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Crystal Structure and Effect of High External Pressures on the Vibrational Spectra of *all-trans*-Hexabenzylcyclohexasilane, $[Si(H)CH_2Ph]_6$

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Hexabenzylcyclohexasilane, $[Si(H)CH_2Ph]_6$ (1), has been synthesized in moderate yield (~35%) by dehydrocoupling benzylsilane in the presence of dimethyltitanocene (Cp_2TiMe_2, Cp = η^5-C_5H_5) catalyst. Compound 1 crystallizes in the trigonal $R\bar{3}$ (C_{3i}^2) space group [a = 25.077(2), c = 5.7031(6) Å; V = 3105.9(4) Å^3; D_{calcd} = 1.157 g cm^{-3} for Z = 3; R_w = 0.040]. It has the flattest Si_6 ring thus far reported for a cyclohexasilane [Si–Si–Si = 117.02(7)°; dihedral Si–Si–Si–Si angle = 33.58(7)°], despite the absence of any transannular interactions. The IR and Raman spectra of 1 have been recorded at various pressures up to ~40 kbar with the aid of diamond-anvil cells. The pressure dependences ($d\nu/dP$) and relative pressure sensitivities ($d\ln\nu/dP$) of the major IR and Raman bands have been determined. From the X-ray crystallographic and vibrational spectroscopic results, there is evidence for rotation of the benzyl groups in the solid state and a pressure-induced phase transition at 20 ± 1 kbar. Moreover, the larger $d\nu/dP$ values for ν_{SiH} and ν_{SiSi}, compared to those for ν_{CH} and ν_{CC} in cyclohexane, suggest that, at least in this particular case, SiH and SiSi bonds are more anharmonic than are CH and CC bonds.

Introduction

Polysilanes constitute a new class of polymeric materials that have been developed in recent years.[1–3] These materials are fundamentally different from conventional organic polymers with CC backbones because of the electronic properties of the Si–Si backbones and the nature of the organic substituents attached to the Si atoms. Polysilanes have been used as precursors to silicon carbide ceramics, as photoresists, as injected positive hole conductors, as NLO materials, and as photoinitiators for vinyl polymerization.[2] Most previous work on cyclic polysilanes has been concerned with the symmetrically-disubstituted compounds, $(R_2Si)_n$,[4,5] although a few studies have been reported for some unsymmetrically-disubstituted derivatives, such as the isomers of $[Si(t\text{-Bu})Me]_4$ and $[Si(Me)Ph]_{5,6}$.[6,7] Part of the problem in studying $[Si(H)R]_n$ compounds is the rapidly increasing number of isomers possible as the value of n is increased and the difficulties is separating the isomers in a pure form. Despite this, however, a pure isomer of hexaphenylcyclohexasilane has been isolated following bromine substitution of the phenyl groups of dodecaphenylcyclohexasilane, $(SiPh_2)_6$, and subsequent reduction of the resulting hexabromo–hexaphenyl compound.[8] On the basis of the singlet appearing for the SiH groups in its ^1H NMR spectrum, this compound was assigned an *all-trans* configuration.

Primary organosilanes undergo facile dehydrocoupling to oligosilanes under the catalytic influence of a variety of titanocene and zirconocene derivatives.[9–11] The products of these reactions are generally mixtures of cyclic and linear oligomers in which either structural form can dominate, depending on which catalyst and/or monomer is being employed. With dimethyltitanocene (Cp_2TiMe_2, Cp = η^5-C_5H_5; ~2 mol %) as the catalyst and benzylsilane as the monomer, a rapid coupling reaction occurs within about 1 day to give mainly cyclic products $[Si(H)CH_2Ph]_n$ (n ~ 6). If the resulting mixture of oligomers is left to stand at room temperature for several weeks, *all-trans*-hexabenzylcyclohexasilane, $[Si(H)CH_2Ph]_6$ (1), is deposited as a white powder in yields approaching 35% based on the starting benzylsilane. Details of the synthesis and X-ray structural characterization of 1 are presented in this paper. Although a number of other partially-substituted cyclosilanes have been synthesized,[8,12] crystallographic data have only been obtained for fully-substituted derivatives.[13–17] The X-ray diffraction data described here for 1 confirm its expected *all-trans* geometry, but unlike other cyclohexasilanes, the Si_6 ring is almost planar, suggesting that the ring is not particularly

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rigid when subjected to the intermolecular forces present in the crystalline solid. Earlier vibrational spectroscopic studies on several alkyl-substituted polysilanes and high polymers have revealed the existence of order–disorder phase transitions in several cases, which take place either above or below room temperature, depending on the conformations of the Si–Si backbones and the nature of the different organic substituents.[18–20] By monitoring the changes that take place in the IR and Raman spectra of a compound, it is often possible to detect phase transitions which are induced by variations in temperature and pressure. The effect of these variables on the chemical bonding and interatomic and intermolecular interactions can also be investigated by this approach. We report here the results of such a high-pressure vibrational spectroscopic study of 1. The ν_{SiSi}, ν_{SiC}, and ν_{SiH} modes (2300–300-cm^{-1} region) were examined chiefly by Raman spectroscopy, while information about the benzyl substituent groups was obtained from IR spectra in the 3200–100-cm^{-1} region. As far as we know, this work represents the first high-pressure vibrational investigation of an organosilicon compound.

