lapping of carbon and silicon π -orbitals. In line with this interpretation, the changes in moments from ethyl- to phenylhalogenosilanes decrease from the tri- to the monohalides for both the chloro and bromo compounds.

The moment of phenyltribromosilane, 2.36, is appreciably greater than that reported for tribromosilane, 0.79,⁵ revealing the very large polarizability (electron release) of the phenyl group. The replacement of a phenyl group by a hydrogen atom in diphenyl dibromosilane, and of two phenyl groups by two hydrogen atoms in triphenylbromosilane result in decreases in moment of 0.43 and 0.19, respectively. These relatively small changes suggest that these replacements relieve steric strains, permitting more favorable orientation of the benzene rings for π -orbital overlapping. A comparison of the moment observed for pmethoxyphenyltribromosilane with a calculated moment, gives evidence of resonance interaction between the p-methoxy and tribromosilyl groups. A value for the moment of this compound, assuming no resonance interaction, was calculated assuming⁶ an angle of 72° between the anisole (μ 1.2) and phenyltribromosilane moment vectors. This calculation leads to a value of 2.97, compared to the observed moment of 3.34. The difference, 0.37 *D*, indicates an appreciable contribution of the structure

to the *p*-methoxyphenyltribromosilane molecule.

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(5) G. L. Lewis and C. P. Smyth, THIS JOURNAL, 61, 3063 (1939). NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Molecular Structures of Mono-, Di- and Trimethylsilane¹

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The sector-microphotometer method has been applied to the electron diffraction study of mono-, di- and trimethylsilane. The results are summarized in Tables II and VI. Notable features are the precision of the Si-C bond length values and their significant increase (~ 0.015 Å.) in the series, as well as the approximate values determined for some of the interatomic vibrational amplitudes.

The wide range of values reported for Si–C bond lengths—Si(CH₃)₄ 1.888 \pm 0.02 Å.,³ Si₂(CH₃)₆ 1.90 \pm 0.02 Å.,⁴ Si(CH₃)₂Cl₂ 1.83 \pm 0.06 Å.,⁵ Si-(CH₃)₃Cl 1.89 \pm 0.03 Å.,⁶ Si(CH₃)₃CH₂Cl 1.88 \pm 0.04 Å.,⁷ methylbromosilanes 1.92 \pm 0.06 Å.,⁸ [(CH₃)₃Si]₂O 1.88 \pm 0.03 Å.,⁹ [(CH₃)₂SiO]₃ 1.88 \pm 0.04 Å.,¹⁰ carborundum 1.89 Å.¹¹—might suggest a considerable sensitivity of this bond length to the nature of the other atoms attached to the silicon atom although, to be sure, the more precise values all lie within 0.01 of 1.89 Å. The present electron diffraction study of the three methylsilanes affords a direct test of the effect of added methyl groups; it was the first study of molecular structure to be made in this Laboratory by the sector–microphotometer method.

Experimental

Preparation of the Silanes.—The corresponding methylchlorosilanes were treated with LiAlH₄ in ether in a manner

(1) From the Ph.D. dissertation of Arthur C. Bond, University of Michigan, 1951.

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(5) R. L. Livingston and L. O. Brockway, ibid., 66, 94 (1944).

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(10) E. H. weiter and S. H. Bauer, tota., 16, 42 (1950).
 (11) N. W. Thibault, Am. Mineral., 29, 249, 327 (1944); L. S.

(11) N. W. Inibalit, Am. Minerat., 29, 249, 521 (1944), Ramsdell, ibid., 29, 431 (1944); 30, 519 (1945). similar to that described 12 for the preparation of SiH4 from SiCl4

(4 - x) LiAlH₄ + 4Si(CH₃)_xCl_{4-x} \longrightarrow

4Si(CH₃)_x $H_{4-x} + (4-x)$ AlCl₃ + (4-x)LiCl; x = 1, 2 or 3 The volatile products were passed through AlCl₃ (which forms a stable, non-volatile etherate) and subjected to repeated fractional condensations until tensiometrically pure. Vapor density measurements checked the calculated values to within 0.5%, and straight line log p vs. 1/T plots of rough vapor pressure measurements (Table I) led to estimated boiling points of 6°, -19° and -57° , in agreement with the literature (9-10°, ¹³ - 20.1°¹⁴ and $-56.8°^{14}$).

