Currently, no information is available on the barriers to internal rotation in silyl amine compounds. Therefore, in the hope of clearing up the existing discrepancies in the vibrational assignment, conclusively establishing either the planarity or nonplanarity of the heavy-atom skeleton, and providing some information on the methyl and silyl torsional barriers, we have undertaken a reinvestigation of the vibrational data for dimethylsilylamine and have further expanded it to include Raman and far-infrared spectral data for both $(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$.

Experimental Section

The samples used in the present work were prepared by the methods of Aylett and Emsley[13] or Sujishi and Witz.[14] Iodosilane, SiH_3I, or bromosilane, SiH_3Br, was allowed to react with either dimethylamine, $(CH_3)_2NH$, or dimethylamine-d_3, CH_3CD_3NH, depending on whether the undeuterated or deuterated dimethylsilylamine was to be prepared. The iodosilane and bromosilane used in the above syntheses were both prepared according to the method of Ward.[15]

Raman spectra were recorded to 4000 cm^{-1} with a Cary Model 82 Raman spectrophotometer equipped with a Spectra-Physics Model 171 argon ion laser. The 5145-Å line was used and the laser power was varied from 0.5 to 5 W at the head depending on the physical state under investigation. A standard Cary gas cell with multipass optics was utilized to obtain the spectra of gaseous dimethylsilylamine and dimethylsilylamine-d_3. Spectra of the liquids were obtained from samples in sealed glass capillaries. The spectra of solid $(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$ were recorded by condensing the sample onto a brass plate maintained at ~77 K in a Cryogenics Technology Inc. Spectrim cryostat equipped with a Lake Shore Cryotronics Model DTL 500 high precision temperature controller. Under these conditions the samples condensed on the plate as a clear glass. The samples were annealed by allowing the temperature to increase to ~245 K, whereupon a white crystalline solid was observed to form, and then quickly lowered to ~100 K, at which temperature all Raman spectra of the solid phase were recorded. Polarization measurements were made using the standard Cary accessories. Frequencies measured for sharp, resolvable bands are expected to be accurate to at least ±2 cm^{-1}.

Infrared spectra were recorded with a Digilab FTS-15B Fourier transform interferometer. Mid-infrared spectra from 3800 to 450 cm^{-1} were obtained using a germanium beam splitter on a KBr substrate and a glower source, while far-infrared spectra from 450 to 80 cm^{-1} were obtained by using a 6.25-μm Mylar beam splitter and a high pressure Hg arc lamp source. Spectra of the gaseous phase were recorded by using a 10-cm cell with KBr windows and ~3 Torr of sample pressure in the mid-infrared, or polyethylene windows and ~600 Torr of sample pressure in the far-infrared. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. Mid-infrared spectra were recorded at an effective resolution of better than 1.0 cm^{-1} and far-infrared spectra at an effective resolution of better than 0.5 cm^{-1} using a modified "boxcar" apodization function for photometric accuracy. As a result, measured frequencies are expected to be accurate to better than ±1 cm^{-1} in the mid-infrared region and approximately ±0.2 cm^{-1} in the far-infrared region.

Vibrational Assignment

The Raman spectra of gaseous, liquid, and solid $(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$ are shown in Figures 1 and 2, respectively. The mid-infrared spectra of gaseous

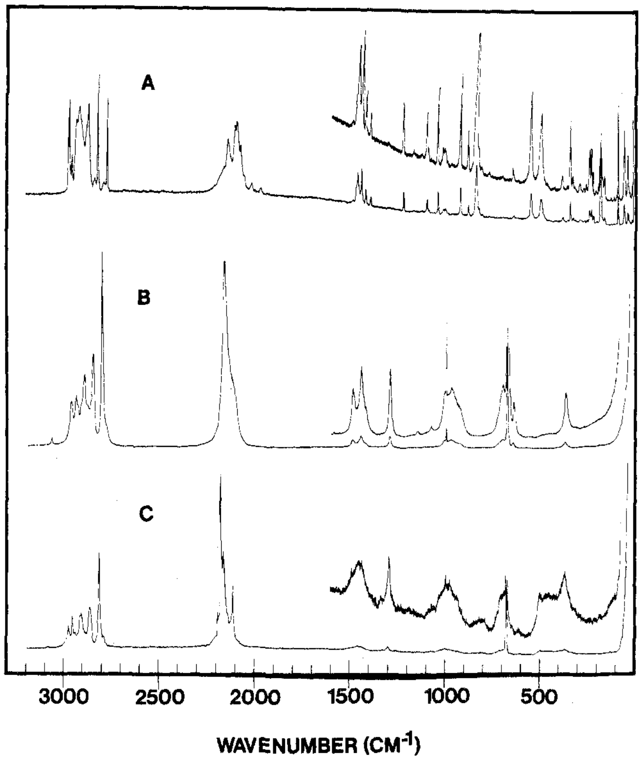

Figure 1. Raman spectra of $(CH_3)_2NSiH_3$: (A) annealed solid, spectral bandwidth 2 cm^{-1}; (B) liquid, spectral bandwidth 1 cm^{-1}; (C) gas, spectral bandwidth 2 cm^{-1}.

