INFRARED AND RAMAN SPECTRA, VIBRATIONAL ASSIGNMENT AND BARRIERS TO INTERNAL ROTATION FOR METHYLDISILYLAMINE

J. R. DURIG and P. J. COOPER*

Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208 (U.S A.)

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ABSTRACT

The Raman spectra of gaseous and liquid $(S_1H_3)_2NCH_3$ and $(S_1H_3)_2NCD_3$ have been recorded to within 10 cm⁻¹ of the exciting line. The IR spectra of $(S_1H_3)_2NCH_3$ and $(S_1H_3)_2NCD_3$ have been recorded from 80 cm⁻¹ to 3800 cm⁻¹ in the gaseous state, and from 80 cm⁻¹ to 450 cm⁻¹ in the solid state. A vibrational assignment has been made, and from the low-frequency vibrational data, an upper limit of 3.3 kcal mol⁻¹ was calculated for the barrier to internal rotation of the silyl groups, whereas a barrier of ~450 cal was calculated for internal rotation of the methyl group. It is concluded that there exists a significantly strong $d_{\pi} - p_{\pi}$ interaction in methyldisilylamine.

INTRODUCTION

The unusual stereochemistry exhibited in compounds containing silicon bonded to three-coordinate nitrogen has resulted in a certain amount of controversy concerning the specific nature of the interactions which contribute to the molecular geometry. Compounds containing three silyl groups, trisilylamine [2] or two silvl groups, disilylamine [3], methyldisilylamine [4], tetrasilylhydrazine [5] and difluoroboryldisilylamine [6] have all been shown to have planar Si_2NX skeletons. Dimethylsilylamine [7], on the other hand, has been found to possess a non-planar heavy-atom skeleton. However, the heavy-atom skeletons of both trifluorosilyldimethylamine [8] and trichlorosilvldimethylamine [8] are planar. Glidewell [9, 10] has rationalized the above geometries, as well as various other structural parameters, solely on the basis of a $d_{\pi} - p_{\pi}$ interaction between the lone electron pair on the nitrogen with the appropriate empty silicon d-orbital [9], and also entirely on the basis of non-bonded interactions [10], as well as a combination of both π -bonding and steric factors [9]. However, the evidence accumulated to date has not been able conclusively to distinguish among the various hypotheses presented.

^{*}See ref. 1.

Dimethylsilylamine has been the subject of a recent investigation in this laboratory [11]. The methyl and silyl torsional frequencies were observed in the far-IR spectrum of the gaseous phase, and the internal rotational barriers about the C—N and Si—N bonds were calculated. Consideration of the magni tudes of the methyl and silyl barriers led to the conclusion that the heavyatom skeleton is indeed non-planar and that a $d_n - p_n$ interaction is not very significant. In order to extend the available data for these interesting compounds and test the various hypotheses concerning their structure and bonding, we have initiated an investigation of methyldisilylamine, (SiH₃)₂NCH₃.

There have been two previous vibrational studies [12, 13] of methyldisilylamine. However, several of the proposed vibrational assignments are quite uncertain and unresolved differences between the two studies exist. Also, if the heavy-atom skeleton is truly planar, then the barrier to internal rotation about the C—N bond is sixfold and expected to be quite small. Should the barrier be sufficiently low, the methyl group would have essentially free rotation which should be easily discernable in the IR spectra of the vapor phase. Therefore, the vibrational spectra of $(SiH_3)_2NCH_3$ and $(SiH_3)_2NCD_3$ have been analyzed in detail and the proposed assignment is discussed together with its consequences.

EXPERIMENTAL

The samples used in the present work were prepared by the method of Emeleus and Miller [14]. Bromosilane, SiH_3Br , was reacted with either methylamine, CH_3NH_2 or methylamine- d_3 , CD_3NH_2 , depending on whether the undeuterated or deuterated methyldisilylamine was to be prepared. The bromosilane used in the above syntheses was prepared according to the method of Ward [15]. Methylamine- d_0 and methylamine- d_3 were obtained commercially (Matheson and Merck, Sharp and Dohme, respectively) and used without further purification.

