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Microwave, Infrared and Raman Spectra, Structure, Dipole Moment, and Vibrational Assignment of Dimethylcyanosilane

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The microwave spectrum of dimethylcyanosilane has been investigated in the region between 18.0 and 40.0 GHz. Only A-type transitions were observed. The R-branch assignments have been made for the ground and three excited vibrational states. With reasonable assumptions made for the structural parameters of the dimethylsilyl moiety and the nitrile bond, the following structural parameters were obtained: $r(\mathrm{Si{-}CN}) = 1.840$ Å, $\angle(\mathrm{CSiC}) = 112.25°$, and an angle between the CSiC plane and the $\mathrm{Si{-}C{\equiv}N}$ bond of 123.97°. The dipole moment components were determined from the Stark effect to be $\mu_a = 3.65 \pm 0.1$ D and $\mu_c = 1.04 \pm 0.1$ D with a total dipole moment of 3.8 ± 0.1 D. The Raman spectra of dimethylcyanosilane have been studied to within 50 $\mathrm{cm^{-1}}$ of the exciting line in all three physical states. The infrared spectra of dimethylcyanosilane have been studied from 200 to 4000 $\mathrm{cm^{-1}}$ in the gaseous state and from 95 to 4000 $\mathrm{cm^{-1}}$ in the solid state. A vibrational assignment has been made, and from the low-frequency vibrational data, an upper limit of 2.8 kcal/mol was obtained for the barrier to internal rotation of the methyl groups.

Introduction

Recently, in this laboratory, microwave studies were completed on dimethylcyanamide, $(\mathrm{CH_3})_2\mathrm{NCN}$,[2] dimethylcyanophosphine, $(\mathrm{CH_3})_2\mathrm{PCN}$,[3] and isopropyl cyanide, $(\mathrm{CH_3})_2\mathrm{CHCN}$[4] in order to determine the effects of the strong electron-withdrawing group CN on the molecular structure. In addition, there exists the possibility of bonding through the nitrogen of the CN group to form the isocyanide compound. A recent investigation of trimethylcyanosilane, $(\mathrm{CH_3})_3\mathrm{SiCN}$, by Durig et al.[5] established the presence of an appreciable amount of the isocyanide at ambient temperature for this sample. As an extension of this work and as a continuation of our studies on the spectra and structure of silicon-containing compounds in general, a microwave investigation of dimethylcyanosilane has been undertaken.

The infrared and Raman spectra of the dimethylhalosilanes $(\mathrm{CH_3})_2\mathrm{SiHX}$ (X = F, Cl, Br, I) have been analyzed in this laboratory,[6] and the torsional barrier heights for each compound reported. Therefore, in order to extend this series, infrared and Raman data were obtained for dimethylcyanosilane and a complete vibrational assignment is presented.

Experimental Section

The sample used in the present work was prepared by the following method. Samples of $(\mathrm{CH_3})_2\mathrm{SiHCl}$ (12 g) and AgCN (6.7 g) were combined together with 70 ml of anhydrous diethyl ether in a round-bottomed flask which was attached to a high-vacuum system employing greaseless stopcocks. The mixture was then stirred at room temperature under an inert atmosphere for 36 hr. Materials volatile at −45° were allowed to distil from the reaction vessel for a period of 6 hr. Fractionation of the involatile materials yielded crude $(\mathrm{CH_3})_2\mathrm{SiHCN}$ in a trap at −78°. Pure $(\mathrm{CH_3})_2\mathrm{SiHCN}$ was obtained using a low-temperature sublimation column. The yield was 48% based on the initial amount of AgCN.

The rotational spectrum of dimethylcyanosilane was recorded in the frequency range 18.0–40.0 GHz using a Hewlett-Packard Model 8460A MRR spectrometer with 33.33-kHz square-wave Stark modulation. The Stark cell was maintained at Dry Ice temperature for all measurements except those of relative intensity, which were performed at room temperature. Sample pressure was held to about 20 μ. The accuracy in the line frequency measurement is estimated to be better than 0.2 MHz. The sample was observed to decompose in the wave guide even at Dry Ice temperature, requiring the sample to be renewed approximately every 20 min.