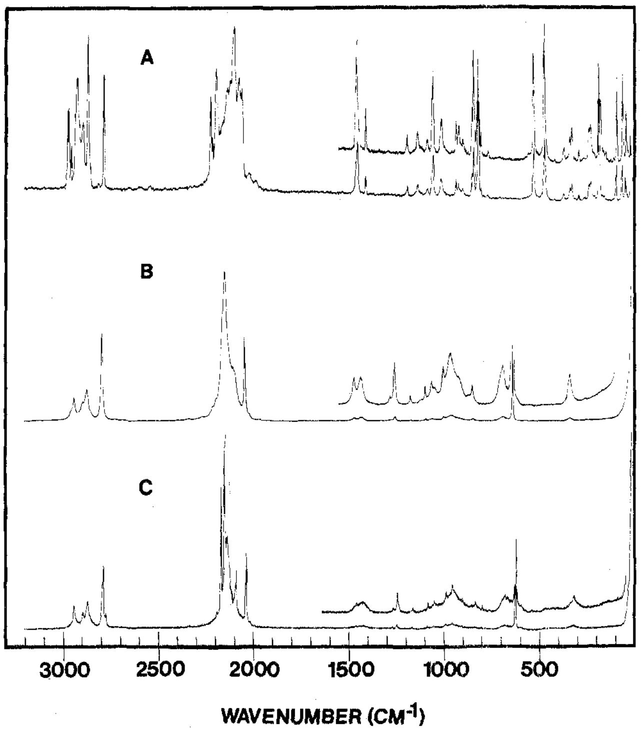

Figure 2. Raman spectra of $CH_3CD_3NSiH_3$: (A) annealed solid, spectral bandwidth 3 cm^{-1}; (B) liquid, spectral bandwidth 1 cm^{-1}; (C) gas, spectral bandwidth 2 cm^{-1}.

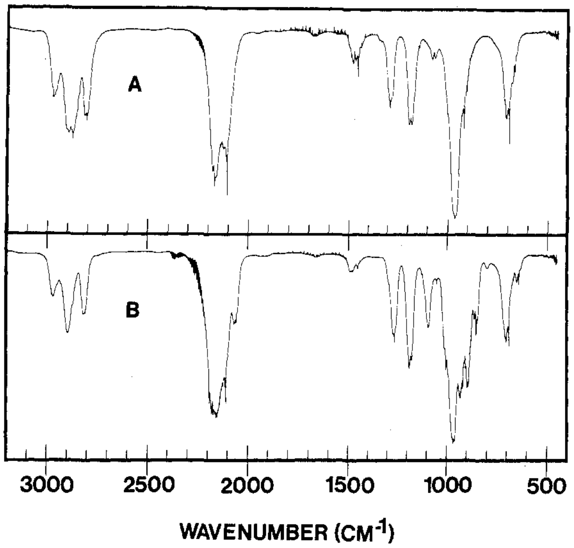

Figure 3. Infrared spectra of gaseous dimethylsilylamine: (A) $(CH_3)_2NSiH_3$; (B) $CH_3CD_3NSiH_3$.

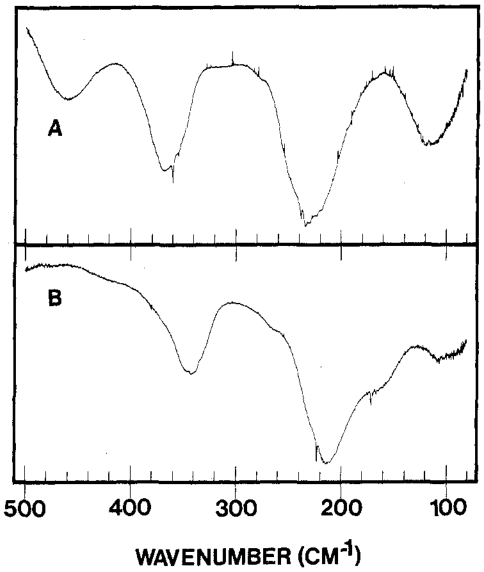

Figure 4. Far-infrared spectra of gaseous dimethylsilylamine: (A) $(CH_3)_2NSiH_3$; (B) $CH_3CD_3NSiH_3$.

$(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$ are both presented in Figure 3, while the far-infrared spectra are shown in Figure 4. It was not possible to conclusively establish either the planarity or nonplanarity of the heavy-atom skeleton solely on the basis of C_s and C_{2v} selection rules. However, it will be shown in the section on torsional assignments that the heavy-atom skeleton is nonplanar for both molecules, and $(CH_3)_2NSiH_3$ will belong to the symmetry group C_s, with 18 A′ and 15 A″ modes predicted, while $CH_3CD_3NSiH_3$ will then belong to the symmetry group C_1. In either case, all 33 normal vibrational modes will be both infrared and Raman active.

The observed frequencies and assignments for $(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$ are given in Tables I and II, together with approximate descriptions of the normal modes. As in the previous vibrational study[11] of $(CH_3)_2NSiH_3$, we too were unable to assign all of the CH_3 stretching fundamentals. However, in addition to the A′ and A″ CH_3 symmetric stretches previously assigned, we also assigned the two CH_3 antisymmetric stretches, ν_1 and ν_{19}, to the band at 2970 cm^{-1} in the gas and 2957 cm^{-1} in the liquid, since the frequency was considered too high to be due to an overtone of one of the CH_3 deformations. This assignment is consistent with the observation of a band at the same frequency in $CH_3CD_3NSiH_3$, corresponding to one of the CH_3 antisymmetric stretches. The assignment of the other two CH_3 antisymmetric stretches, ν_2 and ν_{20}, however, still proves too elusive due to the abundance in the CH_3 stretching region of what must be overtones and combination bands of the CH_3 deformations.