Experimental Section

Synthesis of 1. Benzylsilane (12.0 mL, 82 mmol) was syringed into a toluene solution (26 mL) of dimethyltitanocene (Cp_2TiMe_2; 1.72 g, 8.26 mmol) under argon. After the dark-blue solution was allowed to stand for 6 weeks at room temperature, the white precipitate of 1 which had formed (~3.5 g, ~35% yield) was filtered off and washed with hot toluene. Colorless, crystalline needles of 1, suitable for the X-ray crystallographic and vibrational spectroscopic measurements, were obtained by recrystallization from hot toluene or chlorobenzene. Anal. Calcd for C_7H_8Si: C, 70.0; H, 6.67. Found: C, 69.2; H, 6.95. ^1H NMR (δ, ppm): SiH (br, s) 3.754, CH_2 (br, s) 2.072. IR: ν_{SiH} 2096 w, 2075 s cm^{-1}. MS [*m/e* (%)]: 693 (43), 507 (20), 383 (64), 119 (64), 91 (100). Mp: 213–5 °C.

Crystal Structure of 1. The data set for 1 was collected on an Enraf-Nonius diffractometer controlled by NRCCAD software,[21] using the $\theta/2\theta$ scan mode. All computing was performed by using the NRCVAX crystallographic software.[22] Standard intensities monitored throughout the data set collection showed no decay. The last least-squares cycle was calculated with 16 atoms, 105 parameters, and 678 out of 893 reflections. Merging *R* for 1290 merging pairs of symmetry-related reflections was 2.6%. Weights based on counting statistics were used. In the last D-map, the deepest hole was −0.180 e/Å^3 and the highest peak was 0.30 e/Å^3. The structure was solved by direct methods. Hydrogen atoms were located in a difference map and were refined isotropically. The crystal data and collection parameters are summarized in Table I. The atomic coordinates and anisotropic thermal parameters are listed in Table II, and selected bond distances and angles are given in Table III. An ORTEP-II diagram of 1, showing the atom numbering scheme, is presented in Figure 1, and a packing diagram is shown in Figure 2.

Table I. Crystal Data and Data Collection Parameters for 1

formula	$C_{42}H_{48}Si_6$
fw	721.35
system	trigonal
space group	$R\bar{3}$
a, Å	25.077(2)
c, Å	5.7031(6)
V, Å^3	3105.9(4)
Z	3
F(000)	1153.55
D_{calcd}, g cm^{-3}	1.157
μ(Mo Kα), mm^{-1}	0.22
λ, Å	0.7093
crystal dimens, mm	0.2 × 0.2 × 0.5
temp, °C	20
2θ limits, deg	$3 < 2\theta < 45$
scan speed, deg/min	6
no. of measd reflns	5164
no. of unique reflns	1786
no. of reflns used	1356
R	0.048
R_w	0.040

Table II. Atomic Positional and Anisotropic Thermal Parameters for 1

	x	*y*	*z*	B_{eq},[a] Å^2
Si	0.10355(5)	0.07024(5)	0.96428(23)	3.51(7)
C(1)	0.19720(17)	0.18661(18)	1.1185(7)	3.47(24)
C(2)	0.18350(20)	0.21625(19)	1.2948(8)	4.6(3)
C(3)	0.20171(23)	0.27718(22)	1.2753(9)	6.2(3)
C94)	0.23129(24)	0.31028(21)	1.0862(10)	7.4(4)
C(5)	0.24535(22)	0.28336(22)	0.9107(9)	7.6(3)
C(6)	0.22884(19)	0.22133(21)	0.9224(8)	5.2(3)
C(7)	0.17734(18)	0.11964(18)	1.1341(8)	4.3(3)
H(1)	0.1139(14)	0.0798(14)	0.720(6)	4.5(9)
H(2)	0.1592(14)	0.1926(14)	1.430(5)	4.9(10)
H(3)	0.1901(17)	0.2920(17)	1.408(7)	7.5(11)
H(4)	0.2389(19)	0.3470(19)	1.079(7)	9.5(13)
H(5)	0.2655(16)	0.3043(16)	0.777(6)	5.8(10)
H(6)	0.2373(18)	0.1969(19)	0.800(7)	9.1(13)
H(7)	0.1643(14)	0.1021(14)	1.283(5)	4.2(9)
H(8)	0.2164(17)	0.1123(17)	1.035(6)	7.1(11)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid for atoms refined anisotropically. For hydrogens, $B_{eq} = B_{iso}$.