The Raman spectra were recorded with a Cary Model 82 Raman spectrometer equipped with a Spectra-Physics Model 171 argon ion laser. The 5145-Å line was used and the laser power was varied from 1 to 4 W at the head depending on the physical state under investigation. A standard Cary gas cell with the multipass optics was utilized to obtain the spectrum of gaseous dimethylcyanosilane, while a simple capillary tube was employed to obtain the spectrum of the liquid. The spectrum of solid $(\mathrm{CH_3})_2\mathrm{SiHCN}$ was recorded by subliming the sample onto a standard cold cell maintained at liquid nitrogen temperatures.

The infrared spectra of dimethylcyanosilane between 200 and 4000 $\mathrm{cm^{-1}}$ were recorded with a Perkin-Elmer Model 621 spectrophotometer. A Beckman IR-11 spectrophotometer was used to record the infrared spectra between 33 and 300 $\mathrm{cm^{-1}}$. Both instruments were purged with dry air and calibrated with standard gases.[7] A 25-cm cell equipped with cesium iodide windows was used in recording the

Table I. Rotational Transitions (MHz) of Dimethylcyanosilane in the $v = 0$ and $v_i = 1$ Vibrational States

	$v = 0$		$v_\alpha = 1$		$v_\beta = 1$		$v_\gamma = 1$	
Transition	ν(obsd)	$\Delta\nu$(obsd − calcd)[a]	ν(obsd)	$\Delta\nu$(obsd − calcd)[a]	ν(obsd)	$\Delta\nu$(obsd − calcd)[a]	ν(obsd)	$\Delta\nu$(obsd − calcd)[a]
$4_{04} \leftarrow 3_{03}$	18,485.03	0.46						
$4_{13} \leftarrow 3_{12}$	20,885.67	0.31						
$5_{05} \leftarrow 4_{04}$	22,602.23	0.17						
$6_{16} \leftarrow 5_{15}$	26,522.94	0.16					26,571.13	0.14
$6_{06} \leftarrow 5_{05}$	26,701.89	0.14	26,697.31	0.08			26,732.94	−0.11
$6_{25} \leftarrow 5_{24}$	28,934.82	0.10	28,965.82	0.03	28,990.88	0.12		
$6_{15} \leftarrow 5_{14}$	30,211.34	0.26	30,231.89	0.20	30,265.42	0.09		
$7_{17} \leftarrow 6_{16}$	30,738.32	0.13			30,771.66	0.02		
$7_{06} \leftarrow 6_{06}$	30,824.96	−0.09						
$6_{24} \leftarrow 5_{23}$	31.757.73	0.01	31,840.94	0.11	31,854.93	0.11	31,923.13	−0.19
$7_{26} \leftarrow 6_{25}$	33,427.70	−0.11	33,454.60	−0.13	33,486.34	−0.12		
$7_{16} \leftarrow 6_{15}$	34,428.59	0.07	34,432.83	−0.08	34,476.94	−0.06	34,452.52	−0.05
$7_{25} \leftarrow 6_{24}$	36,912.78	−0.16	36,989.62	−0.11	37,013.50	−0.15	37,064.57	0.21
$8_{27} \leftarrow 7_{26}$	37,817.16	−0.34						
$8_{17} \leftarrow 7_{16}$	38,481.37	−0.27						
$9_{19} \leftarrow 8_{18}$	39,112.74	−0.16						

[a] Calculated from the rotational constants given in Table II.