The two SiH_3 antisymmetric stretches and the SiH_3 symmetric stretch are assigned to the bands near 2170 and 2106 cm^{-1}, respectively, in both the light and heavy compounds. The fine structure appearing on the high frequency side of the SiH_3 stretches, as well as on the low frequency side of the SiH_3 deformations, in the mid-infrared spectra of both compounds is attributed to the presence of SiH_3Br. The closely spaced series of bands centered at 2350 cm^{-1} in the mid-infrared spectrum of $CH_3CD_3NSiH_3$ is due to atmospheric CO_2. The CH_3 deformations, which all occur in the 1400–1500-cm^{-1} region, were assigned on the basis of the Raman polarization data and the results of a previous vibrational assignment[16] of the corresponding modes in dimethylamine.

Assignment of the spectra in the region below 1300 cm^{-1} proved difficult. As first pointed out by Buttler and McKean,[11] not only is there significant coupling between several of the vibrational modes in this region, but the differences between the spectra of the gas and solid phases are considerable. The assignments presented in this study for the gas and liquid phase frequencies are in fairly good agreement with those reported previously.[11] The two A′ CH_3 rocking modes are assigned to the infrared A–C hybrid-type bands at 1293 and 1149 cm^{-1}, while the two A″ CH_3 rocking modes are assigned to the infrared B-type bands at 1189 and 1074 cm^{-1}. The C–N antisymmetric stretch in $(CH_3)_2NSiH_3$ is assigned to the weak shoulder at 1030 cm^{-1} in the Raman spectrum of the liquid. The SiH_3 symmetric and antisymmetric deformations are assigned to the infrared bands near 971 and 922 cm^{-1}, respectively, in both the heavy and light compounds. The A′ SiH_3 rocking mode is assigned to the infrared A–C hybrid-type band at 695 cm^{-1}, and the A″ SiH_3 rocking mode is then assigned to the shoulder at 715 cm^{-1} which appears to be of B-type contour.

Buttler and McKean,[11] in their study of $(CH_3)_2NSiH_3$, assigned the C–N symmetric stretch to a band at 1003 cm^{-1}, and the Si–N stretch to an ill-defined, weak band at 670 cm^{-1}. In a subsequent investigation of the matrix-isolated solid by Goldfarb and Khare,[8] it was argued that the band at 1003 cm^{-1} corresponded to the Si–N stretching frequency, while a band near 900 cm^{-1} in the matrix spectrum was assigned to the C–N symmetric stretch. The observation of a sharp, medium-intense polarized line at 670 cm^{-1} in the Raman spectra of the gas and liquid phases, and of an A–C hybrid-type band at 670 cm^{-1} in the infrared spectrum of $(CH_3)_2NSiH_3$, confirms the initial assignment of Buttler and McKean.[11] The Raman line at 670 cm^{-1} is too intense for an SiH_3 rock and too high in frequency for a skeletal bend. The polarized lines near 1003 cm^{-1} in the Raman spectra of gaseous and liquid $(CH_3)_2NSiH_3$, and the corresponding band of A–C type contour at 1005 cm^{-1} in the infrared spectrum, must, therefore, be assigned to the C–N symmetric stretch. Further evidence for the correctness of this assignment is demonstrated by the occurrence of bands near 642 cm^{-1} and near 1005 cm^{-1} in both infrared and Raman spectra of $CH_3CD_3NSiH_3$. The 642-cm^{-1} band is obviously the analogue of the band at 670 cm^{-1} in the light compound, which is ascribed to the Si–N stretch. The small decrease in frequency can best be attributed to coupling of the Si–N stretch with the C–N stretch, which is already coupled with the highest frequency CH_3 rocking mode. The $(H_3)C$–N stretch in the heavy compound is assigned to the infrared and Raman bands near 1006 cm^{-1}, which are little shifted from the bands near 1003 cm^{-1} assigned to the C–N symmetric stretch in the light compound. This is in agreement with the assignments of the C–N symmetric stretch in dimethylamine-d_0[16] and the $(H_3)C$–N stretch in dimethylamine-d_3[17] to bands at 924 and 925 cm^{-1}, respectively. The differences in the C–N stretching frequencies between the dimethylamines and dimethylsilylamines is, of course, due to the introduction of coupling between the C–N stretch and the Si–N stretch in the dimethylsilylamines. The $(D_3)C$–N stretch in the heavy compound is assigned to the infrared and Raman bands at 855 cm^{-1}, shifted from the frequency of 820 cm^{-1} assigned to the $(D_3)C$–N stretch in dimethylamine-d_3,[17] as a result of coupling with the Si–N stretch.

The A′ C–N–C skeletal deformation in $(CH_3)_2NSiH_3$ is assigned to the far-infrared band at 359.7 cm^{-1}. The Q-branch observed at 354.2 cm^{-1} is thought to be due to the deformation in an excited torsional state. The C–N–C deformation is observed at 342.4 cm^{-1} in the infrared spectrum of the deuterated compound. The broad band occurring at 459 cm^{-1} in the far-infrared spectrum of the light compound is considered to be the result of an impurity on the cell windows, as evidenced by its lack of any recognizable band contour and the absence of any counterpart in the spectrum of the heavy compound. The C–N–Si out-of-plane skeletal deformation is assigned to the band at 268 cm^{-1} in the far-infrared spectrum, shifting to 256 cm^{-1} upon deuteration. The C–N–Si in-plane skeletal deformation, although not directly observed, is estimated to occur at approximately 234 and 215 cm^{-1} in the light and heavy compounds, respectively. The reasoning behind this assignment will be made apparent in the following section of this paper.