Table I

VAPOR PRESSURES OF THE METHYLSILANES IN MILLIMETERS

	OF MLE	ACURY	
<i>t</i> , °C.	Si(CH3)3H	Si(CH ₂) ₂ H ₂	SiCH:H:
-78.5		30.0	244.0
-63.5	25.0	84.0	552.0
-32.0		411.0	
-22.6	233.5	664.0	
-13.5	334.0		
0.0	607.0		

The Sector-Microphotometer Method.—Our apparatus has been described by Bartell.¹⁵ An "r³" sector (a sector with the angular opening proportional to the cube of the radial distance from the center of the sector) mounted 8 mm. in front of the plate (medium-contrast lantern slide) was rotated at 1200 r.p.m. during the exposures. It covered the ranges 3 < s < 30 and 1 < s < 13 at the camera distances, 10 and 25 cm., used; the electron wave length was about 0.059 Å. Five photographs covering a range of exposure times and with maximum optical density usually

(12) A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, 69, 2692 (1947).

- (13) A. G. Taylor and B. V. de G. Walden, ibid., 66, 842 (1944).
- (14) Alfred Stock, Z. Elektrochem., 32, 341 (1926).
- (15) L. S. Bartell, Thesis, University of Michigan, 1951.

less than 0.7 were selected, for microphotometering, for each substance at each camera distance.

A spinning stage,¹⁶ which rotated at 1200 r.p.m., was fitted to the Leeds and Northrup microphotometer. The pen of the Speedomax recorder was set for zero optical density at an unexposed portion of the photograph by adjusting the incident light intensity and for infinite optical density by other appropriate adjustments. The entire pattern was scanned to obtain a symmetrical trace, once with this setting and again, to accentuate the oscillations, with the lowest part of the trace brought to zero by increasing the incident light. It was found that satisfactory "true" density readings could be obtained from the second trace by adding the difference in nominal density between the two traces as read at a particular point.

read at a particular point. Points at equal intervals from the center were marked off on each side of the trace, the corresponding optical densities read, and the symmetrical pairs averaged and added to the appropriate constant to obtain "true" densities. These were converted to intensities, by a method somewhat similar to the Karles',^{17b} and averaged over the five photographs.

Interpretation

The treatment of the data, similar for all three compounds and closely following the Karles' description,^{17a,b,c} will be detailed here only for trimethylsilane.

Curves A (10 cm.) and B (25 cm.) of Fig. 1 show the intensities plotted against s, and curve C shows the 10 cm. intensities as multiplied by const. \times (radius)^{1/1} to emphasize somewhat the outer features. The interpretation of these curves depends on the theoretical scattering function

$$I(s) = I_{at} + I_{mol}$$

$$I_{at} = I_{atomic} = \frac{kI_0N}{s^4} \sum_{i} (Z - F)_i^2 + S_i$$
(1)

$$I_{\text{mol}} = I_{\text{molecular}} = \frac{kI_0N}{s^4} \sum_{ij}' (Z - F)_i (Z - F)_j$$
$$\int_0^\infty P_{ij}(r) \frac{\sin sr}{sr} dr$$

in which $P_{ij}(r)$ represents the probability that atoms i and j shall lie the distance r apart. In order to emphasize the fluctuations of I_{mol} , we use the function

$$M(s) = \frac{I_{\text{mol}}}{I_{\text{at}}} = \sum_{i,j}' C_{ij} U_{ij} \int_0^\infty P_{ij}(r) \frac{\sin sr}{sr} dr \quad (2)$$

$$C_{ij} = Z_i Z_j / \sum_i Z_i (Z_i + 1) \text{ (independent of } s)$$

$$U_{ij} = \frac{(Z - F)_i (Z - F)_j}{\sum_i (Z - F)_k^2 + S_k} \frac{\sum_k Z_k (Z_k + 1)}{Z_i Z_j}$$

In practice there is always some extraneous scattering— $I(\text{background}) = I_{\text{at}} + I_{\text{ext}}$ —while experimentally only a multiple, ρI , of the total intensity is known; the function to be compared with M of eq. 2 is accordingly taken as

$$M_{\rm obsd} = \left(\frac{\rho I}{\rho (I_{\rm at} + I_{\rm ext})} - 1\right) \left(\frac{I_{\rm ext}}{I_{\rm at}} + 1\right) \quad (3)$$

which in practice is further simplified by the approximation that $((I_{ext}/I_{at}) + 1)$ is unity. The (16) I. L. Karle, D. Hoober and J. Karle, J. Chem. Phys., 15, 765L

(1947). (17) (a) I. L. Karle and J. Karle, *ibid.*, **17**, 1052 (1949); (b) J.

(17) (a) I. L. Karle and J. Karle, *ibid.*, **17**, 1052 (1949); (b) J. Karle and I. L. Karle *ibid.*, **18**, 957 (1950); (c) I. L. Karle and J. Karle, *ibid.*, **18**, 963 (1950).



