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The Microwave Spectrum of *trans*-Ethylmethylsilane

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The microwave spectra of $CH_3CH_2SiH_2CH_3$ and $CH_3CH_2SiD_2CH_3$ in the *trans* form were studied. The rotational constants calculated from the spectra can be explained satisfactorily with a model which has structural parameters transferred with only a slight modification, from the values reported for dimethylsilane and ethylsilane. From the observed splittings of the spectra, the barrier to the internal rotation of the $SiCH_3$ group was calculated to be 1520 ± 30 cal/mol, assuming that the coupling effect of the torsional motions of the other groups can be ignored. From the Stark shifts, the dipole moment was determined to be $\mu_a = 0.036 \pm 0.030$, $\mu_b = 0.757 \pm 0.003$, and $\mu_{total} = 0.758 \pm 0.005$ D, making an angle of 2°44′ with the *b* axis for the parent species, while it was determined to be $\mu_a = 0.024 \pm 0.030$, $\mu_b = 0.758 \pm 0.003$, and $\mu_{total} = 0.758 \pm 0.005$ D, making an angle of 1°49′ with the *b* axis for the deuterated species. From these results, the orientation of the dipole moment in the molecule was concluded to be along the direction slightly inclined from the bisector of the CSiC angle toward the ethyl group in the molecule.

Ethylmethylsilane has been investigated by means of microwave spectroscopy as an expression of the current interest in rotational isomerism and in the barriers to internal rotation.

The infrared and Raman spectra of this molecule have also been previously investigated by one of the present authors[1]; they give evidence of the existence of two rotational isomers, which will be published separately. However, the observed microwave spectra were very weak, and assignments are possible for only the *trans* isomer at present.

Therefore, in the present paper, a brief consideration will be given of the structure, the barrier to the internal rotation of the $SiCH_3$ group, and the electric dipole moment of the *trans* isomer.

Experimental

The samples of $CH_3CH_2SiH_2CH_3$ and $CH_3CH_2SiD_2CH_3$ were prepared by the method of reacting CH_3CH_2MgBr with CH_3SiCl_3 in ethyl ether and by subsequently reducing the resultant $CH_3CH_2SiCl_2CH_3$ with $LiAlH_4$ or $LiAlD_4$ in *n*-butyl ether.[2]

The microwave spectra of the samples were measured in the region from 8000 to 36000 MHz with conventional sinu-

TABLE 1. OBSERVED MICROWAVE TRANSITION FREQUENCIES OF *trans*-$CH_3CH_2SiH_2CH_3$ AND $CH_3CH_2SiD_2CH_3$ (MHz)

Transition	$CH_3CH_2SiH_2CH_3$			$CH_3CH_2SiD_2CH_3$		
	ν_A[a]	ν_E[a]	$\Delta\nu$[c]	ν_A[a]	ν_E[a]	$\Delta\nu$[c]
$1_{10} \leftarrow 1_{01}$	12651.59[b]	12650.45	0.00	10230.24[b]	10229.48	−0.01
$2_{11} \leftarrow 2_{02}$	12895.12[b]	12893.67	0.00	10475.60[b]	10474.71	−0.02
$3_{12} \leftarrow 3_{03}$	13266.87[b]	13265.33	0.01	10851.74[b]	10850.77	0.01
$4_{13} \leftarrow 4_{04}$	13774.53	13772.91	0.04	11368.18	11367.11	0.06
$5_{14} \leftarrow 5_{05}$	14428.10	14426.47	0.06	12037.34	12036.25	0.14
$6_{15} \leftarrow 6_{06}$	15239.78	15238.05	0.02	12874.05	12872.87	0.14
$7_{16} \leftarrow 7_{07}$	16223.66	16221.95	−0.01	13895.02	13893.78	0.04
$8_{17} \leftarrow 8_{08}$	17394.92	17393.08	−0.07	15117.86	15116.53	−0.05
$9_{18} \leftarrow 9_{09}$	18769.16	18767.28	−0.23	16559.29	16557.94	−0.33
$10_{19} \leftarrow 10_{010}$	20361.34	20359.28	−0.65	18234.22	18232.72	−0.62
$1_{11} \leftarrow 0_{00}$	17578.12[b]	17576.10	0.02	15061.75[b]	15060.42	0.04
$2_{12} \leftarrow 1_{01}$	22504.58[b]	22502.84	−0.03	19893.14[b]	19892.08	−0.04
$3_{13} \leftarrow 2_{02}$	27312.40[b]	27310.78	0.01	24605.76[b]	24604.80	0.01
$4_{14} \leftarrow 3_{03}$	32005.82	32004.24	0.02	29205.52	29204.58	0.61
$4_{04} \leftarrow 3_{13}$	8805.49	8807.00	−0.01	10841.67	10842.55	−0.03
$5_{05} \leftarrow 4_{14}$	14390.11	14391.55	−0.17	16318.84	16319.72	−0.20
$6_{06} \leftarrow 5_{15}$	20051.50	20052.84	−0.39	21862.78	21863.60	−0.44
$7_{07} \leftarrow 6_{16}$	25773.80	25775.08	−0.80	27454.40	27455.20	−0.71
$8_{08} \leftarrow 7_{17}$	31539.72	31540.92	−1.15	33072.94	33073.60	−0.97