That a specific intermolecular association such as that first proposed by Sujishi and Witz[14] occurs in dimethylsilylamine has been conclusively confirmed by the two previous vibrational studies,[8,11] and the greater disparity between the gas and condensed phase spectra in the region below 1300 cm^{-1} shown to be indicative of involvement of the nitrogen and silicon atoms in the interaction leading to association. The major point of disagreement in those two investigations occurred over the assignments of the C–N symmetric stretch and the Si–N stretch. Since we have already shown the gas phase assignment of Buttler and McKean[11] to be correct, we conclude on the basis of our Raman spectra of the solid that at least one, and possibly both, of the bands observed at 505 and 465 cm^{-1} by Buttler and McKean[11] must correspond to the Si–N stretch. Since no bands of comparable intensity are to be found anywhere nearer the gas phase frequency of 670 cm^{-1} for the Si–N stretch, we assign the bands at 550 and 498 cm^{-1} in the solid phase Raman spectra to the Si–N stretch in the light compound and at 524 and 468 cm^{-1} in the heavy compound. On the basis of their assignment of the Si–N stretch to a much higher frequency, Goldfarb and Khare[8] assigned these bands to deformations of the rigid skeletal framework of the polymerized species. We have assigned the C–N symmetric stretch in the light compound and the $(H_3)C$–N stretch in the heavy compound to bands at 919 cm^{-1} in the solid phase Raman spectra of both compounds. The downward shift in frequency from the gas phase value is in keeping with the decrease in frequency of the Si–N stretch upon condensation, since both modes have already been shown to be coupled in the gas phase molecules. The assignments suggested in this work for the solid phase frequencies are, in most cases, in fair agreement with those proposed by Buttler and McKean.[11]

An X-ray diffraction study by Rudman et al.[18] has shown that crystalline dimethylsilylamine forms cyclic pentamers which consist of ten-membered, slightly skewed rings formed by alternating silicon and nitrogen atoms. Each

TABLE I: Observed Infrared and Raman Frequencies (cm^{-1}) and Assignments for (CH$_3$)$_2$NSiH$_3$[a,b]

Raman				
Gas	Liquid	Solid	Infrared gas	Assignment
	3062 w,p		3077 vw	
		2972 s		
2970 m	2957 m		2970 m	ν_1(A'), ν_{19}(A'') CH$_3$ antisymmetric stretches
		2966 s		
		2953 m		
2946 m	2931 m			
2930 m	2923 m,sh			
		2929 s		
		2915 s		ν_2(A') + ν_{20}(A'') and overtones and combination bands due to CH$_3$ deformations
		2904 s,sh		
	2901 m,sh			
2901 m	2890 m		2983 s	
		2877 s,sh		
	2870 m			
			2873 s	
		2867 s		
2856 m	2843 m			
		2836 w		2 × ν_8
		2818 s		
2807 s	2794 s	2769 s	2803 m	ν_3(A'), ν_{21}(A'') CH$_3$ symmetric stretches
		2789 w		2 × ν_{25}
	2763 w,sh			
2187 m			2189 s	Impurity ?
		2180 w,sh		
2169 vs	2158 s,p	2140 s	2170 s	ν_4(A'), ν_{22}(A'') SiH$_3$ antisymmetric stretches
	2158 w,sh			
2156 s				
2108 m	2105 m,sh,p	2102 s	2106 s	ν_5(A') SiH$_3$ symmetric stretch
		2091 s		
		2074 s		2 × ν_{12}
		2053 w		ν_{12} + ν_{13} or ν_{12} + ν_{29}
		2015 w		ν_{13} + ν_{29}
		1967 w		
		1485 vw		
1485 w,dp	1483, w,dp	1467 m,sh		ν_6(A'), ν_{23}(A'') CH$_3$ antisymmetric deformations
		1460 m		
1471 w,dp		1454 m	1473 w	ν_{24}(A'') CH$_3$ antisymmetric deformation
1453 w,p		1440 m	1455 m	ν_7(A') CH$_3$ antisymmetric deformation
1440 w,p ?	1440 w,p ?	1417 m		ν_8(A') CH$_3$ symmetric deformation
	1419 w,sh,dp?	1392 m		ν_{25}(A'') CH$_3$ symmetric deformation
			1342 w	2 × ν_{15}
1333 vw				
1306 vw,sh				
		1298 vw		
1293 w,p	1289 w,p	1220 m	1293 m	ν_9(A') CH$_3$ rock
		1164 vw	1189 m	ν_{26}(A'') CH$_3$ rock
	1142 vw	1122 vw	1149 w	ν_{10}(A') CH$_3$ rock
1073 vw	1073 vw,dp	1087 vw	1075 w	ν_{27}(A'') CH$_3$ rock
	1030 vw,sh	1096 w		ν_{28}(A'') C-N antisymmetric stretch
1004 w,p	1002 w,sh,p	919 m	1005 m	ν_{11}(A') C-N symmetric stretch
992 w,p	992 w,p			Impurity ?
972 w,p	965 w,sh,p	1039 m	971 vs	ν_{12}(A') SiH$_3$ symmetric deformation
927 w,p	923 w,p	1011 w	922 m	ν_{13}(A'), $_{29}$(A'') SiH$_3$ antisymmetric deformations
		1000 w		
		995 w,sh		
		985 vw		
		878 w	715 m	ν_{30}(A'') SiH$_3$ rock
696 w,p	695 w,p	834 m	695 s	ν_{14}(A') SiH$_3$ rock
		803 vw		
		768 vw		
		696 vw		
670 m,p	670 m,p	550 m	670 m	ν_{15}(A') Si-N stretch
		498 m?		
		642 vw		
640 vw	638 w,p			
			459 m	Impurity
360 w,p	364 w,p	385 w	359.7 m	ν_{16}(A') C-N-C deformation
			354.2 m	
		344 m	268 w,sh	ν_{31}(A'') C-N-Si out-of-plane deformation
			238.5 s	ν_{17}(A') CH$_3$ torsion
			~240[b]	ν_{32}(A'') CH$_3$ torsion
		241 w	~234[b]	ν_{18}(A') C-N-Si in-plane deformation
			115	ν_{33} (A'') SiH$_3$ torsion
		328 w		
		290 vw		