Infrared spectra were recorded with a Digilab FTS-15 B Fourier transform interferometer. The spectrometer housing was purged with dry nitrogen in order to remove any atmospheric water vapor. Mid-IR spectra from 3800 cm⁻ to 450 cm⁻¹ were obtained using a germanium beamsplitter on a KBr substrate and a glower source, while far-IR spectra from 450 cm⁻¹ to 80 cm⁻¹ were obtained by using a 6.25 μ mylar beamsplitter and a high pressure Hg arc lamp source. Spectra of the gaseous phase were recorded using a 10 cm cell with KBr windows and ~ 5 torr of sample pressure in the mid-IR or polyethylene windows and ~ 400 torr of sample pressure in the far-IR. Far-IR spectra of the solid phase were obtained by condensing the samples onto a silicon plate maintained at ~ 60 K in a Cryogenics Technology Inc. Spectrim cryostat equipped with a Lake Shore Cryotronics Model DTL500 high precision temperature controller. Samples were annealed by allowing the temperature to increase slowly to \sim 120 K and then slowly recooling to 60 K. Mid-IR spectra were recorded at an effective resolution of 0.5 cm⁻¹ and far-IR spectra at an effective resolution of 1.0 cm

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 at the head was 6 W for vapor phase samples and 1 W for the liquids. A standard Cary gas cell with the multipass optics was utilized to obtain the spectra of gaseous methyldisilylamine and methyldisilylamine-d₃. Spectra of the liquids were obtained from samples in sealed glass capillaries. Frequencies measured for sharp, resolvable bands are expected to be accurate to at least $\pm 2 \text{ cm}^{-1}$ (see Fig. 1).

VIBRATIONAL ASSIGNMENT

Since methyldisilylamine adopts a planar configuration at the nitrogen atom, the barrier to internal rotation of the methyl group can be expressed in terms of a sixfold potential. Thus, the barrier is expected to be quite low. If the methyl group is assumed to be freely rotating, then the effective symmetry of the disilylamino moiety is really C_{2v} and the local symmetry of the methyl group is C_{3v} . The molecule would then exhibit 33 fundamental vibrations of which 21 can be classified as $(SiH_3)_2N$ modes and 9 as N--CH₃ modes, with the remaining 3 modes corresponding to the in-plane and outof-plane C--N-Si bends and the CH₃ torsion. The vibrations of the $(SiH_3)_2N$ moiety under C_{2v} symmetry would then break down into the following



Fig. 1: Raman spectra of (A) gaseous (SiH₃)₂NCH₃; (B) liquid (SiH₃)₂NCH₃; (C) gaseous (SiH₃)₂NCD₃; (D) liquid (SiH₃)₂NCD₃.



Fig. 2. Infrared spectra of gaseous methyldisilylamine (A) (SiH₃)₂NCH₃; (B) (SiH₃)₂NCD₃.



Fig. 3. Far-IR spectra of methyldisilylamine (A) gaseous (SiH₃)₂NCH₃; (B) solid (SiH₃)₂NCH₃; (C) gaseous (SiH₃)₂NCD₃, (D) solid (SiH₃)₂NCD₃.

symmetry species: $(7A_1 + 4A_2 + 6B_1 + 4B_2)$, while the vibrations of the N-CH₃ moiety would break down into the symmetry species: $(3A_1 + 3E)$. In addition, the degenerate methyl modes would be expected to give rise to bands in the IR spectrum of the gas phase which would exhibit resolvable

fine structure of alternating strong, weak, weak intensity characteristic of perpendicular vibrations of symmetric-top molecules with a three-fold axis of symmetry. However, if the internal rotational barrier is not sufficiently low so that the methyl group is not freely rotating at room temperature, then the molecule will belong to the symmetry group C_s , with 18 A' and 15 A" modes predicted. The symmetry plane would, in this case, be taken as being the plane perpendicular to the heavy-atom plane and coincident with the C-N bond. And, of course, there should be an absence of any fine structure associated with any of the IR bands.

