Electron Diffraction Study of the Molecular Structures of Monomethylsilyl Isocyanate and Monomethylsilyl Isothiocyanate in the Gas Phase

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The molecular structures of the methylsilyl pseudohalides SiH_2MeNCO and SiH_2MeNCS have been determined by electron diffraction in the gas phase. The molecules appear bent at nitrogen, but it is shown that this is probably due to a shrinkage effect caused by a low-frequency, large amplitude bend at nitrogen, as found for the simple silyl analogues SiH_3NCY (Y = O or S). The major structural parameters (r_a, bond lengths in pm, angles in degrees) are: SiH_2MeNCO, r(Si–N) 171.8(2), r(Si–C) 185.3(3), r(N=C) 121.3(23), r(C=O) 116.9(18), Si–N–C 151.7(16), N–Si–C 104.5(21); SiH_2MeNCS, r(Si–N) 172.4(6), r(Si–C) 184.8(8), r(N=C) 119.5(4), r(C=S) 157.8(3), Si–N–C 156.4(16), N–Si–C 108.5(14). In each case the torsion angle between the plane containing the SiC and SiN bonds and that containing the SiN and N=C bonds is close to 90°. Comparisons are drawn with other pseudohalides $MH_nMe_{3-n}NCY$, where M = Si or C and n = 0—3.

The molecular structures of isocyanates and isothiocyanates have been extensively studied since it was shown that SiH_3NCS[1,2] and SiH_3NCO[3,4] had SiNCY (Y = S or O) skeletons that were linear or close to linear at nitrogen. In each case the potential function corresponding to the bending motion at nitrogen is broad,[5] so that the motion has a very high amplitude. For the isocyanate[4,5] there is a low hump in the potential at the linear configuration, the minimum potential energy being at an angle of *ca.* 156°, but the vibrational ground state lies very close to the top of the hump, which is only some 30 cm^{-1} above the minimum.

This sort of molecule poses problems for electron diffraction study, due to the wide range of bond angles at nitrogen accessible to molecules at room temperature. In the simple silyl derivatives[6] electron diffraction studies show bent skeletons if no account is taken of the shrinkage effect, but the deviations from linearity disappear if shrinkage corrections, based on low frequency *harmonic* bending motions, are applied. The shape of non-bonded Si $\cdots$ O peaks in the radial distribution curve of SiH_3NCO, however, could only be accounted for if the vibration was taken to be anharmonic. We have studied some methyl-substituted silyl compounds and find that in $SiMe_3NCO$[7] and $SiMe_3NCS$[8] the skeletons are apparently bent at N, with SiNC angles of 157 and 158°; for $SiHMe_2NCO$ and $SiHMe_2NCS$[9] the angles at N are 154 and 155°. These are all close enough to the apparent bond angles found for SiH_3NCO and SiH_3NCS (152 and 163° respectively) to make it clear that shrinkage corrections would result in linear skeletons if the bending frequency at N was well below 100 cm^{-1}, as for the simple silyl compounds.[5]

Unfortunately, in the methylsilyl compounds, the Si $\cdots$ Y non-bonded peaks in the radial distribution curves are too overlapped by peaks due to other non-bonded distances to provide any information about the harmonic or anharmonic nature of the bending motion at nitrogen. However, for the dimethylsilyl derivatives, the asymmetric nature of the group made it possible to define the (apparent) conformational preference of the NCY group, which was found to eclipse the Si–H bond in each case. This is in marked contrast to the preference found in the substituted alkyl isocyanates and isothiocyanates,[10,11] in which the NCY groups eclipse C–C bonds.

We have now studied monomethylsilyl isocyanate and isothiocyanate, hoping to find whether the skeletons are linear or effectively linear at N, whether there is any evidence of anharmonicity in the bending motions, and what are the preferred conformations or apparent conformations. In addition, the major structural parameters allow a more detailed and systematic analysis to be made of the effects of progressive methyl substitution in the series $SiH_nMe_{3-n}NCY$ (n = 3—0, Y = O or S), and a direct comparison between the ethyl and monomethylsilyl derivatives can also be made.