Table II. Rotational Constants (MHz) and Moments of Inertia (amu A^2)[a] of Dimethylcyanosilane at $v = 0$ and $v_i = 1$ States

	$v = 0$	$v_\alpha = 1$	$v_\beta = 1$	$v_\gamma = 1$
A	5311.22 ± 0.23	5291.62 ± 0.25	5312.26 ± 0.22	5244.22 ± 0.37
B	2845.97 ± 0.02	2855.28 ± 0.02	2856.17 ± 0.02	2862.93 ± 0.02
C	2086.17 ± 0.01	2085.66 ± 0.02	2087.86 ± 0.02	2089.84 ± 0.02
κ	−0.528811	−0.519883	−0.523441	−0.509831
I_a	95.155	95.508	95.137	96.371
I_b	177.581	177.002	176.947	176.529
I_c	242.258	242.317	242.062	241.832

[a] Conversion factor: 505,391 MHz amu A^2.

spectrum of the gas. To obtain the low-temperature spectrum, the sample was slowly sublimed onto either a cesium iodide or a silicon support plate maintained at liquid nitrogen temperatures.

Microwave Spectrum and Results

Preliminary spectral predictions for dimethylcyanosilane were made by using the structure of silyl cyanide[8] combined with the dimethylsilyl group parameters of dimethylsilane.[9] These calculations indicated that dimethylcyanosilane should have the principal axes *a* and *c* lying on the molecular symmetry plane. The angle between the *a* axis and the C≡N bond should be sufficiently small so that strong A-type transitions are expected provided that the total dipole moment lies mainly along the C≡N bond. A projection of the molecule in the principal axis system is given in Figure 1.

The R-band microwave spectrum of dimethylcyanosilane is presented in Figure 2. The observed rotational transitions were assigned mainly on the basis of the rigid-rotor model fit. Around each ground-state line there are many weaker satellite lines which arise from molecules in excited vibrational states of the low-frequency modes.

In Table I are listed the transitional frequencies for the ground and three excited vibrational states and the differences between the observed and calculated frequencies. The observed rotational constants, moments of inertia, and asymmetry parameters for the ground and three excited vibrational states are given in Table II. The relative intensities of the three excited-state satellites with respect to the ground-state line intensity were measured for several transitions. The calculated energy level differences between the ground and excited vibrational states were $\nu_\alpha = 145 \pm 50$ cm^{-1}, $\nu_\beta = 273 \pm 30$ cm^{-1}, and $\nu_\gamma = 303 \pm 15$ cm^{-1}. The quoted errors represent the consistencies of the relative intensity measurements of several transitions.

A complete structural determination is not possible from the available microwave data. However, some quantitative values for the Si—CN bond distance and the angle between the CSiC plane and the Si—C≡N bond can be obtained by assuming reasonable values for the dimethylsilyl parameters and the C≡N bond distance. The assumed parameters were r(Si—C) = 1.867 Å, r(Si—H) = 1.483 Å, r(C—H) = 1.095 Å, r(C≡N) = 1.156 Å, ∠(HSiC) = 109.16°, ∠(HCH) = 108.0°, and ∠(SiCN) = 180°. The methyl groups are assumed to be symmetrical. A linear regression structure was calculated, using the experimental rotational constants, by allowing the Si—CN bond distance and the internal angle between the Si—C≡N bond and the CSiC plane to vary.

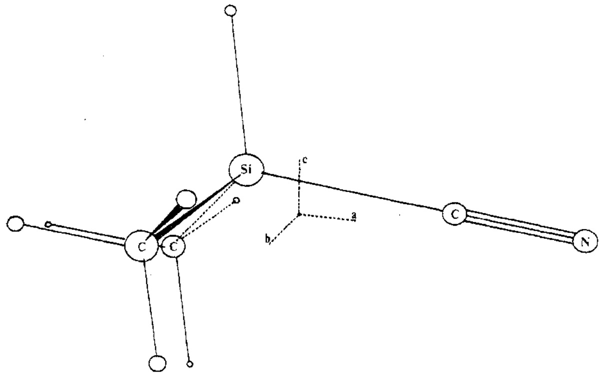

Figure 1. Projection of (CH$_3$)$_2$SiHCN rotated 5° out of its *ac* plane of symmetry.