In the present investigation, the barrier to internal rotation of the methyl group has been concluded to be fairly low, but not low enough so that energy levels above the potential barrier are significantly populated (see "Barriers to internal rotation" and "Discussion" Sections). Also, no discernable fine structure of any kind was observed on any of the asymmetric CH₃ modes despite the rather high resolution (0.5 cm^{-1}) used (see Fig. 2). Therefore, the fundamental vibrations were assigned on the basis of a molecular symmetry of C_s . The observed frequencies and assignments for $(SiH_3)_2NCH_3$ and $(SiH_3)_2NCD_3$ are presented in Tables 1 and 2, respectively, together with approximate descriptions of the normal modes. Although all modes are designated in the Tables in terms of C_s point group symmetry species, we will adopt the practice of Buttler et al. [12] when discussing vibrations of the $(SiH_3)_2N$ moiety and use the corresponding C_{2v} symmetry species $(A' \rightarrow A_1 \text{ or } B_2; A'' \rightarrow A_2 \text{ or } B_1)$ for clarity and the sake of comparison with other molecules containing two silyl groups bonded to a common atom.

In the case of the vibrations for the $(SiH_3)_2N$ group, consideration of the vibrational motions leads to the prediction that vibrations of symmetry class A_1 should give rise to bands of predominantly B-type IR band contours, and those of symmetry classes B_1 and B_2 should result in bands of predominantly A-type and C-type contours, respectively. The two IR bands of A-type contour at 2188 cm⁻¹ and 2148 cm⁻¹ are assigned to the B_1 antisymmetric $[\nu_{20}(A'')]$ and B_1 symmetric $[\nu_{22}(A'')]$ SiH₃ stretching modes, respectively. The presence of three polarized bands in the Raman spectra of the gas phase at 2188 cm⁻¹, 2178 cm⁻¹ and 2155 cm⁻¹ and the observation of a depolarized band at 2146 cm⁻¹, would then seem to indicate that the $A_1[\nu_3(A')]$ and $B_1[\nu_{20}(A'')]$ antisymmetric SiH₃ stretches, as well as the $A_2[\nu_{21}(A'')]$ and $B_{2}[\nu_{4}(A')]$ antisymmetric SiH₃ stretches, are accidentally degenerate, occurring at 2188 cm⁻¹ and 2178 cm⁻¹, respectively. The strong polarized Raman band at 2155 cm⁻¹ is easily assignable as the $A_1[\nu_5(A')]$ SiH₃ symmetric stretch, and the depolarized Raman band at 2146 $\rm cm^{-1}$ must then coincide with the IR band at 2148 cm⁻¹ which has been assigned as the $B_1[\nu_{22}(A'')]$ SiH₃ symmetric stretch. Some fine structure was observed in the mid-IR spectra on the high frequency side of the SiH₃ stretches, as well as on the low frequency side of the SiH₁ deformations, and is attributed to the presence of SiH₃Br.