Experimental

Monomethylsilyl isocyanate was prepared by a modification of the method used for the preparation of SiH_3NCO:[5] HNCO was reacted in the gas phase with a mixture of bis- and tris-(monomethylsilyl)amines, these being generated by the gas-phase reaction of ammonia with methylsilyl chloride. The product was separated and purified by standard vacuum line techniques and characterised by spectroscopic methods (i.r. and multinuclear n.m.r.).

The isothiocyanate was prepared by reaction of 1.5-mol aliquots of methylsilyl bromide with excess solid silver thiocyanate in a tap ampoule, and characterised spectroscopically after fractionation by trap to trap distillation.

Electron diffraction scattering intensities were recorded photographically using the Edinburgh apparatus[12] operating at *ca.* 44 kV. The nozzle and samples were held at room temperature during data collection. Data were converted to digital form using a computer-controlled Joyce–Loebl microdensitometer as described previously.[13] The electron wavelength was determined by analysis of the scattering patterns of gaseous benzene recorded consecutively with those of the compounds. Data reduction[13] and refinement[12] were carried out with established programs, using the complex scattering factors of Schäfer *et al.*[14] The weighting points used in setting up the off-diagonal weight matrix, s ranges, and other pertinent data are given in Table 1. The reduced electron scattering intensities with final difference curves for the two compounds are shown in Figure 1 and 2.

Structural Model and Refinements

The molecules considered here have 10 atoms and 55 independent distances in a structure with overall symmetry C_1. We have constrained the methyl group to have a local three-fold axis, but allowed a tilt of this axis away from the SiC bond direction, and

Table 1. Weighting functions, correlation parameters, and scale factors

Compound	Camera height/mm	Δs	$s_{min.}$	sw_1 nm^{-1}	sw_2	$s_{max.}$	Correlation parameter	Scale factor	Wavelength/pm
SiH_2MeNCO	286.0	2	20	30	120	144	0.110	0.809(8)	5.681
	128.3	4	60	80	300	344	0.137	0.710(14)	5.681
SiH_2MeNCS	285.4	2	20	40	124	144	−0.021	0.864(12)	5.681
	128.3	4	60	80	250	320	0.108	0.691(23)	5.681

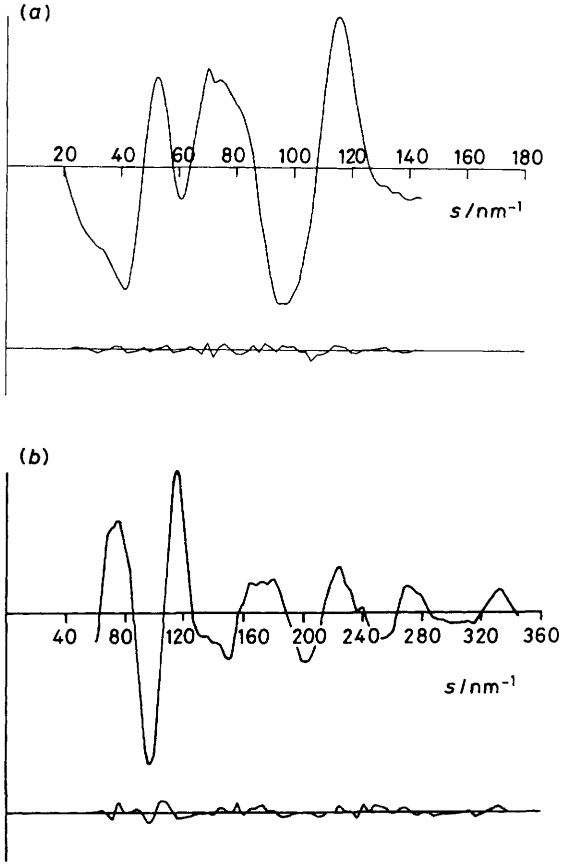

Figure 1. Molecular scattering intensities for monomethylsilyl isocyanate; observed and final difference curves for camera distances of (*a*) 286.0 and (*b*) 128.3 mm