TABLE I (*Continued*)

Raman				
Gas	Liquid	Solid	Infrared gas	Assignment
		257 vw		
		232 w		
		222 w		
		204 vw		
		182 s		Lattice mode
		163 w		
		130 vw		
		104 w		
		99 vw		
		92 m		Lattice mode
		60 m		Lattice mode
		41 m		Lattice mode
		34 vw, sh		Lattice mode
		30 vw, sh		
		18 vw		Lattice mode

[a] Abbreviations used: w, weak, m, medium; s, strong; v, very; sh, shoulder; p, polarized; dp, depolarized. [b] See text for discussion.

nitrogen atom is tetrahedrally bonded, while each silicon atom is five-coordinated in a trigonal bipyramidal arrangement. Therefore, a detailed assignment of the infrared and Raman spectra of solid $(CH_3)_2NSiH_3$ and $CH_3CD_3NSiH_3$ does not seem possible due to the large number of active fundamental vibrational frequencies of the pentamer unit. For the sake of simplicity, we have assigned the solid phase frequencies on the basis of the symmetry of the unassociated molecule.

Because of the coplanarity of the three Si–H bonds around each silicon in the crystalline state, a large disparity between the SiH_3 stretching regions in the gas and solid spectra is expected. However, due to the profuseness of bands in this region, especially in that of the solid, any definitive assignment is impossible. One of the more notable differences in the spectrum of dimethylsilylamine upon condensation is the upward shift in frequency of the SiH_3 deformations, contrary to the usually observed downward shift (e.g., the silyl halides[19]). This unusual upward shift is obviously the result of the trigonal bipyramidal arrangement about the silicon atoms in the solid phase. We observed several bands in the Raman spectrum of the solid phase of the light compound which appeared to have counterparts sufficiently shifted in the deuterated compound so as to be attributable to skeletal deformations of the C_2–N moiety. Therefore, on this basis, the C–N–C deformation and the C_2–N in-plane wag are assigned to the bands at 385 and 344 cm^{-1}, respectively, shifting to 367 and 323 cm^{-1} upon deuteration. The C_2–N out-of-plane rock is assigned to the band at 241 cm^{-1} in the spectrum of the light compound, but its counterpart is not observed in the spectrum of the heavy compound as it is quite possibly obscured by the pair of bands at 232 and 223 cm^{-1}.

Rudman et al.[18] have suggested that the two low frequency bands previously assigned as Si–N stretches are due to in-plane and out-of-plane ring deformational modes. We consider these frequencies, 550 and 498 cm^{-1} in the spectrum of the light compound and 524 and 468 cm^{-1} in the spectrum of the heavy compound, to be too high to be due to such deformational modes. We believe that our assignment of these bands to the Si–N stretch is correct, and the fact that there are two bands is attributable to the existence of in-phase and out-of-phase motions.

Torsional Assignments and Barriers to Internal Rotations

For a molecule such as dimethylsilylamine three torsional vibrations are expected. In the case of $(CH_3)_2NSiH_3$, the torsional oscillations of the two methyl groups will give rise to one A′ and one A″ mode, while the SiH_3 torsion will account for another A″ mode. A–C hybrid band contours are expected for A′ modes, while B-type band contours should result from A″ modes. For $CH_3CD_3NSiH_3$, bands due to the CH_3 and CD_3 torsions should exhibit A–C hybrid band contours, while bands arising from the SiH_3 torsion should be of primarily B-type contour.

The sharp Q branch at 238.5 cm^{-1} in the spectrum of the light compound is assigned as the 1 ← 0 transition of the A′ methyl torsion. The Q branches between 210 and 235 cm^{-1} are expected to be the torsional hot-band series for this mode. In the heavy compound, the sharp bands at 223.3 and 171.3 cm^{-1} are assigned to the 1 ← 0 transitions of the CH_3 and CD_3 tops, respectively. Once again, the bands immediately following on the low frequency side of these transitions are expected to be the torsional hot-band series of the respective torsions. Qualitatively, one would predict the 1 ← 0 transition to be the most intense. However, we observed that several of the torsional hot-band transitions for the CH_3 torsions in both the light and heavy molecules were more intense than the 1 ← 0 transitions. This indicates the existence of a band due to an additional vibrational mode lying beneath these torsional transitions. From the contours of the bands resulting from the CH_3 torsions, we estimate these bands at 234 and 215 cm^{-1} in the light and heavy compounds, respectively, and assign them to the C–N–Si in-plane skeletal deformation. We were unable to observe the A″ CH_3 torsion in the spectrum of the light compound, but based on the small F' value in dimethylsilylamine and the fairly small value of the coefficient of the sine–sine coupling term found for dimethylamine,[17] which should be close to the value for the corresponding quantity in dimethylsilylamine, we can predict that it should occur at a frequency very close to that of the A′ torsion.