a) ν_A and ν_E designate the observed frequencies belonging to the "A" and "E" components of the doublets, respectively and estimated uncertainty of the frequencies is ±0.05 MHz.

b) The observed frequency used for the determination of the rotational constants by the least-squares technique.

c) $\Delta\nu$ = (the observed frequency of the "A" component of the doublet) − (the calculated frequency in the rigid rotor model).

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1) M. Hayashi, K. Ohno, and H. Murata, This Bulletin, **45**, 298 (1972).

2) F. S. Fipping, *Proc. Chem. Soc.*, **20**, 15 (1904); W. Dilthey, *Ber.*, **37**, 319 (1904); A. E. Finhalt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

TABLE 2. ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA OF *trans*-ETHYLMETHYLSILANE

	$CH_3CH_2SiH_2CH_3$	$CH_3CH_2SiD_2CH_3$
Observed rotational constants for the "A" sublevel (MHz)[a]		
A	15114.85±0.20	12645.98±0.20
B	2703.36±0.10	2656.80±0.10
C	2463.25±0.10	2415.73±0.10
Rotational constants for the unperturbed level (MHz)[b]		
A	15113.80	12645.30
B	2703.34	2656.79
C	2463.25	2415.73
Observed and calculated moments of inertia (amu·Å²)		

		Observed[c]	Model I	(δ)[d]	Model II	(δ)[d]
$CH_3CH_2SiH_2CH_3$	I_a	33.4381	33.4720	−0.10	33.4198	0.05
	I_b	186.9454	185.8801	0.57	186.7817	0.09
	I_c	205.1668	204.2243	0.46	205.0770	0.04
$CH_3CH_2SiD_2CH_3$	I_a	39.9656	40.0181	−0.13	39.9790	−0.03
	I_b	190.2209	189.1896	0.54	190.1100	0.06
	I_c	209.2026	208.2991	0.43	209.1837	0.01

a) The rotational constants were determined by the least squares technique from the observed frequencies of the following six transitions; $1_{11}\leftarrow 0_{00}$, $1_{10}\leftarrow 1_{01}$, $2_{11}\leftarrow 2_{02}$, $2_{12}\leftarrow 1_{01}$, $3_{12}\leftarrow 3_{03}$, and $3_{13}\leftarrow 2_{02}$.The root mean square deviations on the calculations were 0.016 and 0.024 MHz for the parent and deuterated species, respectively.

b) The unperturbed rotational constants were calculated by the formulas;
A (unperturbed)$=A$(A sublevel)$-F\alpha^2W_{0A}^{(2)}$, B(unperturbed)$=B$(A sublevel)$-F\beta^2W_{0A}^{(2)}$, C(unperturbed)$=C$(A sublevel)

c) The moments of inertia were calculated from the unperturbed rotational constants. Conversion factor; 505377 MHz/amu·Å².

d) Observed−calculated in %.

TABLE 3. STRUCTURE OF *trans*-ETHYLMETHYLSILANE[a]