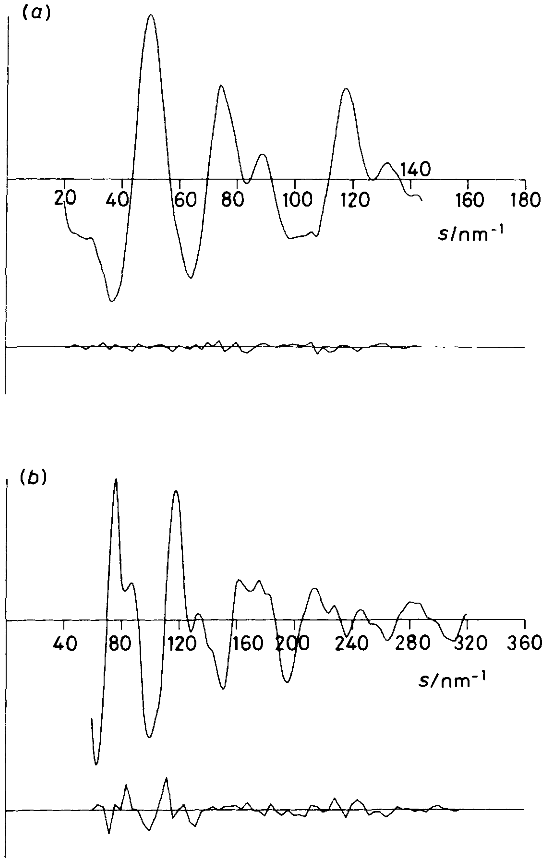

Figure 2. Molecular scattering intensities for monomethylsilyl isothiocyanate; observed and final difference curves for camera distances of (*a*) 285.4 and (*b*) 128.3 mm

assumed the SiH_2 group to be symmetric about the plane containing the C–Si and Si–N bonds. The structure is then defined by six bond lengths, six interbond angles (taken as CSiN, SiNC, NCY, NSiH, HSiH, and HCH), the tilt and torsion of the methyl group, a torsion around the SiN bond, defined to be zero with the NCY group *trans* to the SiC bond, and a torsion about the N=C bond. Of these available parameters those defining the directions of the SiH bonds were fixed throughout, while the tilt and torsion angles of the methyl group were fixed at an early stage of the refinements. The NCY bond angles were kept fixed at 180° in each case, no improvement in the fit being obtained if they were allowed to depart from linearity: the N=C torsion is therefore undefined. The remaining structural parameters (all six bond lengths, SiCH, SiNC, NSiC, and the SiN torsion angle) were free to refine at the final stage, together with the amplitudes of vibration corresponding to all the major peaks in the radial distribution curves. In a few cases this involved refining a single parameter for a group of overlapping peaks, and ratios of vibration amplitudes were fixed. Care was taken to ensure that the final refinements were closely comparable with each other, and as far as possible with those published earlier for the dimethylsilyl pseudohalides.[9] The final fits, on an r_a basis, were good, with R factors of *ca.* 7% (SiH_2MeNCO: $R_G = 0.071$, $R_D = 0.064$; SiH_2MeNCS: $R_G = 0.076$, $R_D = 0.077$). We did not attempt to extend our analysis to an r_α basis because of the difficulty of correctly accounting for the effects of the high amplitude vibrations. The final difference curves associated with the radial distribution curves (Figure 3) show no sign of the presence of another conformer in either case. The final refined parameters are shown in Table 2 and the most important interatomic distances and amplitudes are listed in Table 3. Atomic co-ordinates for all atoms are given in Table 4. Finally, the correlation matrices between refining parameters and amplitudes are shown in Table 5.

Discussion

The bond lengths and angles given in Table 2 may usefully be compared with parameters for other silyl pseudohalides (Table 6). It is clear that the Si–N bonds are lengthened by the introduction of methyl substituents at Si, but the bond lengths for the monomethylsilyl and dimethylsilyl compounds are very similar in both cases. The SiC bond lengths are also similar in the monomethylsilyl and dimethylsilyl compounds, and rather longer in the trimethylsilyl analogues. The apparent bond angles at nitrogen are all rather similar, between 152 and 163°, and the differences between them are barely significant. It is clear, however, that in all cases the shrinkage effect associated with a low-frequency, high-amplitude vibration would be adequate to explain the apparent structures even if the SiNCY chains were all linear. In Table 6 we also show the shrinkages δ(Si $\cdots$ Y), defined as r(SiN) + r(NC) + r(CY) − d(Si $\cdots$ Y), and δ(Si $\cdots$ C), defined as r(SiN) + r(NC) − d(Si $\cdots$ C) for the whole range of silyl pseudohalides. These shrinkages are closely related to the apparent bond angles at nitrogen, and are quite consistent with the suggestion of low-frequency, large amplitude vibrations of essentially linear skeletons. We have performed trial normal co-ordinate analysis calculations on SiH_2MeNCO, assuming a linear SiNCO chain and a rectilinear, harmonic bending motion with various frequencies between 50 and 100 cm^{-1}, and find that a frequency of 60 cm^{-1} results in calculated shrinkages δ(Si $\cdots$ C) and δ(Si $\cdots$ O) of 8.5 and 12.6 pm respectively, very close to the values derived from the electron diffraction results. There is a band at 135 cm^{-1} in the Raman spectrum of the solid; this is a very weak line, and may well be due to the *overtone* of the bend at nitrogen, which is also observed in the Raman spectra of other pseudohalides. Below 100 cm^{-1} the spectrum contains a number of strong peaks,