Vibrational Spectra. Raman spectra (2-cm^{-1} resolution) were recorded on an Instruments S. A. Ramanor spectrometer with a Jobin-Yvon U-1000 double monochromator interfaced to an IBM PS/2 Model 60 computer for data collection and processing. The 514.532-nm green line of a Spectra-Physics Model 164-5W argon ion laser was used as the excitation source. Infrared spectra (2-cm^{-1} resolution) were acquired on a Nicolet 6000 FT-IR spectrometer equipped with a liquid N_2-cooled MCT-B detector. Far-IR data were obtained on a Bruker IFS-88 FT-IR spectrometer equipped with a DTGS detector and a 6-μm Mylar beam splitter.

High-pressure Raman spectra were obtained with the aid of a diamond-anvil cell (dac) from Diacell Products, Leicester, U.K., fitted with Type IIA diamonds. The sample and pressure calibrant (a small ruby chip) were placed in the 300-μm hole of a 400-μm-thick, stainless-steel gasket located between the parallel faces of the diamonds. The dac was located under the 4× objective of a Nachet optical microscope coupled to the spectrometer. The laser power at the sample for the Raman measurements was usually ~30 mW. The dac used for the high-pressure IR measurements was purchased from High Pressure Diamond Optics, Tucson, AZ, and was fitted with Type IIA diamonds. The IR-active, antisymmetric N–O stretching mode of a mixture of $NaNO_3$ in NaBr (5%) was used to calibrate the pressure in the dac.[23] A small amount of the calibrant was loaded together with the sample under an optical microscope into the 400-μm hole of a 200-μm-thick, stainless-steel gasket. The dac was mounted onto an *xyz* optical stage and then aligned in the spectrometer with the aid of a Spectra-Bench (Spectra-Tech) equipped with a 4× beam condenser.

Results and Discussion

Crystal and Molecular Structure of 1. Compound 1 is not particularly soluble in common organic solvents

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Table III. Selected Bond Distances (Å) and Angles (deg) for 1[a]

	Distances		
Si–Sia	2.3318(24)	C(3)–C(4)	1.336(8)
Si–Sib	2.332(3)	C(3)–H(3)	0.95(4)
Si–C(7)	1.899(4)	C(4)–C(5)	1.349(8)
Si–H(1)	1.42(3)	C(4)–H(4)	0.84(4)
C(1)–C(2)	1.392(6)	C(5)–C(6)	1.397(7)
C(1)–C(6)	1.396(6)	C(5)–H(5)	0.92(4)
C(1)–C(7)	1.497(6)	C(6)–H(6)	1.02(4)
C(2)–C(3)	1.363(6)	C(7)–H(7)	0.94(3)
C(2)–H(2)	0.98(3)	C(7)–H(8)	1.22(4)
	Angles		
Sia–Si–Sib	117.01(7)	C(3)–C(4)–C(5)	119.4(4)
Sia–Si–C(7)	109.09(14)	C(3)–C(4)–H(4)	118(3)
Sia–Si–H(1)	107.0(13)	C(5)–C(4)–H(4)	122(3)
Sib–Si–C(7)	109.97(14)	C(4)–C(5)–C(6)	121.0(4)
Sib–Si–H(1)	102.7(13)	C(4)–C(5)–H(5)	122.3(22)
C(7)–Si–H(1)	110.8(13)	C(6)–C(5)–H(5)	116.6(22)
C(2)–C(1)–C(6)	117.4(4)	C(1)–C(6)–C(5)	119.5(4)
C(2)–C(1)–C(7)	121.6(4)	C(1)–C(6)–H(6)	113.4(23)
C(6)–C(1)–C(7)	120.9(4)	C(5)–C(6)–H(6)	127.1(23)
C(1)–C(2)–C(3)	120.4(4)	Si–C(7)–C(1)	111.8(3)
C(1)–C(2)–H(2)	119.4(19)	Si–C(7)–H(7)	99.1(18)
C(3)–C(2)–H(2)	120.1(19)	Si–C(7)–H(8)	105.0(17)
C(2)–C(3)–C(4)	122.2(5)	C(1)–C(7)–H(7)	115.0(19)
C(2)–C(3)–H(3)	112.1(23)	C(1)–C(7)–H(8)	107.4(18)
C(4)–C(3)–H(3)	125.7(23)	H(7)–C(7)–H(8)	117(3)

[a] Atoms flagged a or b are symmetry equivalents. Sia: 0.070 24, −0.033 31, 1.035 72; *y*, −*x* + *y*, 2 − *z*. Sib: 0.033 31, 0.103 55, 1.035 72; *x* − *y*, *x*, 2 − *z*.

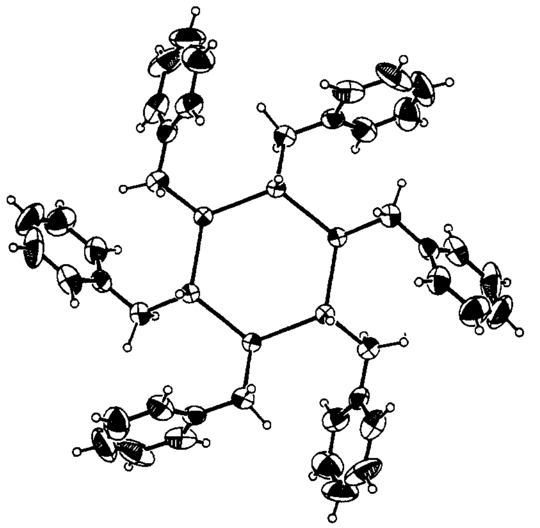

Figure 1. ORTEP-II diagram of a molecule of *all-trans*-[Si(H)CH$_2$Ph]$_6$ showing 50% probability thermal ellipsoids. H atoms are drawn as spheres of arbitrary size for clarity.