Buttler et al. [12] tentatively assigned a band which they observed in the

TABLE 1

Observed^a IR and Raman frequencies (cm⁻¹) and assignments for (SiH₃)₂NCH₃

Raman		IR	
Gas	Liquid	Gas	Assignments
		2949 m	$\nu_1(A'), \nu_{10}(A'')$ CH ₃ antisymmetric stretches
2943 w.p	2930 w.p	2937 m	and/or overtone or combination bands of
2902 w.p	2890 w,p	2907 m	the methyl deformations
2822 m,p	2813 m,p	2823 m	$\nu_2(A')$ CH ₁ symmetric stretch
2188 m,p	2174 m,р	2188 s	$v_3(A')$, $v_{20}(A'')$ SiH ₃ antisymmetric stretch
2178 m.sh.p			$v_4(A')$, $v_{21}(A'')$ SiH ₃ antisymmetric stretch
2155 vs,p	2149 s,p		$\nu_{s}(A')$ SiH ₃ symmetric stretch
2146 w,sh,dp?		2148 vs	$\nu_{22}(A'')$ SiH ₃ symmetric stretch
2133 w,sh,dp?	2130 vw.bd.dp?		
1438 vw.bd		1960 vw	$2 \times v_{26} = 1960$
		1496	$2 \times v_{13} = 1494$
	1455 vw,bd,dp	1447 v w	$v_6(A')$, $v_{23}(A'')$ CH, antisymmetric stretch
	1433 vw,p	1418 vw	$\nu_{\tau}(A')$ CH ₃ symmetric deformation
		1222 m.sh	v _s (A') CH ₁ rock
		1202 m	v24(A") CH, rock
1095 vw,p	1088 vw.p	1095 s	v ₀ (A') CN stretch
995 v w, dp	989 vw.dp	994 s.sh	$v_{2s}(A'')$ SI-N-Si antisymmetric stretch
		980 s	v ₂₆ (A") SiH ₃ antisymmetric deformation
972 vw			v _{io} (A') SiH ₃ symmetric deformation
957 vw.p?	040 3		$v_{11}(A')$ SiH ₃ antisymmetric deformation
947 vw.dp	949 vw.ap		$v_{-1}(A')$, $v_{-1}(A'')$ SiH, antisymmetric deformation
926 vw.sh.dp?	925 vw.dp	930 s	V. (A") SiH, symmetric deformations
747 vw.p	745 vw.p	747 m	V.,(A') SiH, rock
708 vw.dp?	710 vw.sh.dp?	712 s	V. (A') SiH, rock
694 vw.dp	701 vw.dp		V10(A") SiH, rock
_	659 vw.dp?		vun(A") SiH, rock
560 m.p	562 m,p		$\nu_{is}(A')$ Si-N-Si symmetric stretch
		392 vw,sh	-
		369 w	$2 \times v_{17} = 374$
262 vw,dp	273 vw.dp	279 m (270) ^b	v _u (A") C-N-Si bend
223 vw,p?	214 vw.p?	(236) ^b	$\nu_{16}(A')$ SI-N-Si bend
189 vw	192 vw	187 s (205) ^b	v ₁₇ (A') C-N-Si bend
178 vw		(170)	$\nu_{18}(A'), \nu_{32}(A'')$ SiH ₃ torsions
		(~140 vw,bd) ^b	$v_{33}(A'')$ CH ₃ torsion

^av, very; s, strong; m, medium; w, weak; sh, shoulder; bd, broad; p, polarized; dp, depolarized. ^bFrequencies in parentheses are for the solid phase.

Raman spectrum of the liquid at 990 cm⁻¹ to the A_1 symmetric SiH₃ deformation. We too observed this band in both the gas and liquid phase Raman spectra of $(SiH_3)_2NCH_3$ and $(SiH_3)_2NCD_3$, and it appeared to be depolarized. Therefore, we prefer to assign this band to the antisymmetric Si-N-Si stretch. The two infrared bands of A-type contour at 980 cm⁻¹ and 930 cm⁻¹. in the spectrum of $(SiH_3)_2NCH_3$, shifting to 971 cm⁻¹ and 936 cm⁻¹ in the spectrum of $(SiH_3)_2NCD_3$, are assigned to the B_1 antisymmetric $[\nu_{26}(A'')]$ and B_1 symmetric $[\nu_{22}(A'')]$ SiH₃ deformations. The $A_1[\nu_{10}(A')]$ symmetric SiH₃, deformation is then assigned to the band at 972 cm⁻¹ in the Raman spectrum of the gas. It should be noted that this assignment is in disagreement with corresponding assignments in $(SiH_3)_2CH_2$ [16] and $(SiH_3)_2S$ [17], where the A_1 and B_1 symmetric deformations were assigned to the highest and lowest