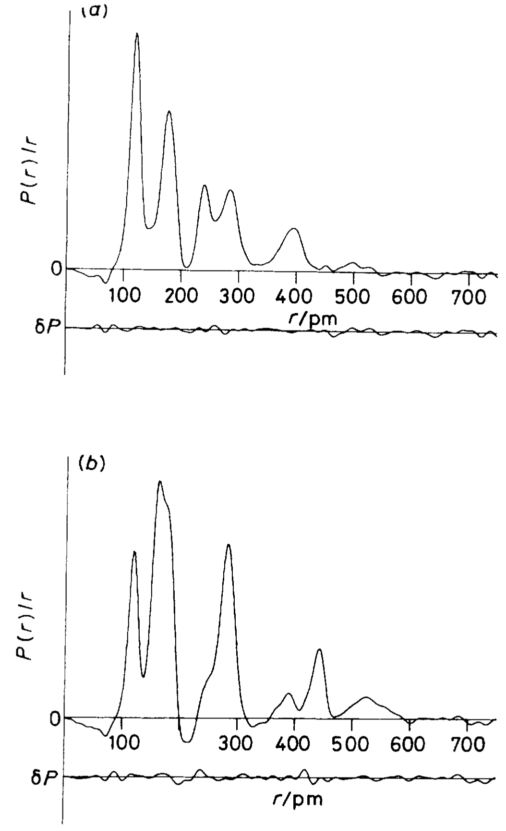

Figure 3. Observed and final difference radial distribution curves $P(r)/r$ for (*a*) SiH_2MeNCO and (*b*) SiH_2MeNCS. Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.000\,02s^2/(Z_N - f_N)(Z_{Si} - f_{Si})]$

Table 2. Molecular parameters (in pm or °)

Parameter		SiH_2MeNCO	SiH_2MeNCS
p_1	r(C–H)	112.0(9)	113.6(14)
p_2	r(Si–C)	185.3(3)	184.8(8)
p_3	r(Si–H)	152.3(10)	148.9(16)
p_4	r(Si–N)	171.8(2)	172.4(6)
p_5	r(N=C)	121.3(23)	119.5(4)
p_6	r(C=Y)	116.9(18)	157.8(3)
p_7	H–C–H	112.9(14)	108.5(16)
p_8	CH_3 tilt[a]	2.0 (fixed[b])	2.0 (fixed[b])
p_9	CH_3 twist[a]	−22.0 (fixed[b])	25.5 (fixed[b])
p_{10}	H–Si–H	109.0 (fixed)	109.0 (fixed)
p_{11}	N–Si–H	112.0 (fixed)	112.0 (fixed)
p_{12}	Si–N–C	151.7(16)	156.4(16)
p_{13}	N–C–Y	180.0 (fixed)	180.0 (fixed)
p_{14}	N–Si–C	104.5(21)	108.5(14)
p_{15}	Si–N twist[a]	86.4(97)	82.2(80)

[a] For definition, see text. [b] Optimum value found in early refinements. Errors quoted in parentheses in Tables 1—3 are estimated standard deviations obtained in the least-squares analysis.