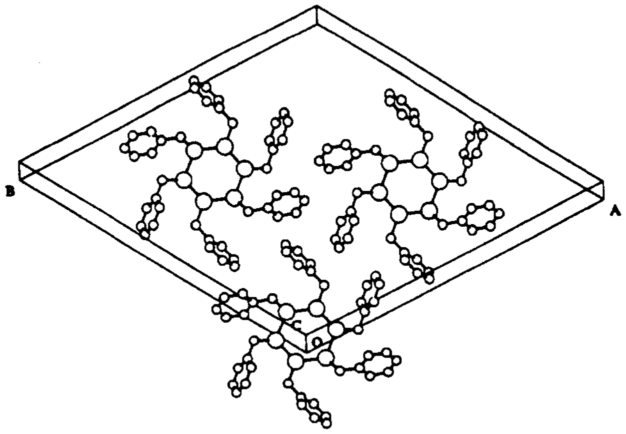

Figure 2. ORTEP-II packing diagram showing the arrangement of molecules in the unit cell.

at room temperature, and at no time during its synthesis was it detected in solution by ^{1}H NMR spectroscopy. In fact, it is probably this low solubility which allows reversion of the kinetic products to a single isomer in such a high yield in the first place. Compound 1 can be recrystallized from boiling toluene or THF solutions, but the crystals are small and fibrous and generally unsuitable for X-ray crystallography. Good-quality crystals are best obtained by very slow recrystallization from hot chlorobenzene. Apart from its aesthetic qualities, the molecule illustrated in Figure 1 is particularly interesting for its flattened Si$_6$ ring, with a Si–Si–Si angle of 117.01(7)° and a dihedral Si–Si–Si–Si angle of 33.58(7)°. Other bond angles and the bond lengths are quite normal [e.g.: Si–Si = 2.332(2) and Si–C = 1.899(4) Å; Si–Si–C = 109.5°]. The flattening is more exaggerated than in the structures of the fully-substituted cyclohexasilanes reported in the literature [(SiMe$_2$)$_6$, Si–Si–Si$_{av}$ = 111.9(4)°;[13] [Si(Me)Ph]$_6$, Si–Si–Si$_{av}$ = 111.1°;[15] (SiPh$_2$)$_6$, Si–Si–Si$_{av}$ = 113.8° [14]]. In the odd number cyclics (SiMe$_2$)$_n$, n = 7 and 13, the average Si–Si–Si angles are 116.2 and 115.7°, respectively.[15] It has been suggested that the opening of the bond angle in these cases is due to a reduction in the transannular methyl–methyl repulsions.[15] However, there are no significant transannular interactions in 1—the benzyl groups are oriented roughly in the plane of the molecule and the system is strain-free. This arrangement most likely maximizes the van der Waals interactions along the needle axis ($\bar{3}$), while flattening of the ring minimizes the repulsive interactions between the methylene protons of one benzyl group and the phenyl group of a vicinal benzyl group. The fiberlike crystals, with their low solubility and high melting point, suggest relatively strong packing forces along the $\bar{3}$ axis.

High-Pressure Vibrational Spectroscopic Studies. The IR and Raman spectra of 1 and three other related cyclic polysilanes were recently thoroughly examined at ambient temperature and pressure.[24] The values of the pressure dependences (dν/dP) and the relative pressure dependences (d ln ν/dP) of the main Raman and IR bands, together with the proposed vibrational assignments, are listed in Tables IV and V, respectively. Typical plots of wavenumber versus pressure (P) for the bands assigned to the Raman-active ν_{SiSi} and ν_{SiC} modes and the IR-active ν_{CH} and ν_{CC} modes are shown in Figures 5 and 6, respectively. With few exceptions (e.g., the 660-cm^{-1} band in the Raman), most of the bands exhibit distinct breaks in the slopes of the ν–P plots at 20 ± 1 kbar, suggesting a pressure-induced phase transition. Extensive high-pressure vibrational work on organometallic and organic crystals by Adams and co-workers[25,26] has shown that such discontinuities indicate the occurrence of phase transitions. Apart from sample melting, no ΔH changes were detected for 1 by differential scanning calorimetry (dsc) throughout the 600–165 K range. Since the lowest temperature obtainable in these dsc measurements was 165 K and the transition pressure was quite high (~20 kbar), it is possible either that there is a further ΔH change below 165 K or that no ΔH change occurs at all because the phase transition is second order. In the latter case, the space groups of the two phases would be quite similar.