Model I. Structural parameters transferred from those for $(CH_3)_2SiH_2$ and $CH_3CH_2SiH_3$.									
CH_3–(C)		–CH_2–		CH_3–(Si)		–SiH_2–		skeleton	
r(CH)	1.093 Å	*r*(CH)	1.097 Å	*r*(CH)	1.095 Å	*r*(SiH)	1.483 Å	*r*(CC)	1.540 Å
∠(H_sCC)	111°57′	∠(HCH)	105°46′	∠(H_sCSi)	110°56′	∠(HSiH)	107°50′	*r*(CH_2–Si)	1.867 Å
∠(H_aCC)	111°41′	∠(CCH)	109°28′	∠(H_aCSi)	110°56′	∠($HSiCH_2$)	109°30′	*r*(CH_3–Si)	1.867 Å
∠(H_sCH_a)	107°15′	∠(SiCH)	109°28′	∠(H_sCH_a)	108°	∠($HSiCH_3$)	109°30′	∠(CCSi)	113°11′
∠(H_aCH_a)	106°59′			∠(H_aCH_a)	108°			∠(CSiC)	110°59′
Model II. Structural parameters adjusted.									
∠(CCSi)	114°11′			∠($HCCH_3$)	109°13′			∠(SiCH)	109°13′
Other structural parameters remain unchanged.									

a) H_s and H_a designate the hydrogen atoms in the molecular plane and out of the plane, respectively.

soidal and square wave Stark modulation spectrometers at the temperature of dry ice.

Results and Discussion

Spectra and Structure of the Molecule. Although *b*- and *a*-type transitions are expected for *trans*-ethylmethylsilane, the observation of the *a*-type spectra was impossible because of the small dipole moment component along the *a* axis.

As is shown in Table 1, the observed *b*-type spectra are doublets resulting from the internal rotation of the $SiCH_3$ group.

The "A" components of the doublets can be explained by an asymmetric rotor model with the rotational constants of $A=15114.85$, $B=2703.34$, and $C=2463.25$ MHz for the parent species and of $A=12645.98$, $B=2656.80$, and $C=2415.73$ MHz for the deuterated species, with reasonable centrifugal distortion contributions.

These rotational constants were determined by the least-squares technique from the observed frequencies of the "A" components of the doublets for the following six transitions; $1_{11}\leftarrow 0_{00}$, $1_{10}\leftarrow 1_{01}$, $2_{12}\leftarrow 1_{01}$, $2_{11}\leftarrow 2_{02}$, $3_{12}\leftarrow 3_{03}$, and $3_{13}\leftarrow 2_{02}$.

From these rotational constants, the unperturbed rotational constants were calculated by subtracting the contributions due to the internal rotation for the "A" sublevel.

As is shown in Tables 2 and 3, the moments of inertia obtained from the unperturbed rotational constants can be explained by a model (Model I in Table 3) which has structural parameters transferred from the reported values for $(CH_3)_2SiH_2$[3] and $CH_3CH_2SiH_3$.[4] Furthermore, a very good agreement is obtained between the calculated and the observed moments of inertia if the CCSi angle is increased by about 1° from the original value and if the CCH and SiCH angles are decreased by about 15′ (Model II in Table 3). Although the models described above should be tested further by

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3) L. Pierce, *J. Chem. Phys.*, **34**, 498 (1961).

4) D. H. Petersen, Doctoral thesis, The University of Notre Dame (1961).

means of the observed rotational constants for other isotopic species which have not yet been measured, the agreement is so good and so reasonable that the structure of Model II may be proposed as the best structure for *trans*-ethylmethylsilane.

Internal Rotation of the $SiCH_3$ Group. The analysis of the fine structures of the observed spectra has been carried out by the principal-axis method.[5]

A preliminary analysis indicates that the doublet structures of the observed spectra originate mainly from the coupling of the over-all rotation and the internal rotation of the $SiCH_3$ group if the barriers are taken to be equal to the reported value for the similar molecules.

On the assumption that the coupling terms among the internal rotation of the $SiCH_3$ group, that of the CH_3CH_2 group and the skeletal torsion of the C–SiH_2–CH_2–C part of the molecule, can be neglected, the effective Hamiltonian for the v-th torsional state of the $SiCH_3$ group is given as;

$$H_{v\sigma} = H_r + F\sum_n W_{v\sigma}^{(n)}\mathscr{P}^n$$

$$H_r = AP_\mathrm{a}{}^2 + BP_\mathrm{b}{}^2 + CP_\mathrm{c}{}^2,\ \mathscr{P} = \alpha P_\mathrm{a} + \beta P_\mathrm{b}$$

$$\alpha = \lambda_\mathrm{a} I_\alpha / I_\mathrm{a},\ \beta = \lambda_\mathrm{b} I_\alpha / I_\mathrm{b}$$

$$F = \hbar^2/2rI_\alpha,\ r = 1 - \lambda_\mathrm{a}\alpha - \lambda_\mathrm{b}\beta$$

where I_α is the moment of inertia of the $SiCH_3$ group around the top axis and where the λ's are the direction cosines between the internal top axis and the principal axes of the entire molecule. σ stands for either the "A" or "E" sublevel.