An attempt was made to fit the data for the CH_3 and CD_3 tops in both the light and heavy compounds to a two-dimensional potential function based on a new theoretical treatment by Groner and Durig[20] of the torsional vibrations in $(CH_3)_2X$-type molecules having C_s symmetry. All such endeavors, however, met with failure for both the deuterated and undeuterated compounds. In the case of $(CH_3)_2NSiH_3$, the kinetic top–top interactions between the two methyl groups is expected to be moderately large and the coefficient of at least the cosine–cosine coupling term should be significant. We were severely limited though in the amount of data available for the light compound as we were only able to unambiguously assign the 1 ← 0 transition of the A′ CH_3 torsion and were unable to observe

TABLE II: Observed Infrared and Raman Frequencies (cm^{-1}) and Assignments for $CH_3CD_3NSiH_3$[a,b]

Raman				
Gas	Liquid	Solid	Infrared gas	Assignment
		2973 s		
2967 w,sh	2957 m,sh		2971 m	ν_1 CH_3 antisymmetric stretch
		2966 s		
2957 m	2943 m			2 × ν_{11} or ν_2 CH_3 antisymmetric stretch ?
		2954 m		
		2933 s		
		2922 s		
2909 m	2899 m			
		2891 s		
2886 m	2877 m		2890 m	2 × ν_{12}
		2865 vs		
		2807 vw		
2805 m	2797 s	2782 s	2805 m	ν_3 CH_3 symmetric stretch
2791 m				
	2728 vw			
		2638 vw		
		2590 vw		
		2536 vw		
	2343 vw			
		2220 s		
	2216 w			
		2212 m		
2208 w	2200 w			2 × ν_{15}
		2190 s		
2184 m	2172 m,sh		2189 s	Impurity?
2168 s	2155 vs	2133 s	2170 s	ν_6, ν_7 SiH_3 antisymmetric stretches
2155 m				
		2119 s		
2107 m	2106 m,sh	2098 vs	2105 s	ν_8 SiH_3 symmetric stretch
		2073 s		
		2055 s		
2054 m	2047 s		2054 m	ν_9 CD_3 symmetric stretch
2033 w	2025 w			
		2017 w		
		1982 w		
	1490 vw,sh	1459 m,sh		ν_{10} CH_3 antisymmetric deformation
1450 w,bd	1472 w	1452 m	1480 w,bd	ν_{11} CH_3 antisymmetric deformation
	1438 w	1407 w	1448 w	ν_{12} CH_3 symmetric deformation
1284 w	1284 vw		1290 m	2 × ν_{27}
1263 w	1260 w	1188 w	1264 m	ν_{13} CH_3 rock
1182 vw	1177 vw	1121 vw	1185 s	ν_{14} CH_3 rock
			1160 w	
	1124 vw			
1104 w	1100 vw	1133 w	1104 m	ν_{15} CD_3 deformation
1067 w	1065 vw	1082 w		ν_{16} CD_3 deformation
	1049 vw		1053 w	ν_{17} CD_3 deformation
1008 w	1004 w	919 w	1007 s	ν_{18} (H_3) C-N stretch
973 w	968 w	1057 m,sh 1053 m	974 vs	ν_{19} SiH_3 symmetric deformation
930 w		933 w		ν_{20} CD_3 rock
922 w	924 w,sh	1010 w	923 s	ν_{21}, ν_{22} SiH_3 antisymmetric deformations
	875 vw,sh	896 w		ν_{23} CD_3 rock
855 w	852 vw	816 vs	855 m	ν_{24} (D_3) C-N stretch
819 w				
			801 w	
		801 w		
		765 vw		
		706 vw		
703 w		848 w	711 m	ν_{25} SiH_3 rock
686 w	693 w	839 m	693 m	ν_{26} SiH_3 rock
	669 vw		668 w	
641 m	642 s	524 m 468 m?	643 w	ν_{27} Si-N stretch
612 vw	612 vw,sh			
586 vw				
560 vw	560 vw			
	539 vw			
	360 vw,sh			
337 w	340 w	367 w	342.4 m 333.0 m,sh	ν_{28} C-N-C deformation
	260 vw,bd	323 w	256 w,sh	ν_{29} C-N-Si deformation
			223.3 s	ν_{30} CH_3 torsion
			~215[b]	ν_{31} C-N-Si deformation
			171.3 m	ν_{32} CD_3 torsion
			103 m,bd	ν_{33} SiH_3 torsion

TABLE II (*Continued*)

Raman				
Gas	Liquid	Solid	Infrared gas	Assignment
		332 w		
		287 w		
		256 vw		
		232 w		
		223 w		
		205 vw		
		179 vs		Lattice mode
		160 vw		
		123 vw		
		105 w		
		94 w		
		89 m		Lattice mode
		58 m		Lattice mode
		40 w		Lattice mode
		34 w,sh		
		30 w,sh		
		18 w		Lattice mode