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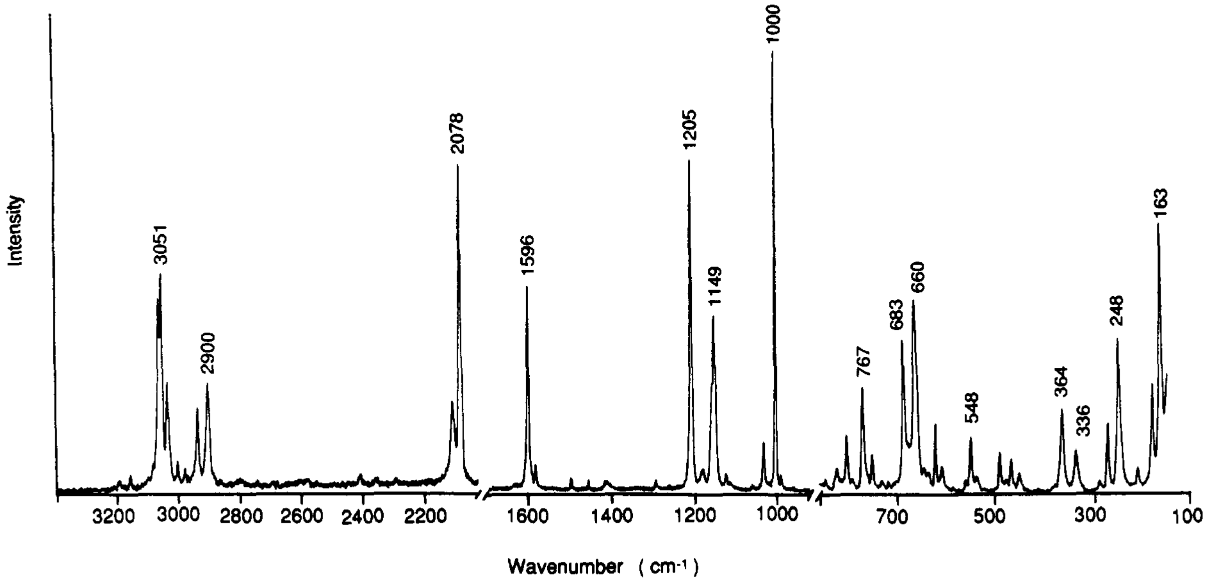

Figure 3. Raman spectrum of *all-trans*-[Si(H)CH_2Ph]$_6$ in the 3300–100-cm^{-1} region under ambient pressure at room temperature.

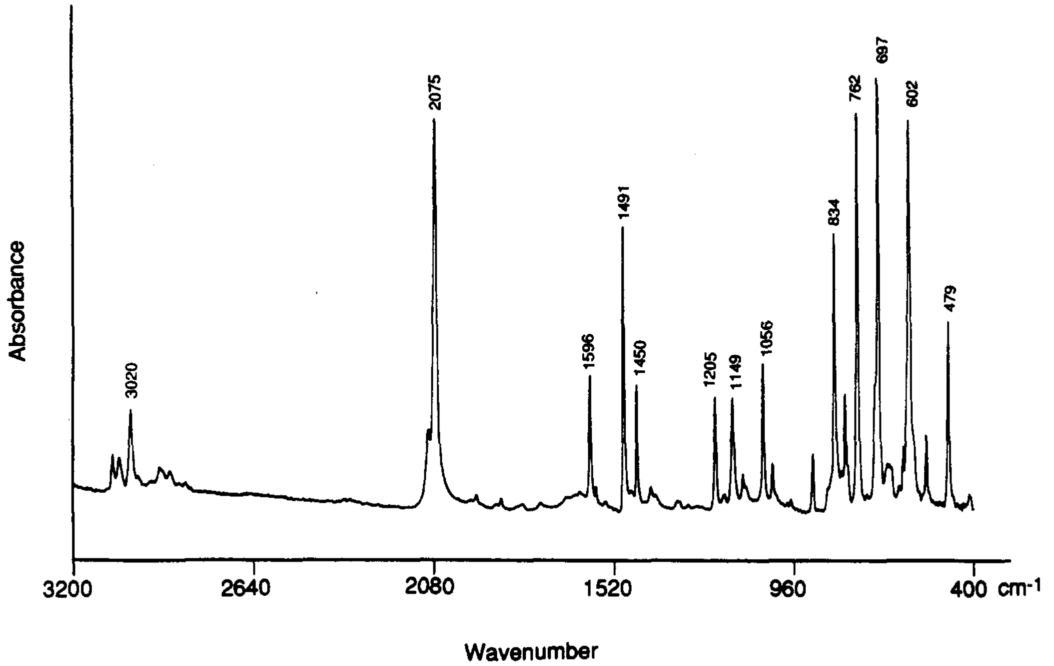

Figure 4. IR spectrum of *all-trans*-[Si(H)CH_2Ph]$_6$ in the 3200–400-cm^{-1} region under ambient pressure at room temperature.