I_α was calculated from the structural parameters of Model II, and the λ's were obtained on the assumption that the top axis coincides with the SiC bond.

According to the bootstrap method,[5] the perturbation coefficients, $W_{v\sigma}^{(n)}$, are simply proportional to a quantity, w_1, for a reasonably high barrier if the corrections due to the shape of the barrier are negligible.

By the least-squares technique, the w_1's were determined from the observed frequency splittings of the spectra, neglecting the terms higher than the fourth-order in the effective Hamiltonian for both parent and deuterated species. Then, the reduced barrier s's ($=4V_3/9F$) were obtained by the interpolation of the values of w_1 *vs.* s in the table.[6]

The barrier V_3's calculated from the interpolated s values are found to be 1522 and 1515 cal/mol, respectively, for the two species; the agreement between the two species is good within the limit of experimental error. The results are shown in Table 4.

As the analysis described above was made on the assumption that the coupling can be neglected among the torsional motion of the $SiCH_3$ group and those of the other groups, any comparison with the reported values for the similar molecules would be rather invalid. However, it is noticeable that the barrier of the $SiCH_3$ group in *trans*-ethylmethylsilane is lower than those of methylsilane[7] (1595 cal/mol), dimethylsilane[3] (1640 cal/mol), and trimethylsilane[8] (1830 cal/mol).

TABLE 4. OBSERVED AND CALCULATED SPLITTINGS ($\nu_A-\nu_E$) OF *trans*-ETHYLMETHYLSILANE (MHz)

Transition	$CH_3CH_2SiH_2CH_3$		$CH_3CH_2SiD_2CH_3$	
	Obsd	Calcd	Obsd	Calcd
$1_{10}\leftarrow 1_{01}$	1.14	1.11	0.76	0.73
$2_{11}\leftarrow 2_{02}$	1.45	1.44	0.89	0.94
$3_{12}\leftarrow 3_{03}$	1.54	1.54	0.97	1.01
$4_{13}\leftarrow 4_{04}$	1.62	1.60	1.07	1.06
$5_{14}\leftarrow 5_{05}$	1.63	1.66	1.09	1.11
$6_{15}\leftarrow 6_{06}$	1.73	1.72	1.18	1.17
$7_{16}\leftarrow 7_{07}$	1.76	1.79	1.24	1.23
$8_{17}\leftarrow 8_{08}$	1.84	1.86	1.33	1.31
$9_{18}\leftarrow 9_{09}$	1.88	1.95	1.35	1.39
$10_{19}\leftarrow 10_{010}$	2.06	2.04	1.50	1.49
$1_{11}\leftarrow 0_{00}$	2.02	2.04	1.33	1.30
$2_{12}\leftarrow 1_{01}$	1.74	1.73	1.06	1.11
$3_{13}\leftarrow 2_{02}$	1.62	1.64	0.94	1.05
$4_{14}\leftarrow 3_{03}$	1.58	1.59	0.94	1.02
$4_{04}\leftarrow 3_{13}$	−1.51	−1.52	−0.88	−0.94
$5_{05}\leftarrow 4_{14}$	−1.44	−1.44	−0.88	−0.88
$6_{06}\leftarrow 5_{15}$	−1.34	−1.36	−0.82	−0.82
$7_{07}\leftarrow 6_{16}$	−1.28	−1.29	−0.80	−0.75
$8_{08}\leftarrow 7_{17}$	−1.20	−1.21	−0.66	−0.69
R.M.S.[a]	0.02_4		0.04_4	
I_α (amu·Å^2)	3.1635		3.1635	
λ_a	0.8645		0.8562	
λ_b	0.5095		0.5166	
s	41.07		41.44	
V_3 (cal/mol)	1522±30		1515±30	

a) Root mean square deviation (MHz)

Dipole Moment. The electric dipole moments were quantitatively determined from Stark-effect measurements of $1_{11}\leftarrow 0_{00}$, $1_{10}\leftarrow 1_{01}$, and $2_{11}\leftarrow 2_{02}$ ($M=2$) transitions. For the deuterated species, very fast Stark shifts were found for $1_{11}\leftarrow 0_{00}$ and the $M=1$ lobe of $2_{11}\leftarrow 2_{02}$ transitions, since the energy levels of 1_{11}, 2_{02}, and 1_{10} are, accidentally in near degeneracy.