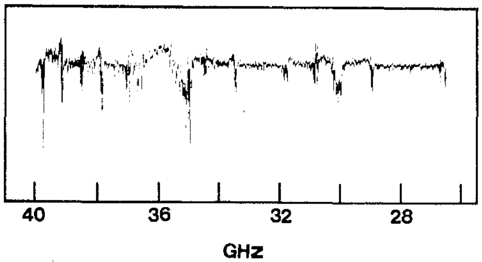

Figure 2. Microwave spectrum of dimethylcyanosilane.

Table III. Observed Fundamental Frequencies (cm^{-1}) and Assignments for Dimethylcyanosilane[a]

Raman			Infrared		
Gas	Liquid	Solid	Gas	Solid	Assignment
2978 m, dp	2977 m, dp	2987 s	2983 m	2988 sh	ν_1 (a'), ν_{18} (a'') CH_3 antisym str
		2977 s		2977 m	ν_2 (a'), ν_{19} (a'') CH_3 antisym str
2917 m, p	2912 s, p	2912 s	2918 w	2915 w	ν_3 (a'), ν_{20} (a'') CH_3 sym str
		2222 s		2218 s	$\nu_{21} + \nu_{25} = 2223$ (a')
2183 s, p	2190 s, p	2188 vs	2185 s	2191 s	ν_4 (a') C≡N str
2174 m, p	2175 sh, p				ν_5 (a') Si–H str
		1441 w		1447 w	ν_{21} (a'') CH_3 antisym def
	1421 w, p?	1422 w	1421 w	1425 m	ν_6 (a')
		1408 w		1407 m	ν_{22} (a'') CH_3 antisym def
	1405 w, p?	1398 w		1398 m	ν_7 (a')
		1262 w		1263 sh	ν_8 (a') CH_3 sym def
1268 w, p?	1258 w, p	1253 w	1264 m	1248 s	ν_{23} (a'')
	898 w, dp	889 w	887 s	889 s	ν_{24} (a'') CH_3 rock
	879 w, p?	870 w		868 s	ν_9 (a') CH_3 rock
	847 w, p	851 vw	850 m	846 s	ν_{10} (a') Si–H in-plane bend
	782 w, dp	782 m	782 m	782 s	ν_{25} (a'') Si–C antisym str
741 w, p	743 w, p	756 m	741 m	749 s	ν_{11} (a') Si–C sym str
669 m, p	669 s, p	672 s	670 w	672 s	ν_{12} (a'), ν_{26} (a'') CH_3 rocks
	637 w, dp	639 m	634 w	633 s	ν_{27} (a'') Si–H out-of-plane bend
560 m, p	550 m, p	543 w	562 m	536 s	ν_{13} (a') Si–CN str
337 w	345 w, p	352 w	342 w	352 w	ν_{14} (a') C–Si–C(N) bend
	252 vw, p			244 w	ν_{15} (a') Si–C_2 def
	222 m, dp	228 m		227 vw	ν_{28} (a'') Si–C≡N bend
	208 sh, dp	206 vw			ν_{16} (a'), ν_{29} (a'') CH_3 torsion
	176 m, p?	180 m			ν_{17} (a') Si–C≡N bend
	138 m, dp	144 m		150 s	ν_{30} (a'') C–Si–C(N) bend
		117 m			Lattice mode

[a] Abbreviations used w, weak; m, medium; s, strong; v, very; sh, shoulder; p, polarized; dp, depolarized.