Table IV. Pressure Dependences of the Main Raman Bands Observed for 1

low-pressure phase			high-pressure phase			
ν, cm^{-1}	dν/dP, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^{-3}	ν, cm^{-1}	dν/dP, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^{-3}	assignment[a]
336 w	0.66	2.00	349	0.00	0.00	ν_{SiSi}
364 m	0.56	1.50	368	0.41	1.10	ν_{SiSi}, ϕ_{CC}(phenyl)[b]
660 m	0.49	0.70	664	0.37	0.56	
			669	0.65	0.97	ν_{SiC}
684 m	0.55	0.80	687	0.12	0.17	
767 m	0.24	0.30	771	0.00	0.00	δ_{SiH}
1000 s	0.38	0.40	1008	0.20	0.20	ring breathing (phenyl)
1149 m	−0.45	−0.40	1141	−0.14	−0.12	
1155 sh	0.26	0.23	1161	0.10	0.09	β_{CH}(phenyl)
1177 w	0.28	0.24	1182	0.22	0.19	
1204 s	0.67	0.56	1217	0.04	0.03	
2078 s	1.47	0.71	2108	0.99	0.47	ν_{SiH}

[a] From ref 24. [b] Alternative assignment suggested by a reviewer; see ref 35.

Earlier investigations of the conformational changes occurring in polysilanes have shown that the energy barriers for C_{sp^3}–Si–Si–C_{sp^3} torsional rotations are small compared to those for the analogous carbon systems, C_{sp^3}–C–C–C_{sp^3}.[27] In addition, Sundararajan[28] recently calculated the conformational energies associated with the

Table V. Pressure Dependences of the Main IR Bands Observed for 1

low-pressure phase			high-pressure phase			
ν, cm^{-1}	dν/dP, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^{-3}	ν, cm^{-1}	dν/dP, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^{-3}	assignment[a]
479 m	0.40	0.84	486	0.07	0.14	ν_{SiSi}, ϕ_{CC}(phenyl)[b]
547 w	0.30	0.43	551	0.18	0.26	ν_{SiC}
697 s	0.21	0.38	701	0.04	0.07	γ_{CH}(phenyl)
762 s	0.08	0.10	763	0.19	0.25	δ_{SiH}
800 w	0.39	0.49	807	0.35	0.43	CH$_2$ rocking
834 s	0.08	0.10	836	0.48	0.57	
1056 m	0.24	0.23	1061	0.18	0.17	
1149 m	−0.55	−0.48	1142	−0.06	0.05	β_{CH}(phenyl)
			1156	−0.24	−0.21	
1205 m	0.57	0.47	1216	0.48	0.39	
1450 m	0.25	0.17	1455	0.19	0.13	ν_{CC}(phenyl)
1491 s	0.21	0.14	1495	0.11	0.07	
1578 w	0.40	0.25	1585	0.34	0.21	
1596 m	0.44	0.28	1606	0.37	0.23	
2900 w	0.98	0.34	2920	0.79	0.27	ν_{CH}(CH$_2$)
2927 m	1.28	0.44	2961	0.93	0.31	
3020 w	0.77	0.25	3036	0.43	0.14	ν_{CH}(phenyl)
3058 w	0.64	0.21	3072	1.42	0.46	
3079 w	0.74	0.24	3092	0.71	0.23	

[a] From ref 24. [b] Alternative assignment suggested by a reviewer; see ref 35.

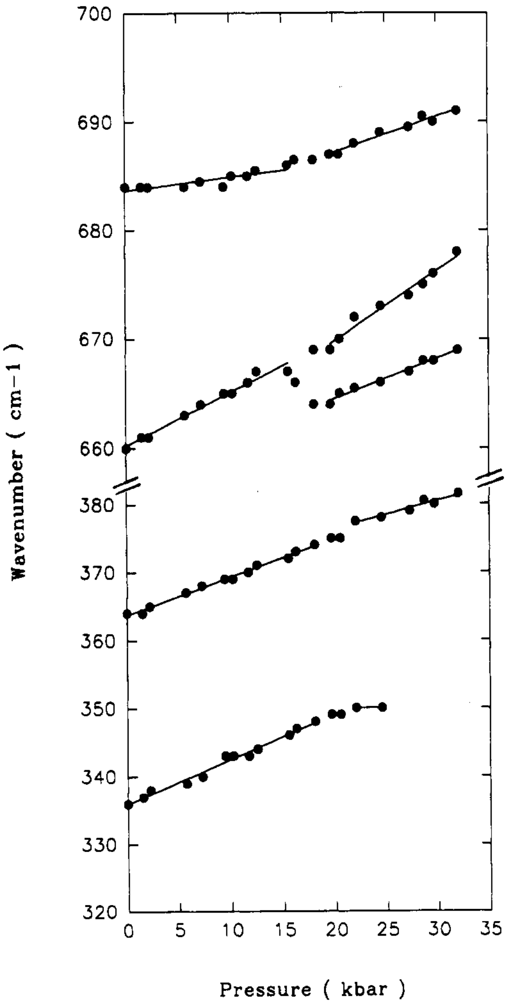

Figure 5. Pressure dependences of some of the observed Raman bands of *all-trans*-[Si(H)CH$_2$Ph]$_6$.