[a] Abbreviations used: w, weak; m, medium; s, strong; v, very; sh, shoulder. [b] See text for discussion.

any of the torsional double jumps in the Raman spectrum of the gas phase. In $CH_3CD_3NSiH_3$, we expect the kinetic top–top interaction between the CH_3 and CD_3 tops to be fairly small and, hence, on the basis of the results for dimethylamine-d_3,[17] the coefficient of the cosine–cosine coupling term to be somewhat smaller than that for the light compound and the coefficient of the sine–sine coupling term to be negligible. Here too we were hampered in obtaining the necessary data by not being able to observe the torsional double jumps in the Raman spectrum of the gas. Also, the possibility that the CD_3 torsion is significantly coupled to the SiH_3 torsion must be examined.

The bands at 115 and 103 cm^{-1} in the light and heavy compounds, respectively, both have contours attributable to a series of overlapping B-type bands and are, thus, assigned to the SiH_3 torsion. To the best of the authors' knowledge this is the first observation of a torsional frequency of a silyl group bonded to nitrogen. Taking into consideration the experimental uncertainty in frequency measurement due to the broadness of the bands and the difference in F numbers in the light and heavy compounds, we conclude that this difference between the SiH_3 torsional frequencies in the light and heavy compounds is real and that, more specifically, it is a result of coupling between the SiH_3 top and the CD_3 top in the heavy compound. In the light compound it is expected that coupling of the SiH_3 top with the two methyl tops is insignificant. Such coupling would, of course, invalidate any results obtained by using a two-dimensional potential function to fit the CH_3 and CD_3 top data in the heavy compound.

Therefore, all torsional data were fit by neglecting all top–top interactions and using a one-dimensional periodic potential function. The torsional assignments together with the results of all calculations are summarized in Table III. Since coupling between the CH_3 and SiH_3 tops is expected to be almost nonexistent in the light compound and since coupling between the CH_3 and CD_3 tops is expected to be small in the heavy compound, we consider the barrier to internal rotation of 1.51 kcal/mol calculated for the SiH_3 top in the light compound as best approximating the actual silyl barrier and the value of 3.23 kcal/mol calculated for the CH_3 top in the heavy compound as best approximating the actual methyl barrier.

If the heavy-atom skeleton were indeed planar, then the internal rotational barrier about the Si–N bond would be sixfold and we would expect the silyl top to be essentially freely rotating. Also, we would predict rotational fine structure in the form of bands of alternating strong–weak–weak intensity to be exhibited on the antisymmetric SiH_3 stretch. The fact that we observed the SiH_3 torsion and found the barrier to internal rotation to be appreciable, and were unable to observe any fine structure on the antisymmetric SiH_3 stretch, is clearly evidence of the nonplanarity of the heavy-atom skeleton.

TABLE III: Observed Torsional Frequencies and Potential Constants for Dimethylsilylamine

	$(CH_3)_2NSiH_3$	$CH_3CD_3NSiH_3$
Methyl torsions		
ν, cm^{-1} (CH_3 τ)	238.5	223.3
ν, cm^{-1} (CD_3 τ)		171.3
F,[a] cm^{-1} (CH_3 top)	5.531	5.503
F',[a] cm^{-1}	−0.0183	−0.0230
F,[a] cm^{-1} (CD_3 top)		2.863
V_3, kcal/mol (CH_3 top)	3.65	3.23
V_3, kcal/mol (CD_3 top)		3.52
	$(CH_3)_2NSiH_3$	$CH_3CD_3NSiH_3$
Silyl torsions		
ν, cm^{-1}	115	103
F,[a] cm^{-1}	3.155	3.113
V_3, kcal/mol	1.51	1.25

[a] All F numbers calculated from the structural parameters presented in ref 12.

Discussion

Of particular interest in the silyl amine compounds is the possibility of a d_π–p_π interaction between the lone pair electrons on the nitrogen and the d orbitals of the silicon atom. Certain controversy exists concerning the strength of such an interaction in dimethylsilylamine. Glidewell et al.[12] reported the Si–N bond distance in methyldisilylamine to be shorter by 0.010 ± 0.007 Å than that in trisilylamine, and the Si–N bond distance in dimethylsilylamine to be shorter by 0.011 ± 0.005 Å than that in methyldisilylamine. The authors speculated that these differences might reflect the enhancement of (p $\rightarrow$ d)π bonding between nitrogen and silicon as the number of silyl groups decreases. While we feel that such an explanation is reasonable for trisilylamine and methyldisilylamine, which are both planar, we do not think it valid to extend it to a molecule such as dimethylsilylamine whose structure is nonplanar. We tend to believe that the nonplanarity of the heavy-atom skeleton in dimethylsilylamine would not be very agreeable to sufficient p and d orbital overlap for a strong d_π–p_π interaction. Also, any significant amount of (p $\rightarrow$ d)π bonding should manifest itself in a change in the hybridization of the nitrogen atom with a resultant change in the C–N–C bond angle. That these angles are almost identical in dimethylsilylamine[12] and dimethylamine[21,22] argues against any appreciable d_π–p_π interaction. We are thus inclined to attribute the differences in the Si–N bond distance between methyldisilylamine and dimethylsilylamine to the difference in electronegativity of the nitrogen atom in the two molecules.

