Microwave Spectrum of Propyl Silane

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The microwave spectra of propyl silane and its four deuterated species were measured. The structure of the antiperiplanar isomer was so obtained as to reproduce the observed moments of inertia. The dipole moment and its direction were determined by Stark-effect measurements of several low J transitions.

In continuation of studies on the molecular structures of organosilicone molecules such as allyl silane[1] and ethyl fluorosilane,[2] the antiperiplanar isomer of propyl silane has been investigated by means of microwave spectroscopy.

The infrared and Raman spectra of the molecule were obtained by Murata *et al.*[3] who gave evidence of the existence of two rotational isomers, the antiperiplanar and synclinal isomers, in the gaseous phase. According to their Raman spectra, the antiperiplanar isomer is more stable than the synclinal isomer in the liquid state. We expected the structure of the synclinal isomer to be adequate for comparing it with that of allyl silane, but the observed microwave spectra of the synclinal isomer were so weak that assignments were possible for only the antiperiplanar isomer. In the present paper, the structure and the dipole moment of the antiperiplanar isomer are discussed.

Experimental

Samples of propyl silane and its deuterated species $CH_3CH_2CH_2SiD_3$ were prepared by reducing propyl trichlorosilane with lithium aluminium hydride or deuteride in dibutyl ether. Samples of $CD_3CH_2CH_2SiH_3$, CH_3CD_2-CH_2SiH_3, and $CH_3CH_2CD_2SiH_3$ species were prepared by reacting appropriate propyl Grignard reagents with iodosilane.

The Grignard reagents were prepared in dibutyl ether from appropriate deuterated propyl bromides (98 atom % D, Merck Sharp & Dohme, Canada). Iodosilane was prepared by the method of Sternbach and MacDiarmid.[4]

The microwave spectra of the samples were measured in the region 8000—35000 MHz with a conventional Stark modulation spectrometer at the temperature of Dry Ice.

Results and Discussion

Microwave Spectra. The antiperiplanar isomer of propyl silane is a nearly prolate symmetric top molecule with the μ_a and μ_b-dipole moment components. However, the b-type transitions are actually very weak because of the smallness of the μ_b-dipole component. The observed frequencies of the transitions are given in Table 1. The rotational constants were obtained by a least-squares fit of all the observed frequencies with use of a rigid rotor formula modified by adding the first term of the centrifugal distortion $-d_J[J(J+1)]^2$. The results are given in Table 2.

Molecular Structure. The present data are not sufficient to determine the r_s structure by the substitution method. Only a part of the r_s coordinate values of the hydrogen atoms could be obtained from the solutions of the Kraitchman equations. They are given in Table 4.

In order to find a plausible structure of the molecule, five skeletal parameter values alone were adjusted so as to well reproduce the fifteen observed moments of inertia, the other parameter values being transferred from those of analogous molecules.

For the CCH_2SiH_3 part of the molecule, a set of parameter values was transferred from those of ethyl silane.[5] Since the reported parameter values of the methyl group for propane[6] gave a slightly asymmetric group, the parameter values were so corrected as to give a symmetric methyl group before the transfer of the values to the CH_3C part of our molecule.

As regards the parameter values of the CCH_2C part, r(CH) and α(HCC) values were transferred from those of the corresponding parameter values of the methyl group in ethyl silane. Since the α(CCC) value to be adjusted was related closely to the other five angle values, the change of α(CCC) was compensated by the change of α(HCH). The parameter values are given in Table 3.

When the r_s structure of a molecule is well established, the differences between the observed and calculated moments of inertia are small positive values and approximately constant for all the measured species. This was taken into consideration for the adjustment of the skeletal parameter values.

The differences between the observed and calculated moments of inertia (Table 2) are considered to be as small as those usually obtained from the r_s structure. The coordinate values of the hydrogen atoms calculated from the set of the skeletal parameter values reproduce the r_s coordinate values (Table 4).