Several calculations were carried out assuming different values in the range 105–117° for the CSiC bond angle in the dimethylsilyl moiety. Minimization of the root-sum-square of the deviations between the observed and calculated moments of inertia, $[\sum_g(\Delta I_g)^2]^{1/2}$, $g = a, b, c$, yielded the following results. The optimum value for the CSiC bond angle was found to be 112.25°. The Si–CN bond distance and the internal angle were calculated to be 1.840 Å and 123.97°, respectively.

Similar calculations were carried out using an assumed Si–C bond distance of 1.880 Å. The results are $\angle$(CSiC) = 111.10°, r(Si–CN) = 1.817 Å, and an internal angle of 125.12°. Considering the fairly large value assumed for the Si–C bond distance in the second case, the corresponding results in these two sets do not differ appreciably. Such agreement lends confidence in the obtained results and appears to indicate a fairly small uncertainty in the calculated structural parameters. However, due to the lack of data for any isotropically substituted species and the large number of assumed parameters used, meaningful error limits could not be assigned to the calculated structural parameters.

Dipole Moment

The electric dipole moment of dimethylcyanosilane has been determined by measurement of the quadratic Stark effect for the $|M| = 2$ components of the $4_{04} \leftarrow 3_{03}$ and $4_{13} \leftarrow 3_{12}$ transitions, the $|M| = 0$ component of the $5_{05} \leftarrow 4_{04}$ transition, and the $|M| = 1$ component of the $6_{15} \leftarrow 5_{14}$ transition. The electric field was calibrated by using the $J = 3 \leftarrow 2$, $|M| = 2$, transition of OCS with its dipole moment taken to be 0.71521 D.[10] The components of the electric dipole moment along the a and c axes and the estimated error limits are 3.65 ± 0.1 and 1.04 ± 0.1 D, respectively. The total dipole moment is 3.8 ± 0.1 D.

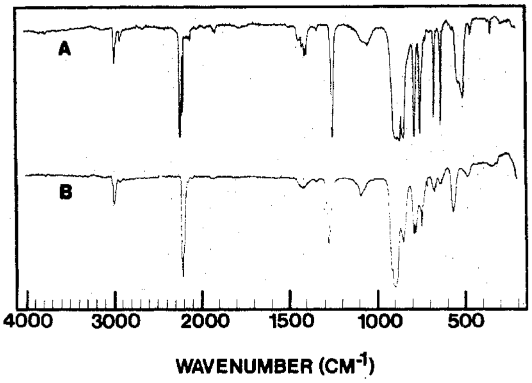

Figure 3. Infrared spectra of dimethylcyanosilane: (A) annealed solid at −195°; (B) gas, room temperature, 2 mmHg.

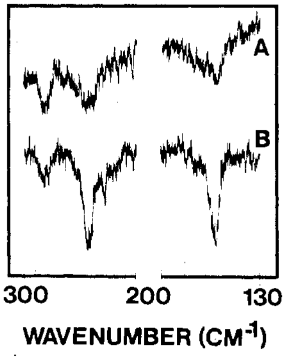

Figure 4. Far-infrared spectrum of dimethylcyanosilane: (A) background; (B) annealed solid at −195°.

Vibrational Spectra and Results

The infrared and Raman spectra of $(CH_3)_2SiHCN$ are shown in Figures 3–5. The molecule belongs to the symmetry group C_s, and from group theory, one predicts the molecule to have 17 a' and 13 a'' modes. The CH_3 motions should give rise to 18 of the fundamental modes, the Si–H motions, to another 3, and motions of the skeletal framework should account for the remaining 9 vibrations. The complete vibrational assignment is presented in Table III.