Table 3. Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm)*

		Distance		Amplitude	
		SiH_2MeNCO	SiH_2MeNCS	SiH_2MeNCO	SiH_2MeNCS
r_1	C–H	112.0(9)	113.6(14)	7.0 (fixed)	7.0 (fixed)
r_2	Si–C	185.3(3)	184.8(8)	5.4(5)	5.8(15)
r_3	Si–H	152.3(10)	148.9(16)	8.8 (fixed)	8.8 (fixed)
r_4	Si–N	171.8(2)	172.4(6)	4.8(4)	5.8 (tied to u_2)
r_5	N=C	121.3(23)	119.5(4)	3.3(16)	3.4(8)
r_6	C=Y	116.9(18)	157.8(3)		4.0(7)
r_7	N $\cdots$ Y	238.2(5)	277.3(6)	5.2(7)	7.7(9)
r_8	Si $\cdots$ C	284.5(18)	285.9(3)	9.9(4)	8.1(9)
r_9	C $\cdots$ N	282.5(41)	289.9(24)	12.4 (tied to u_8)	10.2 (tied to u_8)
r_{10}	Si $\cdots$ H	239.3(21)	246.2(17)	12.8(17)	9.6(12)
r_{11}	Si $\cdots$ H	241.2(21)	248.3(17)		
r_{12}	Si $\cdots$ H	244.2(21)	251.0(17)		
r_{13}	Si $\cdots$ Y	397.8(11)	440.7(4)	11.3(11)	10.4(4)
r_{14}	C $\cdots$ C	377.3(25)	388.8(13)	10.8(29)	12.5(20)
r_{15}	C $\cdots$ Y	480.1(40)	532.5(25)	30.0 (fixed)	29.1 (fixed)

* Other C $\cdots$ H, N $\cdots$ H, Si $\cdots$ H, Y $\cdots$ H, and H $\cdots$ H distances were included in the refinements, but are not listed here.

probably due to lattice modes, but it is quite possible that one is due to the bend at nitrogen. Given the uncertain influence of neighbouring molecules on the bending potential in the solid, this is certainly not inconsistent with a fundamental near 60 cm^{-1}. We may therefore conclude that the electron diffraction results may be accounted for by the effects of shrinkage in molecules with linear SiNCY groups.

Table 4. Atomic co-ordinates/pm

	SiH_2MeNCO			SiH_2MeNCS		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
H(1)	−150.0	188.1	−40.3	−60.5	216.8	−105.3
H(2)	−38.5	212.9	106.6	−160.0	288.2	45.5
H(3)	29.7	228.0	−66.2	15.2	238.6	59.7
C(4)	−46.4	179.4	0.0	−57.2	175.7	0.0
Si(5)	0.0	0.0	0.0	0.0	0.0	0.0
H(6)	−57.0	−67.6	−124.0	−55.9	−66.2	−121.5
H(7)	−57.0	−67.6	124.0	−55.9	−66.2	121.5
N(8)	171.8	0.0	0.0	172.4	0.0	0.0
C(9)	278.6	−3.6	−57.4	281.8	−8.3	−47.6
Y(10)	381.4	−7.0	−112.8	426.2	−19.2	−110.4

Table 5. Least-squares correlation matrices (×100) for (*a*) SiH_2MeNCO and (*b*) SiH_2MeNCS*

(*a*)

	p_6	p_7	p_{12}	p_{14}	p_{15}	u_2	u_6	u_{10}	u_{14}
p_4						59			
p_5	−98	−63	−55	−84	−70		−98	55	
p_6		60	52	84	69		97	−52	
p_7				69	61		58		
p_{12}							53		−71
p_{14}					84		82		
p_{15}							68		
u_4						71			
u_6								−54	
u_7								−59	
u_{13}									69

(*b*)

	p_3	p_4	p_5	p_6	p_7	p_{12}	p_{15}	u_2	u_5	u_6	u_7	u_8
p_1	59		−73		−60				67			
p_2		−84		−65		68		−89		−55		
p_3					−57							
p_4				68		−80		92		58		53
p_5						−52						61
p_6						−76		76				52
p_{12}								−79				−65
p_{14}							91				−72	−71
p_{15}											−67	−64
u_2										73		54
k_1												56

* Only elements with absolute values >50 are included. Parameters p_n are defined in Table 2, amplitudes u_n are defined in Table 3.