The present set of skeletal parameter values can be regarded as the best set but their reliability cannot be shown clearly since the ambiguity arising from the transfer of the parameter values between molecules prevents estimation of the definite reliability of the values obtained.

However, even when maximum uncertainty is assumed, the r(CC) value of the CH_3C group is greater than that of propane, and the r(CC) value of the CH_2CSi group smaller than that of ethyl silane. The r(SiC) value is much greater than those of methyl silane[7] (1.8668 Å) and ethyl silane (1.866 Å).

The angle values are almost equal to those of the corresponding angle values for analogous molecules.

Dipole Moment. The dipole moments were determined by Stark-effect measurements of six low J transitions for the antiperiplanar isomers of propyl

Table 1. Observed frequencies of propyl silane (MHz)[a)]

	$CH_3CH_2CH_2SiH_3$	$CH_3CH_2CH_2SiD_3$	$CD_3CH_2CH_2SiH_3$	$CH_3CD_2CH_2SiH_3$	$CH_3CH_2CD_2SiH_3$
$2_{11}\leftarrow1_{10}$	8922.47(−8)	8291.30(−5)	8008.37(−9)	8782.71(−5)	8848.24(1)
$2_{02}\leftarrow1_{01}$	8826.73(−9)	8210.08(−4)		8680.83(−2)	8740.07(0)
$2_{12}\leftarrow1_{11}$	8731.83(−2)	8129.63(5)		8580.04(7)	8633.08(−1)
$3_{13}\leftarrow2_{12}$	13097.48(−3)	12194.14(10)	11783.68(0)	12869.62(2)	12949.23(−1)
$3_{03}\leftarrow2_{02}$	13239.20(−4)	12314.27(−4)	11897.12(−4)	13019.95(−2)	13108.59(−3)
$3_{12}\leftarrow2_{11}$	13383.52(−3)	12436.80(1)	12012.53(4)	13173.77(−2)	13271.98(2)
$4_{14}\leftarrow3_{13}$	17462.82(−2)	16258.38(−2)	15711.24(3)	17158.84(1)	17264.93(1)
$4_{04}\leftarrow3_{03}$	17650.40(−7)	16417.42(−1)	15861.55(−1)	17357.53(0)	17475.38(1)
$4_{13}\leftarrow3_{12}$	17844.20(−2)	16581.92(−2)	16016.30(1)	17564.36(−3)	17695.15(−5)
$5_{15}\leftarrow4_{14}$	21827.72(−1)	20322.29(0)	19638.43(0)	21447.52(2)	21580.06(8)
$5_{05}\leftarrow4_{04}$	22060.04(−9)	20519.16(1)	19824.77(−5)	21692.95(−4)	21839.76(3)
$5_{14}\leftarrow4_{13}$	22304.47(2)	20726.73(3)	20019.79(1)	21954.44(0)	22117.80(−1)
$6_{15}\leftarrow5_{14}$	26764.19(7)	24871.04(6)	24022.87(0)	26343.75(−2)	26539.61(1)
$6_{06}\leftarrow5_{05}$	26467.79(−2)	24619.16(4)	23786.62(−5)	26025.84(−2)	26201.15(3)
$6_{16}\leftarrow5_{15}$	26192.07(−2)	24385.67(−5)	23565.27(0)	25735.52(3)	25894.31(3)
$7_{17}\leftarrow6_{16}$	30555.90(9)	28448.58(−1)	27491.73(7)	30022.71(4)	30207.75(9)
$7_{07}\leftarrow6_{06}$	30873.21(9)	28717.04(5)	27746.81(−1)	30355.63(−3)	30558.98(4)
$7_{16}\leftarrow6_{15}$	31223.25(13)	29014.73(5)	28025.51(3)	30732.27(4)	30960.47(5)
$8_{17}\leftarrow7_{16}$		33157.76(8)	32027.57(4)	35119.73(5)	
$8_{08}\leftarrow7_{07}$		32812.50(9)	31705.04(4)	34681.80(8)	
$8_{18}\leftarrow7_{17}$		32510.86(4)	31417.58(7)	34309.01(9)	
$1_{10}\leftarrow1_{01}$	17905.89(−8)			15148.35(−3)	14845.45(−3)
$2_{11}\leftarrow2_{02}$	18001.72(2)	14468.83(1)	16023.66(−10)	15250.24(−4)	14953.58(−6)
$3_{12}\leftarrow3_{03}$	18145.96(−5)	14591.29(−1)	16139.03(−6)	15404.04(−6)	15116.97(−1)
$4_{13}\leftarrow4_{04}$	18339.73(−2)	14755.80(−9)	16293.78(−4)	15610.98(1)	15336.81(0)
$5_{14}\leftarrow5_{05}$	18584.15(8)	14963.33(−2)	16488.81(3)	15872.46(5)	15614.90(2)
$6_{15}\leftarrow6_{06}$	18880.35(−4)	15215.23(2)	16725.03(5)	16190.39(6)	15953.40(3)
$7_{16}\leftarrow7_{07}$	19230.46(7)	15512.93(3)	17003.67(3)	16567.03(7)	16354.90(5)
$8_{17}\leftarrow8_{08}$	19636.07(3)	15858.20(3)	17326.23(6)	17004.98(7)	16822.35(6)
$9_{18}\leftarrow9_{09}$	20099.58(2)	16253.02(3)	17694.20(3)	17507.10(−1)	17359.06(2)
$10_{19}\leftarrow10_{010}$	20623.36(−3)	16699.60(3)	18109.38(−4)	18076.74(−2)	17968.71(−4)
$2_{12}\leftarrow1_{01}$		22436.35(7)			
$3_{13}\leftarrow2_{02}$	30813.12(−5)	26420.25(−4)		27815.58(−12)	27580.08(−8)
$4_{14}\leftarrow3_{03}$		30364.30(−9)	31392.61(−6)	31954.45(−11)	31736.34(−12)
$5_{15}\leftarrow4_{04}$		34269.10(−14)			
$6_{06}\leftarrow5_{15}$	9314.03(12)	10869.02(−1)	8441.94(−1)	11674.33(1)	
$7_{07}\leftarrow6_{16}$	13994.91(−3)	15200.40(10)	12623.52(3)	16294.44(1)	16864.39(−5)
$8_{08}\leftarrow7_{17}$	18714.77(−3)	19564.04(−9)	16836.83(−1)	20953.44(−4)	21569.29(−12)
$9_{09}\leftarrow8_{18}$	23471.07(−5)	23958.26(−11)	21080.21(−5)	25648.28(−2)	
$10_{010}\leftarrow9_{19}$	28261.17(−5)	28380.61(−3)	25351.78(−5)	30375.26(−10)	