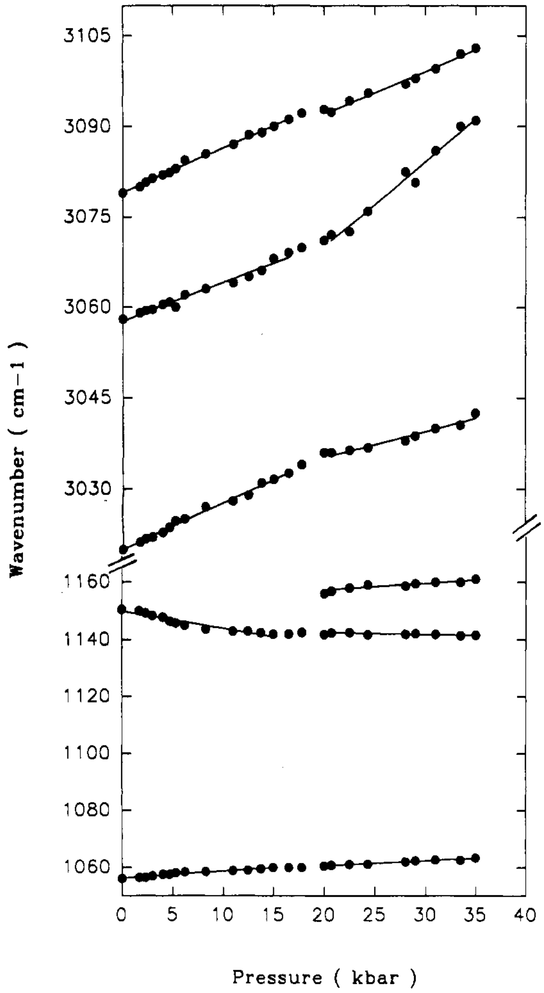

Figure 6. Pressure dependences of some of the observed IR bands of *all-trans*-[Si(H)CH$_2$Ph]$_6$.

different possible skeletal motions and side group rotations in poly(di-*n*-hexylsilane) and poly(silastyrene). The torsional barriers for rotation around the Si–Si bonds in poly(silastyrene) are ~1.2 kcal mol^{-1}, which can occur together with Ph side group rotations about the Si–C$_{ipso}$ axis. These side group rotations were varied from −40 to +40° in each of the skeletal rotational states so that the Ph groups could be placed in their minimum-energy positions. The observed dν/dP values for ν_{SiSi}, ν_{SiH}, and ν_{SiC} indicate that the compressibility of the skeletal framework of [Si(H)CH$_2$-

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$Ph]_6$ is high and that the density of the crystal increases dramatically with increasing pressure. The structure of the crystal under high pressure may be influenced by close-packing effects resulting from the higher crystal density. In general, face-to-face molecular packing in stacks is favored for many large planar molecules since such stacking arrangements maximize the dispersion forces between planar molecules which have delocalized π-electron frameworks.[29] The larger thermal motions of the CH_2Ph groups, the lower crystal density, and the larger volume difference between a H atom and a CH_2Ph substituent at ambient pressure, together with the comparatively smaller rotational barriers for the silicon backbone, apparently permit some benzyl group rotation under high pressure. When the applied pressure is sufficiently high to overcome the rotational barriers in the crystal, a rearrangement of the planar side groups may take place leading to a pressure-induced phase transition.

Most internal vibrational modes of molecular crystals have $d\nu/dP$ values that are less than 1.0 cm^{-1}/kbar, while values of 1–3 cm^{-1}/kbar are typical for external modes.[30] In almost every case, the internal and external modes are blue-shifted (i.e., shifted to higher wavenumbers) when compared to the band positions at ambient pressure. Similar $d\nu/dP$ values and behavior were found for the internal vibrational modes of 1 in our work. No Raman data could be obtained for the external modes because they were obscured by the strong fluorescence background of the diamonds in the dac. On the basis of the $d\nu/dP$ (and associated $d \ln \nu/dP$) values, shown in Tables IV and V for the Raman and IR spectra, respectively, the low-pressure phase of 1 is apparently more compressible than is the high-pressure one.

There are two bands in the ν_{SiH} region of the Raman spectrum at 2104 (w) and 2078 (s) cm^{-1} and two bands in the IR spectrum at 2096 (w) and 2075 (s) cm^{-1}.[24] Although the differences between these band positions are quite small (8 and 3 cm^{-1}, respectively), the bands are clearly not coincident, in agreement with the proposed D_{3d} local symmetry of the silicon ring for which two Raman-active (a_{1g} + e_g) and two IR-active (a_{2u} + e_u) ν_{SiH} modes are predicted. Unfortunately, because of the low solubility of 1 in common organic solvents at room temperature, detailed assignments for the ν_{SiH} modes are not possible, but it is reasonable to assume that the stronger Raman peak at 2078 cm^{-1} is the a_{1g} ν_{SiH} mode, while the weaker one at 2104 cm^{-1} is the e_g ν_{SiH} mode. High-pressure Raman measurements were performed only on the a_{1g} ν_{SiH} mode. No high-pressure IR measurements were possible for the ν_{SiH} modes because the bands were completely masked by a strong absorption in the 2200–1800-cm^{-1} region, due to the diamonds in the dac.