Goldfarb and Khare,[8] assuming a strong d_π–p_π interaction (i.e., greater double bond character, hence a greater force constant), erroneously placed the Si–N stretching frequency over 300 cm^{-1} higher than it actually occurs. We have confirmed the relatively low Si–N stretching frequency of 670 cm^{-1}, although coupling of the Si–N stretch with the C–N stretch has definitely been shown to exist in this molecule. Such a low frequency, even considering the effect of coupling, is consistent with the lack of any significant d_π–p_π interaction.

One of our major concerns is the interplay of bonded and nonbonded interactions on barriers to internal rotations. If the extent of $(p \rightarrow d)\pi$ bonding were considerable in dimethylsilylamine, then the silyl barrier would be expected to be fairly large. The silyl barrier calculated for dimethylsilylamine (1.51 kcal/mol) is within experimental error of that calculated for silylphosphine (1.512 ± 0.026 kcal/mol).[23] Such a low value for the silyl barrier in dimethylsilylamine essentially rules out the possibility of any extensive double bond character in the Si–N bond. Although one might expect a higher barrier in dimethylsilylamine than in silylphosphine due to the fact that the Si–P distance (2.249 Å)[23] is longer than the Si–N distance (1.715 Å),[12] the result is not unreasonable when the rather large C–N–Si bond angle in dimethylsilylamine (120.0°)[12] and the small H–P–Si angle in silylphosphine (92.8°)[23] are considered. The methyl barrier calculated in dimethylsilylamine (3.23 kcal/mol) is comparable to that in dimethylamine (3.007 ± 0.035 kcal/mol).[17] This is to be expected since the structural parameters of the dimethylamino moiety are nearly identical in both compounds. Also, the methyl hydrogens in dimethylsilylamine approach the silyl hydrogens to approximately the same distance that the methyl hydrogens in dimethylamine approach the hydrogen bonded to the nitrogen, 2.34 Å vs. 2.23 Å.

It is interesting to note that the apparent lack of any appreciable intramolecular d_π–p_π interaction can help account for the strong intermolecular d_π–p_π interaction observed for dimethylsilylamine in the solid phase.

Glidewell[24,25] has recently discussed the structural trends in the silyl amines in terms of steric factors. Thus, the increase in bond angles and Si–N bond distances in the series $(CH_3)_2NSiH_3$, $(SiH_3)_2NCH_3$, and $(SiH_3)_3N$ is interpreted on the basis of increasing nonbonded interactions with increasing SiH_3 substitution. While our results are in agreement with the steric model presented by Glidewell,[24,25] we by no means preclude the possibility of perhaps a very weak d_π–p_π interaction in dimethylsilylamine.

Acknowledgment. The authors gratefully acknowledge the financial support given this work by the National Aeronautics and Space Administration through Grant NGL-41-002-003. Acknowledgment is also given to the National Science Foundation for funds to purchase the Digilab FTS-15B interferometer by Grant MPS-75-06296.

References and Notes

(1) Taken in part from the thesis of P. J. Cooper, to be submitted to the Department of Chemistry in partial fulfillment of the requirements for the Ph.D. degree.
(2) D. W. Robinson, *J. Am. Chem. Soc.*, **80**, 5924 (1958).
(3) E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, **13**, 202 (1958).
(4) V. H. Kriegsmann and W. Forster, *Z. Anorg. Allg. Chem.*, **298**, 212 (1959).
(5) T. D. Goldfarb and B. N. Khare, *J. Chem. Phys.*, **46**, 3379 (1967).
(6) K. Hedberg, *J. Am. Chem. Soc.*, **77**, 6491 (1955).
(7) M. J. Buttler, D. C. McKean, R. Taylor, and L. A. Woodward, *Spectrochim. Acta*, **21**, 1379 (1965).
(8) T. D. Goldfarb and B. N. Khare, *J. Chem. Phys.*, **46**, 3384 (1967).
(9) C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, **4**, 215 (1969).
(10) D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, and J. J. Monaghan, *J. Chem. Soc. A*, 1224 (1969).
(11) M. J. Buttler and D. C. McKean, *Spectrochim. Acta*, **21**, 485 (1965).
(12) C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, **6**, 231 (1970).
(13) B. J. Aylett and J. Emsley, *J. Chem. Soc. A*, 652 (1967).
(14) S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, **76**, 4631 (1954).
(15) G. L. Ward, *Inorg. Syn.*, **11**, 159 (1968).
(16) G. Gamer and H. Wolff, *Spectrochim. Acta, Part A*, **29**, 129 (1973).
(17) J. R. Durig, M. Griffin, and P. Groner, *J. Chem. Phys.*, in press.
(18) R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *J. Am. Chem. Soc.*, **89**, 5157 (1967).
(19) D. F. Ball, M. J. Buttler, and D. C. McKean, *Spectrochim. Acta*, **21**, 451 (1965).
(20) P. Groner and J. R. Durig, *J. Chem. Phys.*, submitted for publication.
(21) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968).
(22) B. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, **64**, 2561 (1968).
(23) J. R. Durig, Y. S. Li, M. M. Chen, and J. D. Odom, *J. Mol. Spectrosc.*, **59**, 74 (1976).
(24) C. Glidewell, *Inorg. Chim. Acta Rev.*, **7**, 69 (1973).
(25) C. Glidewell, *Inorg. Chim. Acta*, **12**, 219 (1975).