a) Figures in parentheses indicate the deviation of the observed frequency from the calculated one attached to the last significant figures.

Table 2. Rotational and centrifugal distortion constants of propyl silane[a)] (MHz) and moments of inertia (amu·Å^2)[b)]

	$CH_3CH_2CH_2SiH_3$	$CH_3CH_2CH_2SiD_3$	$CD_3CH_2CH_2SiH_3$	$CH_3CD_2CH_2SiH_3$	$CH_3CH_2CD_2SiH_3$
A	20065.10 (23)	16399.77 (20)	17892.13 (18)	17268.03 (20)	16976.86 (20)
B	2254.478(13)	2093.062(11)	2021.186(9)	2221.042(11)	2238.955(12)
C	2159.131(16)	2012.176(12)	1944.914(12)	2119.647(14)	2131.382(13)
$d_J\times10^3$	0.57 (14)	0.40 (12)	0.39 (9)	0.49 (11)	0.45 (19)
$I_a(\Delta I_a)$	25.1868(0.0462)	30.8160(0.0125)	28.2457(0.0143)	29.2666(0.0625)	29.7685(0.0375)
$I_b(\Delta I_b)$	224.1654(0.3359)	241.4530(0.3395)	250.0393(0.4535)	227.5400(0.3226)	225.7200(0.3022)
$I_c(\Delta I_c)$	234.0645(0.2444)	251.1589(0.1886)	259.8449(0.3628)	238.4246(0.2295)	237.1118(0.1817)

a) Figures in parentheses indicate the uncertainties calculated from 2.5 times standard deviations attached to the last significant figures. b) Figures in parentheses indicate the difference between the observed and calculated moments of inertia. $\Delta I_g=I_g(\text{obsd})-I_g(\text{calcd})$.