The two a' and two a'' antisymmetric CH_3 stretches are assigned to the bands centered at 2987 and 2977 cm^{-1} in the

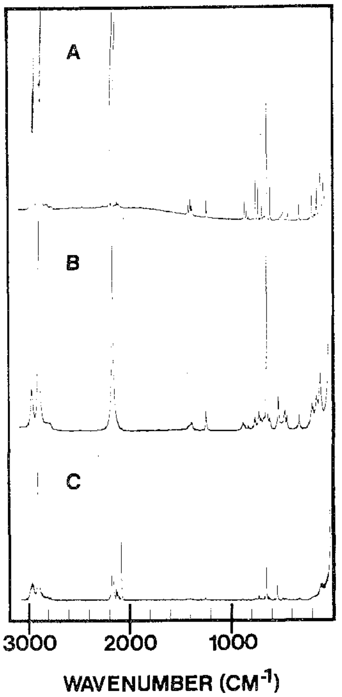

Figure 5. Raman spectra of dimethylcyanosilane: (A) annealed solid at −195°, spectral bandwidth 3 cm^{-1}; (B) liquid, room temperature, spectral bandwidth 1 cm^{-1}; (C) gas, room temperature, spectral bandwidth 5 cm^{-1}.

Raman spectrum of the solid. The a' and a'' symmetric CH$_3$ stretches are assigned to the Raman line at 2912 cm^{-1}. Distinguishing between the Si—H stretch and the C$\equiv$N stretch provided some difficulty. Both stretches are expected to give rise to fairly intense infrared and Raman bands. The assignment was further complicated by the appearance of several relatively intense bands in the Si—H and C$\equiv$N stretching region in both the infrared and Raman spectra. In trimethylcyanosilane, Booth and Frankiss[11] observed the line corresponding to the C$\equiv$N stretch at 2190 cm^{-1} in the liquid phase. Since one would expect the C$\equiv$N stretching frequency to be relatively insensitive to the substitution of a hydrogen for one of the methyl groups, the band at 2190 cm^{-1} in the Raman spectrum of liquid dimethylcyanosilane is assigned to the C$\equiv$N stretch. The Si—H stretch can then be assigned to the Raman band at 2175 cm^{-1}, consistent with the observation that the Si—H stretching frequencies for the dimethylhalosilanes are all within the range 2155–2172 cm^{-1} and that the C—H stretching frequency in isopropyl cyanide (2888 cm^{-1}) is not substantially different from those reported in the isopropyl halides (2875–2882 cm^{-1}).[12] The intense Raman line which appears at 2222 cm^{-1} only in the spectrum of the annealed solid is assigned as a combination between one of the CH$_3$ antisymmetric deformations and the Si—C antisymmetric stretch. The rather large frequency difference, 34 cm^{-1}, between this band and the closest band to it, that assigned to the C$\equiv$N stretch, makes it unlikely that it is a consequence of factor group splitting.

The antisymmetric CH$_3$ deformations are assigned to the Raman lines at 1441, 1422, 1408, and 1398 cm^{-1}. The a' and a'' symmetric deformations are assigned to the Raman lines at 1262 and 1253 cm^{-1}, respectively. The two Raman bands centered at 889 and 870 cm^{-1} are assigned to the a'' and a' CH$_3$ rocks, respectively. The in-plane Si–H bend is assigned to the Raman line at 847 cm^{-1}. The Raman line at 782 cm^{-1} is assigned to the Si–C antisymmetric stretch, while the Si–C symmetric stretch is assigned to the Raman line at 743 cm^{-1}. The remaining a' and a'' CH$_3$ rocks are assigned to the intense Raman band at 669 cm^{-1}. Although the methyl rocks are split more than is generally assumed, these splittings are, however, consistent with those observed in propane[13] and the dimethylhalosilanes.[6] The out-of-plane Si–H bending motion is assigned to the Raman line at 637 cm^{-1}. The Si–C(N) stretch gives rise to a polarized Raman line at 550 cm^{-1}.