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TABLE 2

Observed^a IR and Raman frequencies (cm⁻¹) and assignments for (SiH₁),NCD₃

Raman		IR	
Gas	Liquid	Gas	Assignments
2245 w.p	2233 w,p		$2 \times \nu_7 = 2248$
2188 m.p	2174 m.p	2188 s	$v_1(A')$, $v_{20}(A'')$ S1H, antisymmetric stretch
2178 m.sh.p			$\nu_1(A'), \nu_{11}(A'')$ SiH, antisymmetric stretch
2156 VS.D	2149 s.p		$\nu_{i}(A')$ SiH, symmetric stretch
2146 w.sh.do?		2148 vs	$\nu_{\rm m}(A'')$ SiH ₁ symmetric stretch
2135 w.dp?	2128 vw.sh.dp?		$\nu_1(A'), \nu_{10}(A'')$ CD, antisymmetric stretches
2066 m.p	2058 m.p	2067 m	$v_{1}(A')$ CD, symmetric stretch
		1960 vw	$v_{12} + v_{14} = 1962$
		1355 vw	$v_{1,2} + v_{2,3} = 1355$
		1293 vw	13 14
1124 vw.p	1116 vw.p	1124 s	$v_{-}(A')$ CD, symmetric deformation
		1088 s	$v_{1,1}(A'')$ CD, antisymmetric deformation
	1070 vw.sh		$\nu_{i}(A')$ CD, antisymmetric deformation
1055 vw.p	1051 vs.p	1057 s	$v_0(A')$ C—N stretch
988 vw.dp	988 vw.dp	991 s.sh	$v_{i}(A'')$ Si-N-Si antisymmetric stretch
		971 s	$\nu_{10}(A'')$ SiH ₃ antisymmetric deformation
971 vw.sh			$\nu_{10}(A')$ SiH ₃ symmetric deformation
944 vw,dp	962 vw.sh.p?		$\nu_{i}(A')$ SiH, antisymmetric deformation
	936 vw.sh	936 s	$\nu_{12}(A'')$ SiH ₁ symmetric deformation
	930 vw.dp		$v_{12}(A'), v_{22}(A'')$ SiH, antisymmetric deformations
		888 m	v.(A') CD, rock
	801 vw.dp?	808 s	$\nu_{14}(A'')$ CD, rock
738 vw.p	737 vw.p	738 m	$v_{13}(A')$ SiH ₁ rock
711 vw.dp?	715 vw,sh,dp?	707 s	$\nu_{is}(A')$ SiH ₃ rock
692 vw,dp	701 vw.dp		$v_{29}(A'')$ SiH ₃ rock
673 vw.dp	659 vw.dp		$v_{10}(A'')$ SiH ₃ rock
547 m,p	549 m,p		v ₁₅ (A') S1—N—S1 symmetric stretch
		290 vw,bd	
237 vw.dp?	244 vw,dp?	251 m (246)	$v_{31}(A'')$ C–N–Si bend
225 vw	217 vw,p?	(232) ^D	v ₁₆ (A') Si-N-Si bend
179 vw	183 vw	176 s (198)	v ₁₇ (A') C–N–Si bend
168 vw		(169) ⁶	$v_{18}(A'), v_{32}(A'')$ S1H ₃ torsions
		(~110 vw.bd) ⁰	$v_{33}(A'')$ CD ₃ torsion

*Abbreviations used: see Table 1. ^bFrequencies in parentheses are for the solid phase.