The conclusion might appear to make the question of the conformation meaningless, but this is only so if a static picture of the molecules is employed. In the real molecules, even if they are linear at nitrogen, the bending motion at nitrogen has a large amplitude, and will actually have two non-degenerate components, depending on whether the SiNC angle bends in the plane of the C–Si–N group or is perpendicular to it. The electron diffraction results suggest that the greater amplitude is in the motion perpendicular to the CSiN plane, as the apparent torsion angle about the SiN bond is close to 90° in each case. If we look at the molecules along the SiN bond, with the SiC bond in a vertical plane [Figure 4(*a*)] the largest amplitude motion is the bending at nitrogen from side to side, resulting in an apparent preferred conformation with the NCY group close to eclipsing one of the SiH bonds.

In the dimethylsilyl pseudohalides[9] we found an apparent tendency for the NCY group to eclipse the single SiH bond in each case, suggesting that in these molecules the lowest frequency, highest amplitude motion is in the mirror plane of the $SiHMe_2$ group, with a greater tendency for the NCY group to be close to the SiH bond than between the two SiC bonds [Figure 4(*b*)], although there was some suggestion that a proportion of the molecules may be in the conformation where the NCY group lay between the two SiC bonds [Figure 4(*c*)].

In both the monomethylsilyl and the dimethylsilyl pseudohalides, then, there is evidence that the lowest frequency bend is that in which the NCY group avoids the methyl group or groups. This is probably an electrostatic effect, the (positively charged) carbon of the NCY group being repelled by the

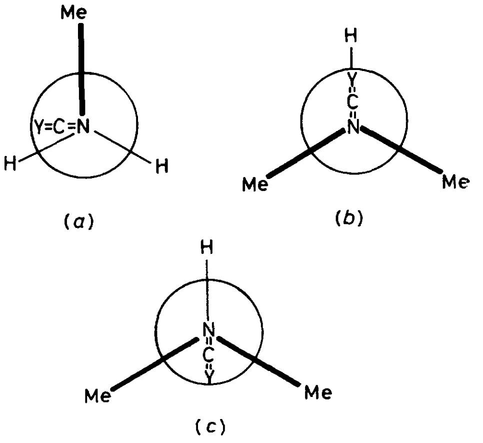

Figure 4. Preferred conformations for (*a*) SiH_2MeNCY (Y = O or S) and (*b*) $SiHMe_2NCY$ (Y = O or S). The possible second conformer found for $SiHMe_2NCS$ is illustrated in (*c*)

Table 6. Structural parameters and shrinkages

Compound	*r*(Si–N)/pm	*r*(Si–C)/pm	*d*(Si···C)/pm	Si–N–C/°	δ(Si···C)*/ pm	δ(Si···Y)*/ pm	Ref.
SiH_3NCO	170.3(4)		283.3(6)	152	8.6	12.0(5)	6
SiH_2MeNCO	171.8(2)	185.3(3)	284.5(18)	151.7(16)	8.6	12.2	This work
$SiHMe_2NCO$	171.9(5)	185.8(3)	286.1(6)	153.5(13)	6.9	11.3	9
$SiMe_3NCO$	174.0(3)	186.4(1)	288.4(13)	156.8(23)	5.8	15.7	7
SiH_3NCS	170.4(6)		287.3(6)	163	2.8	4.2(8)	6
SiH_2MeNCS	172.4(6)	184.8(8)	285.9(3)	156.4(16)	6.0	9.0	This work
$SiHMe_2NCS$	172.3(8)	185.9(5)	286.6(7)	154.7(22)	6.9	9.9	9
$SiMe_3NCS$	174.3(4)	186.6(1)	288.3(6)	158.2(7)	5.1	9.6	8

* For definition see text.

hydrogens of the methyl group(s), or attracted to the negatively charged hydrogen(s) on Si. The fact that the NCY group in ethyl and isopropyl pseudohalides shows the opposite preference [10,11] suggests that the methyl groups are less important than the SiH or CH hydrogens in this respect.

Taken together, the results for the monomethylsilyl and dimethylsilyl derivatives suggest that the true structures are at least as dynamic as those of the simple silyl compounds, but we cannot say whether the potential functions within which the bending motions at nitrogen occur have local maxima where the bond angle SiN=C is 180°, as for SiH_3NCO, or true minima at this point, as for SiH_3NCS. In any case the two-dimensional potential must be unsymmetrical because of the asymmetry of the substituents on silicon. We hope to study the low-frequency motions further using vibrational and microwave spectroscopy.

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