The Raman-active a_{1g} ν_{SiH} mode at 2078 cm^{-1} and the ν_{SiSi} mode tentatively assigned to a band near 336 cm^{-1} have much larger $d\nu/dP$ values in the low-pressure phase than do the corresponding ν_{CH} and ν_{CC} modes in cyclohexane (1.47 vs 0.85 and 0.66 vs 0.35 cm^{-1}/kbar, respectively).[31,32] According to Sherman and Wilkinson,[33] in a completely harmonic approximation, where the force constant operating between any two masses is truly a constant and is independent of the distance between the masses, the application of pressure would cause no observable frequency shift effects at all. Thus, the study of pressure-induced frequency changes is the study of the anharmonicity of atomic or molecular interactions. All force constants can be expected to show significant anharmonicity for even very small changes in bond length. Consequently, the larger $d\nu/dP$ values observed in our work for the ν_{SiH} and ν_{SiSi} vibrations of 1, compared to the values for the corresponding ν_{CH} and ν_{CC} vibrations of cyclohexane, suggest that the SiH and SiSi bonds are affected more by high pressures than are CH and CC bonds, and that the SiH and SiSi bonds are more anharmonic in this particular case.

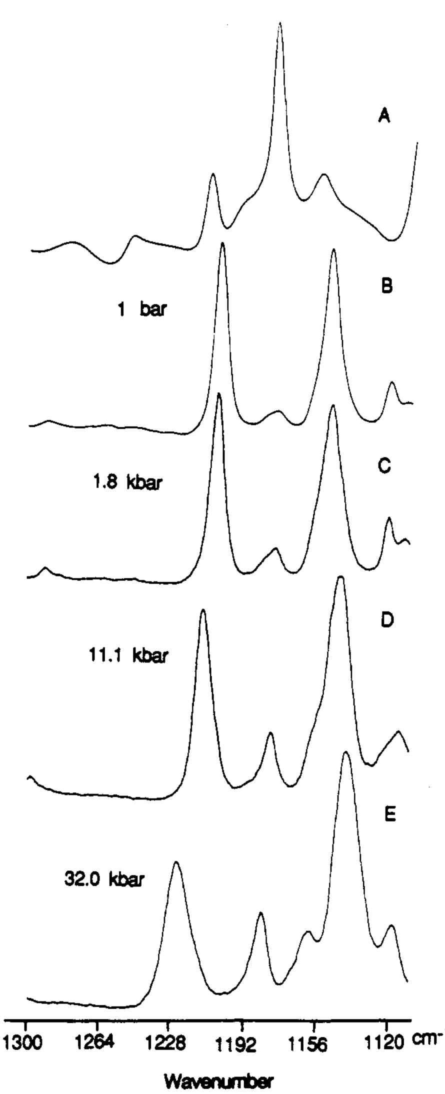

Figure 7. IR spectra of (A) toluene at ambient pressure and (B–E) *all-trans*-$[Si(H)CH_2Ph]_6$ at 1 bar, 1.8 kbar, 11.1 kbar, and 32.0 kbar.

The high-pressure data for most of the vibrational modes associated with the CH_2Ph groups are normal. Coffer and co-workers[34] have shown that the pressure dependences of certain IR-active vibrational modes in a series of hydrocarbon ligands bonded to a triosmium metal carbonyl

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framework decrease in the order CH stretching > CC stretching > CH bending. From Table V, the dν/dP values for the vibrational modes of the benzyl groups in 1 follow a similar order: C$_{sp^3}$H stretching > C$_{aromatic}$H stretching > CC stretching > CH bending.

The relative intensities of the two IR-active β_{CH}(phenyl) modes of 1 at 1204 and 1177 cm^{-1} are reversed from those for the related modes in toluene (Figure 7). The increased intensity of the 1204-cm^{-1} band may possibly be due either to a solid-state effect or to accidental overlap with the first overtone of the δ_{SiH} mode (602 cm^{-1}). The dν/dP value for the 1204-cm^{-1} band is approximately 3 times greater than is that for the 1177-cm^{-1} band. Application of pressure leads to an increase in the intensity of the 1177-cm^{-1} band compared to that of the 1204-cm^{-1} band.

Conclusions

Single-crystal X-ray diffraction has confirmed the *all-trans* stereochemistry of the benzyl groups in 1. In addition, an analysis of the IR and Raman spectra of 1 under high pressures has shown that there is a pressure-induced phase transition at 20 ± 1 kbar and that the benzyl groups rotate in the solid state. Furthermore, the larger dν/dP values for the ν_{SiH} and ν_{SiSi} modes in the low-pressure phase of 1 compared to the values for the ν_{CH} and ν_{CC} modes of cyclohexane suggest that in this particular case the SiH and SiSi bonds are more anharmonic than are the corresponding CH and CC bonds. High-pressure vibrational spectroscopy is clearly a useful method for studying the effects of high external pressures on the geometrical conformations of organosilicon compounds.

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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