observed frequencies, respectively. Buttler et al. [12] mentioned the possibility that there may be two bands superimposed at 990 cm⁻¹, but we could find no evidence of such a superimposition of bands. Also Goldfarb and Khare [13] observed the two highest frequency bands in this region at 986 cm⁻¹ and 966 cm⁻¹ in the IR spectrum of the matrix-isolated solid, and assigned the higher frequency band to the Si-N-Si antisymmetric stretch. Therefore, we believe the present assignment of the B_1 antisymmetric SiH₃ deformation to a higher frequency than the A_1 symmetric SiH₃ deformation to be correct. The shift in frequency of the two B_1 modes upon deuteration is probably indicative of some sort of coupling with the methyl rocks. The B_2 SiH₃ symmetric rocking mode [$\nu_{14}(A')$] is assigned to the C-type IR band at 712 cm⁻¹; while the A_1 symmetric rock [$\nu_{13}(A')$] is assigned to the shoulder which appears to be a band of B-type contour at 747 cm⁻¹, shifting to 738 cm⁻¹ upon deuteration. Buttler et al. [12] assigned the two antisymmetric SiH₃ rocks to bands which they observed at 660 cm⁻¹ and 592 cm⁻¹ in the Raman spectrum of the liquid. We were unable, however, to observe the band at 592 cm⁻¹, while both bands appeared to be absent in the IR spectrum of the matrix-isolated solid [13]. On the basis of Raman spectra of the gaseous and liquid phase, we assign the two antisymmetric SiH₃ rocks to the bands at 701 cm⁻¹ and 659 cm⁻¹. The Si—N—Si symmetric stretch is then unambiguously assigned to the medium intense bands at 560 cm⁻¹ in the Raman spectra of the gas and liquid phases, which are observed to shift to 547 cm⁻¹ in the spectra of the deuterated species.

In the CH₃ stretching region, only the CH₃ symmetric stretch can be assigned with any degree of certainty. The two B-type bands at 2823 cm^{-1} and 2067 cm⁻¹ in the IR spectra of (SiH₃)₂NCH₃ and (SiH₃)₂NCD₃, respectively, are assigned to the CH_3 and CD_3 symmetric stretches. The assignment of the methyl deformations is essentially the same as that reported previously [12]. While the CH₃ symmetric deformation is generally the lowest frequency methyl deformation, the usual reversal is observed upon deuteration so that the CD₃ symmetric deformation becomes the highest frequency methyl deformation. The IR A-type band at 1202 cm⁻¹ is assigned to the CH₃ antisymmetric rocking mode, while a shoulder on its high frequency side at 1222 cm^{-1} , which appears to represent a band of B-type contour, is assigned to the symmetric CH₃ rocking mode. The C-N stretch is assigned to the polarized Raman band at 1095 cm⁻¹, which shifts to 1055 cm⁻¹ upon deuteration. This unusually large downward shift in frequency is attributed to coupling of the C-N stretch with the CD₃ symmetric deformation in the deuterated species. The shift in frequency exhibited by the A_1 symmetric SiH₃ rock $[\nu_{13}(A')]$ upon deuteration is then most likely a result of its being coupled to some extent with the Si-N-Si symmetric stretch, which also exhibits a downward shift probably due to coupling with the C-N stretch.

Three skeletal deformations are expected for methyldisilylamine: two modes in which the planarity of the heavy-atom skeleton is preserved and one mode in which it is destroyed. We have designated the two modes which maintain planarity as corresponding to, primarily, an A' Si-N-Si bending motion and an A" C-N-Si bending motion, while the remaining mode is designated as an A' C-N-Si bend. The A' Si-N-Si bend is easily assigned to the Raman band in the spectrum of the gas at 223 cm^{-1} which appears to be polarized, and which is observed to not shift significantly upon deuteration. Assignment of the remaining two modes, however, proved to be somewhat more difficult. In addition to the band at 223 cm⁻¹ in the Raman spectrum of gaseous $(SiH_3)_2NCH_3$, bands were also observed at 262 and 189 cm⁻¹. In the IR spectrum of the gas, however, bands were observed at 279 and 187 cm⁻¹ (Fig. 3). The IR band at 187 cm⁻¹ is easily recognized as corresponding to the Raman band at 189 cm⁻¹. At first it was believed that the Raman band at 262 cm⁻¹ and the IR band at 279 cm⁻¹ corresponded to two different fundamental modes, there being an understandable reluctance to assign them to