Table 3. Sturctural parameters of propyl silane and related molecules[a)]

	$CH_3CH_2CH_2SiH$	$CH_3CH_2CH_3$	$CH_3CH_2SiH_3$
CH_3C group			
r(CC) (Å) (adjusted)	1.534	1.526	
$r(CH_s)$ (Å)	1.094	1.089	
$r(CH_a)$ (Å)	1.094	1.094	
$\alpha(H_sCC)$	110° 8′	111°48′	
$\alpha(H_aCC)$	110° 8′	110°36′	
$\alpha(H_sCH_a)$	108°48′	108° 6′	
$\alpha(H_aCH_a)$	108°48′	107°18′	
CCH_2C group			
r(CC) (Å) (adjusted)	1.528	1.526	1.540
r(CH) (Å)	1.093	1.096	1.093
α(CCC) (adjusted)	112°10′	112°24′	
α(HCC)	109°34′	109°34′	111° 2′
α(HCH) (balanced)	106°20′	106° 6′	106°59′
CCH_2Si group			
r(SiC) (Å) (adjusted)	1.886		1.866
r(CH) (Å)	1.097		1.097
α(CCSi) (adjusted)	113°11′		113°11′
α(CCH)	110°10′		110°10′
α(HCSi)	108°46′		108°46′
α(HCH)	105°46′		105°46′
SiH_3 group			
$r(SiH_s)$ (Å)	1.483		1.483
$r(SiH_a)$ (Å)	1.480		1.480
$\alpha(H_sSiC)$	110° 3′		110° 3′
$\alpha(H_aSiC)$	110° 3′		110° 3′
$\alpha(H_aSiH_s)$	109° 9′		109° 9′
$\alpha(H_aSiH_a)$	108°20′		108°20′

a) (adjusted) indicates the parameter value which was adjusted and (balanced) indicates the parameter value used as the balance of the change of the adjusted parameter value.

Table 4. Coordinate values for hydrogen atoms (Å)

Atom		r_s[a)]	Model[b)]
$H_a(CH_3)$[c)]	x_c	±0.885	±0.890
$H(CCH_2C)$	x_a	−0.960	−0.965
	x_b	1.142	1.141
	x_c	±0.877	±0.874
$H(CCH_2Si)$	x_a	−0.071[d)]	−0.165
	x_b	−1.245	−1.249
	x_c	±0.876	±0.873
$H_a(SiH_3)$[c)]	x_c	±1.203	±1.200

a) Solved by the Kraitchman equation. b) Obtained from the structure given in Table 3. c) H_a indicates the hydrogen atom located out of the symmetry plane. d) This Kraitchman coordinate value is unreliable because of the smallness of the absolute value.

silane and its two deuterated sepcies ($CH_3CH_2CH_2SiD_3$ and $CH_3CD_2CH_2SiH_3$). The spectrometer was calibrated with OCS[8)] on the measurements. The results are given in Table 5.

The dipole moment of the $CH_3CH_2CH_2SiH_3$ species is slightly larger than that of the $CH_3CH_2CH_2SiD_3$ species though 99% reliability intervals of the dipole moments for these species slightly overlap each other. Thus the silyl group is considered to be situated at the side of the negative pole of the dipole moment.[9)]

There are two possible directions for the dipole moment (Table 5), making angles of i) 5°46′ and ii) 143°54′ with the SiC bond, respectively. The angle between the b-inertial axis and the SiC bond of the $CH_3CD_2CH_2SiH_3$ species is smaller by ca. 40′ than that of the $CH_3CH_2CH_2SiH_3$ species. The angle of $\alpha((C\text{–}Si)\times\mu)$ for the $CH_3CH_2CH_2SiH_3$ and $CH_3CD_2CH_2SiH_3$ species agree with each other within experimental error for i), and disagree beyond experimental error for ii).