The spectrometer was calibrated with OCS[9] on the measurements.

The Stark shifts of the "A" and "E" components of the doublets were found to be essentially the same, and the averaged values were used for the calculations.

However, it was found that some of the observed Stark coefficients, $\Delta\nu/E^2$, show slight but regular variations with the field strength, E, beyond the limit of experimental error. This is probably due to the presence of the higher-order terms, since the second-order perturbation sums for the μ_a component are possibly considerably influenced by the contributions from the μ_b component as the field strength becomes stronger.

Considering the contributions from the higher-order terms as well as from the first-order term, which is especially significant for the $1_{11}\leftarrow 0_{00}$ transition of the deuterated species, the theoretical Stark shifts were calculated by the direct diagonalization of the energy

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[5] D. R. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959).

[6] M. Hayashi and L. Pierce, "Tables for the Internal Rotation Problem," Department of Chemistry, The University of Notre Dame, South Bend, Ind. (1961).

[7] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).

[8] L. Pierce and D. H. Petersen, *ibid.*, **33**, 907 (1960).

[9] J. S. Muenter, *ibid.*, **48**, 4544 (1968).

Table 5. Stark coefficients and dipole moments[a)]

Transition	Stark coefficient[b)] ($\Delta\nu/E^2$) $\times 10^5$(MHz/(V/cm)^2) Obsd	Calcd
$CH_3CH_2SiH_2CH_3$		
$1_{11}\leftarrow 0_{00}$ ($M=0$)	3.818	3.831
$1_{10}\leftarrow 1_{01}$ ($M=1$)	2.601	2.605
$2_{11}\leftarrow 2_{02}$ ($M=2$)	2.914	2.894
$\mu_a=0.036\pm0.030$, $\mu_b=0.757\pm0.003$		
$\mu_{total}=0.758\pm0.005$D		
The angle between the *b* axis and μ, 2°44′		
$CH_3CH_2SiD_2CH_3$		
$1_{11}\leftarrow 0_{00}$ ($M=0$)	−22.578	−22.911
$1_{10}\leftarrow 1_{01}$ ($M=1$)	3.082	3.096
$2_{11}\leftarrow 2_{02}$ ($M=2$)	3.541	3.522
$\mu_a=0.024\pm0.030$, $\mu_b=0.758\pm0.003$		
$\mu_{total}=0.758\pm0.005$D		
The angle between the *b* axis and μ, 1°49′		

a) The measurements were made on the recorder at five or six different field strengths in the range from 0 to 600 V/cm except the $1_{11}\leftarrow 0_{00}$ transition of the deuterated species for which the range was from 0 to 150 V/cm.

b) In order to simplify the table, the observed and theoretical Stark coefficients are shown, though the frequency shifts were actually used for the determination of the diplole moments. These coefficients are the averaged values of the quantities $\Delta\nu/E^2$ for different field strengths.

matrices instead of by the usual perturbation calculation.[10)] The energy matrices were truncated at the terms with $J=4$ and higher after the negligible influences of the truncation were confirmed.

Since more elaborate considerations are required for the application of the least-squares technique to this procedure, the dipole moments were determined by changing the magnitudes of the μ_a and μ_b components little by little until the minimum values of the $S=\sum_i(\Delta\nu_{i\text{obsd}}-\Delta\nu_{i\text{calcd}})^2$ quantity were obtained for each of the two species. The details of the procedures will be reported elsewhere.

As is shown in Table 5, the dipole moments were determined to be $\mu_a=0.036\pm0.030$, $\mu_b=0.757\pm0.003$, and $\mu_{total}=0.758\pm0.005$ D for the parent species, which makes an angle of 2°44′ with the *b* axis, while they were determined to be $\mu_a=0.024\pm0.030$, $\mu_b=0.758\pm0.003$, and $\mu_{total}=0.758\pm0.005$ D for the deuterated species which makes an angle of 1°49′ with the *b* axis.

The structural calculation indicates that the bisector of the CSiC angle makes angles with the *b* axis of 3°53′ for the parent species and 3°24′ for the deuterated species.

The values obtained from these observations lead to the conclusion that the orientation of the dipole moment of the molecule is along the direction making an angle of about 1°20′ with the bisector of the CSiC angle toward the ethyl group in the molecule.

As the reported value for dimethylsilane is 0.75 D[3)], the dipole moment of *trans*-ethylmethylsilane can be said to be equal to that for dimethylsilane.

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[10)] S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).