the same mode because of the rather large disparity in frequency. However, analysis of the far-IR spectrum of the solid phase revealed the existence of only one band at 270 cm⁻¹, with the closest band to it being at 236 cm⁻¹. This band at 236 cm⁻¹ must correspond to the Raman band in the spectrum of the gas at 223 cm⁻¹, which has already been assigned to the S1-N-Si bend. Therefore, the existence of only one band at 270 cm⁻¹ in the IR spectrum of the solid would seem to indicate that the band at 262 cm^{-1} in the Raman spectrum of the gas and the band at 279 cm^{-1} in the IR spectrum of the gas do indeed correspond to the same vibrational mode. We believe that the explanation for the large difference between the IR and Raman frequencies lies in the possibility that some of the sample adsorbed onto the polyethylene windows, which were used in obtaining the far-IR spectra of the gas. It should be noted that all the bands observed in the far-IR spectra of the gas are relatively broad and lack distinct band contours, as might be expected in such a situation. Support for the above interpretation is presented by the observation of the same effect in the spectra of the deuterated species. Thus, we assign the A'' C–N–Si bend to the band in the Raman spectrum of the gas at 262 cm^{-1} , shifting to 270 cm⁻¹ in the solid. In the Raman spectrum of the gas and IR spectrum of the solid of the deuterated species, this band occurs at 237 cm⁻¹ and 246 cm⁻¹, respectively. The A' C-N-Si bend is assigned to the gas phase Raman band at 189 cm⁻¹, shifting to 179 cm⁻¹ upon deuteration. The corresponding bands in the solid phase spectra of the light and heavy species occur at 205 cm^{-1} and 198 cm^{-1} , respectively.

TORSIONAL ASSIGNMENTS AND BARRIERS TO INTERNAL ROTATION

Three torsional vibrations are predicted for a molecule such as methyldisilylamine. The torsional oscillations of the two silyl groups should give rise to one A' and one A" mode, while the methyl torsion will account for another A" mode. The A' and A" SiH₃ torsions are both assigned to the band in the Raman spectrum of the gas at 178 cm⁻¹, shifting to 168 cm⁻¹ in the deuterated compound. In the solid phase this band is observed at 170 cm⁻¹ in the light species and 169 cm⁻¹ in the heavy. It appears then that the two SiH₃ torsions are degenerate or, at least, very nearly so. On the assumption that there is no interaction between the two tops, a periodic barrier of 3.3 kcal mol⁻¹ is calculated as an upper limit, using a torsional frequency of 170 cm⁻¹ and an F value of 3.04 cm⁻¹, calculated from structural parameters obtained in a previous investigation [4].

In the far-IR spectrum of solid $(SiH_3)_2NCD_3$ there appears to be a very weak, broad band at approximately 110 cm^{-1} . We have assigned this band to the CD₃ torsion. In the IR spectrum of $(SiH_3)_2NCH_3$ there appears to be a very weak, very broad absorption centered at ~140 cm⁻¹, approximately where the CH₃ torsion is expected, but it is extremely ill-defined. The assignment of the CH₃ and CD₃ torsions should be considered very tentative. Using an F value of 2.95 cm⁻¹ and a torsional frequency of 110 cm⁻¹, the six-fold CD₃ barrier is calculated to be ~450 cal in the solid phase.

DISCUSSION

Several hypotheses have been advanced to account for the stereochemistries exhibited in various silvlamine compounds. The planarity at the nitrogenatom in trisilylamine [2], disilylamine [3] and methyldisilylamine [4], has most popularly been attributed to the existence of a strong $d_{\pi} - p_{\pi}$ interaction involving the unshared electron pair in a nitrogen 2p orbital and an appropriate silicon 3d orbital [18]. Thus, it would appear that the presence of two or three silicon atoms bonded to nitrogen is sufficient to confer planarity upon the nitrogen atom, while a single silicon atom is insufficient [9], as evidenced by the non-planarity of dimethylsilylamine [7]. The planarity of trifluorosilyldimethylamine [8] and trichlorosilyldimethylamine [8] is then rationalized in terms of a *d*-orbital contraction [19]. Alternatively, Glidewell [10] discussed the geometries of first row atoms strictly in terms of non-bonded interactions, dividing closed shell molecules into three separate categories in which, respectively, inter-electron repulsions dominate, electronic and nuclear terms are in balance, and inter-nuclear repulsions dominate. Still another hypothesis [9] suggests that steric factors are the primary determinants of the geometries observed in the silylamines, and that $(p \rightarrow d)\pi$ bonding is then enhanced in those cases in which planarity at the nitrogen atom occurs.