The dipole moment of the antiperiplanar isomer of propyl silane is thus concluded to incline by 5°46′ from the SiC bond towards the SiH bond in the symmetry plane.

The dipole moment of the antiperiplanar isomer of propyl silane (0.811 D) is close to that of ethyl silane (0.81 D),[5)] larger than that of methyl silane (0.7351 D).[9)] The angle between the dipole moment and the SiC bond is much larger than that for ethyl silane (1°18′).

Spectra due to the Excited Vibrational States. Several groups of spectra attributable to those in the excited vibrational states can be found around the ground state lines. Among them, the group of spectra

TABLE 5. DIPOLE MOMENTS AND STARK COEFFICIENTS OF PROPYL SILANE[a)]

		$CH_3CH_2CH_2SiH_3$		$CH_3CH_2CH_2SiD_3$		$CH_3CD_2CH_2SiH_3$	
Stark coefficient $(\Delta\nu/E^2)$[b)]							
	|M|	obsd	calcd	obsd	calcd	obsd	calcd
$2_{02}\leftarrow1_{01}$	0	−0.539(16)	−0.542	−0.561(8)	−0.562		
	1	0.441(4)	0.441	0.467(4)	0.454	0.437(3)	0.440
$2_{12}\leftarrow1_{11}$	0	0.450(2)	0.447	0.484(6)	0.484	0.466(5)	0.476
$2_{11}\leftarrow1_{10}$	0	0.435(4)	0.443	0.455(3)	0.446	0.437(5)	0.432
$2_{03}\leftarrow2_{02}$	0					−0.137(1)	−0.137
	1			−0.059(1)	−0.059	−0.063(1)	−0.063
	2	0.168(1)	0.166	0.162(2)	0.156	0.152(0)	0.149
$3_{13}\leftarrow2_{12}$	0	−1.498(18)	−1.496			−0.137(1)	−0.137
	1			1.379(12)	1.413	1.119(6)	1.136
$3_{12}\leftarrow2_{11}$	0					−0.024(0)	−0.025
	1	−1.248(14)	−1.306	−1.452(6)	−1.476	−1.179(8)	−1.203
Dipole moment (Debye)							
μ_a		0.783(7)		0.766(8)		0.776(6)	
μ_b		0.212(8)		0.215(22)		0.227(4)	
μ_{total}		0.811(8)		0.796(10)		0.809(6)	
$\alpha(\mu\times b)$[c)]		74°50′(45′)		74°20′(1°53′)		73°40′(25′)	
$\alpha((C\text{-}Si)\times\mu)$[d)]		5°46′ or 143°54′		5°05′ or 143°35′		5°14′ or 142°02′	
$\alpha(b\times(C\text{-}Si))$[e)]		69°01′		69°12′		68°24′	

a) Figures in parentheses indicate the uncertainties calculated from 2.5 times standard deviations attached to the last significant figures. b) In 10^{-5} MHz $(cm/V)^2$ unit. c) The angle between the dipole moment and the b-inertial axis. d) The angle between the dipole moment and the C-Si bond. e) The angle between the b-inertial axis and the C-Si bond.

predictable by the rotational constants (A, B, C)= (19700, 2251, 2158) MHz for the normal species were assigned to that arising from the first excited skeletal torsional state. Actually, rough measurements of the relative intensity of the spectra gave the vibrational frequency of *ca.* 100 cm^{-1} which is close to the observed Raman frequency (102 cm^{-1}) in the liquid state for the $CH_3CH_2CH_2SiD_3$ species.[3)]

Assignments of the spectra attributed to those of the excited CH_3 and SiH_3 torsional states were attempted in order to evaluate the barrier to internal rotation of the CH_3 and SiH_3 groups. However, we have found no spectra with reasonable splittings.

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