The polarized Raman line at 345 cm^{-1} is assigned to the a' C—Si—C(N) bend. The Si—C$_2$ deformation is assigned to the polarized Raman line at 252 cm^{-1}. The out-of-plane (a'') and in-plane (a') Si—C$\equiv$N bending modes are assigned to the Raman lines at 228 and 180 cm^{-1}, respectively. The very weak band centered at 206 cm^{-1} in the Raman spectrum of the solid is tentatively assigned to the two methyl torsions. The a'' C—Si—C(N) bend is then assigned to the depolarized Raman line at 138 cm^{-1}. While the splitting between the a' and a'' C—Si—C(N) bending modes may seem unusually large, it is, however, consistent with the splitting of the two corresponding modes in isopropyl cyanide.[12]

Discussion

The results of the structural calculations indicate that the angle between the CSiC plane and the Si—C$\equiv$N linkage is not very sensitive to changes in the CSiC angle. Also as one increases the CSiC angle, the Si–CN distance increases smoothly to compensate for this change. The Si–CN bond distance (1.840 Å) obtained for dimethylcyanosilane is shorter than the normal Si–C distance (1.867 Å) in dimethylsilane[9] by about the same amount that the C–CN bond distance (1.501 Å) in isopropyl cyanide[4] is shorter than the normal C–C distance (1.526 Å) in propane.[14] Therefore, such a decrease in bond distance is better accounted for by the fact that the Si–CN bond is sp^2–sp^3 hybridized, and, thus, expected to be somewhat shorter than the normal Si–C bond which is sp^3–sp^3 hybridized, than to any explanation involving d_π–p_π delocalization.

It has previously been observed[4] that the dipole moment increases in the series methyl, ethyl, isopropyl, *tert*-butyl cyanide. Such an increase in the dipole moment with increased methyl substitution has also been observed in the corresponding halide series and attributed to the inductive effect. The dipole moment of silyl cyanide[8] has been found to be comparable with that of methyl cyanide (3.92 ± 0.06 D).[15] The dipole moment of 3.8 ± 0.1 D obtained for dimethylcyanosilane appears then to be essentially the same, within experimental error, as that of silyl cyanide. This would seem to indicate that a methyl inductive effect is negligible or at least not quite as important a factor in the cyanosilanes. This is somewhat reasonable if one considers the longer bond distances over which any inductive effect would have to operate in the silicon compounds. Whether or not the same holds true in the case of substitution by larger alkyl groups, which might be expected to exert a stronger inductive effect, one cannot say in the absence of any data for such compounds. It would also be interesting to determine if the same situation exists for the corresponding halosilanes, but, so far, dipole moment data are also lacking for these compounds.

The excited vibrational states $\nu_\alpha = 145 \pm 50$ cm^{-1}, $\nu_\beta = 273 \pm 30$ cm^{-1}, and $\nu_\gamma = 303 \pm 15$ cm^{-1} which were determined from the microwave relative intensity study cannot be unambiguously assigned. As stated previously in the Experimental Section, the sample was observed to decompose in the wave guide even at Dry Ice temperature. At room temperature, sample decomposition was even faster, thus making fairly consistent relative intensity measurements unobtainable. The ν_α mode is most likely an excited state of either the a'' C—Si—C(N) or a' Si—C$\equiv$N bending mode. The ν_β mode is probably an excited state of the Si—C$_2$ deformation, and ν_γ is probably an excited state of the a' C—Si—C(N) bending mode. Attempts to assign the rotational transitions in the torsionally excited states were unsuccessful.