The barrier calculated here for methyldisilylamine (3.3 kcal mol⁻¹) is substantially greater than that found for dimethylsilylamine (1.51 kcal mol⁻¹) [11], despite the longer Si—N bond distance in methyldisilylamine (1.726 Å vs. 1.715 Å) [4, 7]. We believe that the magnitude of the silyl barrier in methyldisilylamine is indicative of a relatively strong $d_{\pi} - p_{\pi}$ interaction. Therefore, on the basis of the evidence presented here and on evidence from photoelectron spectroscopy [20, 21] for the existence of $(p \rightarrow d)\pi$ bonding, it is concluded that any hypothesis relying solely on steric factors is not valid. However, it is still impossible to establish whether the $d_{\pi} - p_{\pi}$ interaction is the cause of the planarity in those silylamines exhibiting planar heavy-atom skeletons or if it is only a consequence of a planar geometry which is caused by steric interactions.

The possible consequences of a freely rotating methyl group in methyldisilylamine in terms of selection rules and effects on the IR spectra have been discussed (see "Vibrational assignment" Section). If the sixfold barrier of ~450 cal mol⁻¹ calculated for the methyl group is correct, then the absence of any observable fine structure due to free internal rotation is explained by the fact that at least the ground and first excited vibrational states of the methyl torsion would lie below the potential barrier and that at room temperature, therefore, the energy levels above the potential well corresponding to free rotation would then be largely inaccessible to the vast majority of the molecular population. Qualitatively, a value of 450 cal mol⁻¹ seems to us to be quite high for a sixfold barrier. For example, V₆ was found to equal only 13.94 cal mol⁻¹ in toluene [22]. However, for N-methylpyrrole [23]. which is a much closer analogue to methyldisilylamine than toluene, $V_6 = 128.9$ cal mol⁻¹ ($V_{12} = 47.7$ cal mol⁻¹), which is substantially higher than the V_6 term found in toluene [22] and is probably a result of the shorter C—N bond compared to the C—C bond. We feel that the higher methyl barrier in methyl-disilylamine may be a result of the increased number of non-bonded inter-actions in methyldisilylamine as compared to N-methylpyrrole.

We have hitherto neglected the possibility that the heavy-atom skeleton may be non-planar within the experimental error of the previous electron diffraction study [4]. In such a case the methyl barrier would be threefold and expected to be much higher. Using the same data as with the calculations for the V_6 potential, we estimate a threefold barrier of ~1.5 kcal mol⁻¹, which does not seem too unreasonable. However, in light of the rather high SiH_3 barrier which has been taken as evidence of a fairly strong $d_{\pi} - p_{\pi}$ interaction, we believe the heavy-atom skeleton to be truly planar and, hence, the methyl torsion to be governed by a sixfold potential. It should be stressed that our belief in a truly planar structure is based more on intuitive feeling than on the available experimental data. The barrier of 450 cal mol^{-1} was obtained for the molecule in the solid phase. Since such barriers are generally higher than those obtained from gas phase data, we might reasonably expect the gas phase methyl barrier in (SiH₃)₂NCH₃ to be less than 450 cal, in which case we we probably should have observed evidence for free rotation of the methyl group if the heavy-atom skeleton were indeed planar. A comparison of the SiH₃ torsional barriers between methyldisilylamine and trisilylamine could be extremely useful at this stage, but, unfortunately, such data for the trisilylamine compound is not available.

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