The existence of small amounts of trimethylisocyanosilane in equilibrium with the cyano isomer has already been established,[5,11] and similar equilibria have been found for the triethyl and triisopropyl compounds.[16] Recently, evidence has also been presented[17] for the existence of approximately 5% of the isocyanide in trimethylcyanogermane. Booth and Frankiss[11] have observed the N=C stretch in trimethylisocyanosilane at 2095 cm^{-1}. Therefore, one would expect that the N=C stretch in dimethylisocyanosilane should give rise to a band at approximately the same frequency. A weak band at 2097 cm^{-1} was observed in the infrared spectrum of gaseous dimethylcyanosilane that had counterparts in the gas- and liquid-phase Raman spectra at 2094 and 2089 cm^{-1}, respectively. However, a band at 712 cm^{-1} was observed in the infrared spectrum of the gas, and a band at 3308 cm^{-1} was observed in the Raman spectrum of the gas. Furthermore, the relative intensity of the gas-phase Raman bands at 2094 and 3308 cm^{-1} was observed to increase with time. There also appeared in the Raman spectrum of the gas a series of equally spaced lines of low intensity extending from the exciting line for about 130 cm^{-1}. Calculations indicated that these lines were assignable to the rotational transitions of HCN. Therefore, the bands at 3308 and 712 cm^{-1} obviously correspond to the C—H stretch and H—C≡N bend in HCN, which must be a decomposition product of dimethylcyanosilane. The bands observed around 2095 cm^{-1} in the infrared and Raman spectra must, therefore, be assigned to the C≡N stretch in HCN, rather than to the N=C stretch in dimethylisocyanosilane. None of the three fundamental frequencies of HCN were observed in the spectra of the solid, which is as expected, since decomposition should be negligible at such low temperatures. Also, no evidence was found for the existence of the isocyanide during the course of the microwave investigation. However, our results cannot, of course, exclude the presence of the isocyano isomer in very low concentration.

We are currently interested in the barriers to internal rotation of methyl groups in organosilanes. Unfortunately, no barrier information was available from the microwave study on dimethylcyanosilane. Barrier calculations[18] were carried out by assuming that the interaction between the two tops is zero. It was observed for the dimethyldihalosilanes[6] that the two torsions are essentially degenerate. This is in contrast to the isopropyl halides[19] where considerable coupling between the two tops was observed. The assumption of zero interaction between the two tops in dimethylcyanosilane is reasonable on the basis of the increased distance between the two tops and is further supported by earlier observations for the trimethylsilanes.[20] Using an F value of 5.42 cm^{-1} calculated from the proposed structure and a torsional frequency of 206 cm^{-1} one calculates a periodic barrier of 2.8 kcal/mol as an upper limit. This value is in qualitative agreement with the barriers to internal rotation of methyl groups in the dimethylhalosilanes[6] which are in the range 2.07–2.56 kcal/mol. It should be pointed out that the calculation of a valid barrier to internal rotation is dependent on the correct assignment of the torsional modes, and since no data were available for the deuterium-substituted molecule, this assignment is to be considered tentative.

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Registry No. $(CH_3)_2SiHCl$, 1066-35-9; AgCN, 506-64-9; $(CH_3)_2SiHCN$, 18192-18-2.

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Vibrational Spectra and Structure of Biphosphine and Biphosphine-d_4

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Infrared and Raman spectra have been obtained for biphosphine and biphosphine-d_4 in both solid and vapor phases. From the spectral data it is concluded that only one conformer exists in both solid and fluid phases and that this is the gauche conformer. A normal-coordinate analysis has also been performed, in which the 24 vibrational frequencies of the two isotopes have been fitted by 10 force constants to an overall average error of 1.0%. The PED indicates that there is practically no mixing of the normal modes in the P_2H_4 molecule but the P–P stretch and the PD_2 wagging modes are extensively mixed for the P_2D_4 molecule.

Introduction

In recent years compounds of the general formula X_2Y_4 have been the subject of considerable spectroscopic investigation.[1] For the diboron X_2Y_4 molecules the planar (D_{2h}) and staggered (D_{2d}) forms have been shown to be the most stable conformers, whereas for the group 5A (nitrogen, phosphorus, and arsenic) compounds the trans (C_{2h}) and gauche (C_2) forms are the only observed conformations. No cis (C_{2v}) conformers have been observed, apparently due to molecular strains induced by the eclipsed positions of the electron pairs and substituents.

While the structures of several substituted biphosphine compounds have been well determined by spectroscopic techniques, the structure of the simplest diphosphorus analog,