Fig. 1.—Experimental and theoretical intensity curves for tri-, di- and monomethylsilane.

proportionality factor, ρ , includes the sector function, the (radius)^{1/2} factor, the sector calibration correction, etc. In principle, of course, ρ cancels out, and in the procedure actually followed it does not have to be explicitly determined: smooth background lines (the solid background curves of B and C of Fig. 1) are drawn in such a way as to cut off approximately equal adjacent areas and are used as an approximation to the term $\rho I_{\rm at} + \rho I_{\rm ext}$ in eq. 3. The continuous M_3 curve of Fig. 2, $\pi < s$ $< 10\pi$, was so obtained from B and C. Next, a



Fig. 2.—Radial distribution curves for the methylsilanes: A, curves preliminary; B, curves final (see text).

radial distribution curve is calculated from M_3 assuming¹⁸ $U_{ij}(s) = 1$.

$$P(r)/r = \sum_{i,j} C_{ij} P_{ij}(r)/r = \int_0^\infty s M(s) \sin sr \, \mathrm{d}s \quad (4)$$

This is modified in practical calculation to

$$f(r) = \sum_{0}^{s(\max)} sM(s) \exp(-l^2 s^2/2) \sin r s \Delta s \quad (5)$$

with M(s) read at intervals $\Delta s = \pi/10$ from M_3 for $\pi < s < 10\pi$ and from a suitable zeroth order theoretical intensity curve for $0 < s < \pi$, and with l chosen to make exp $(-l^2s^2/2)$ equal to 0.1 at $s = 9\pi$ (B curves and A curve for trimethylsilane in Fig. 2) and 0.5 at $s = 10\pi$ (A curves for mono- and dimethylsilane in Fig. 2).

The result, curve A for trimethylsilane (Fig. 2), provided equilibrium distance. r_{ij} , and root-meansquare vibrational amplitude, $l_{ij} = 1/2(\delta r_{ij}^2)^{1/2}$, values for arriving at a molecular model and a new theoretical curve, which was nearly identical to M_3 . Each peak of curve A for trimethylsilane in Fig. 2 was fitted to a Gaussian term^{17a} $B_{ij} \exp \left[-(r - r_{ij})^2/2\sigma_{ij}^2\right]$ by adjusting B_{ij} , σ_{ij} and r_{ij} ; and eq. 2, under the additional assumption $U_{ij}(s) = 1$, was correspondingly modified^{17a} to

$$M(s) = \sum_{ij} C_{ij} \exp \left[-l_{ij}^2 s^2/2 \right] \sin r_{ij} s/r_{ij} r \quad (6)$$

with $l_{ij}^2 + l^2 = \sigma_{ij}^2$. A punched card method^{17b} was used for the calculations.

On the basis of node positions in the new theoretical curve new background and M(obsd.) curves (shown as dashed portions in curves B, C and M_3 of Fig. 1) were drawn wherever necessary, and a new radial distribution curve (B for trimethylsilane in Fig. 3 was calculated, this time with the data for $0 < s < \pi$ supplied from the new theoretical intensity curve. The new radial distribution curve is different from (and superior to) the first chiefly in the inconsequential region below 1A, and although further improvements in the background line could no doubt be made, they would have little effect on our final results. First (A curves) and final (B curves) radial distribution curves for di- and monomethylsilane are also shown in Fig. 2. The A curve Fig. 2 for dimethylsilane is based upon the continuous line M_2 curve of Fig. 1 while the B curve is based upon the dashed M_2 curve. In the case of monomethylsilane it was found that background lines could be drawn through the experimental intensity curves less arbitrarily if these curves were multiplied by $r^{1/3}$ and M_1' of Figure 1 was obtained in this manner while M_1 was obtained from an experimental curve multiplied by the usual $r^{1/2}$ factor. The A curve Fig. 2 for monomethylsilane is based upon M_1 and the B curve upon M_1' .

The Gaussian components into which the radial distribution curves were resolved are shown dotted in Fig. 2; their areas are compared with the theoretical areas nZ_iZ_j/r_{ij} (*n* is the multiplicity of r_{ij} in Table II, which also summarizes the peak identifications, positions and widths. The agreement is generally very good and might perhaps be improved if the less important distances here ignored were taken into account. The l_{ij} , it will be noted, were assumed not to vary from compound to compound, as is reasonable and was verified for Si-C. The C-C, Si-C and C-H values were actually obtained from curve B for trimethylsilane; the Si-H_c value from curve B for dimethylsilane; and the Si-H and C-H_{Si} from curve B for monomethylsilane. These are our final l_{ij} values; our final bond length and bond angle values are given in Table VI.

TABLE II

SUMMARY OF RADIAL DISTRIBUTION DATA

	1::/	, (CH3)3S	iH	(C	H ₃) ₂ Si	H_2	(C	H3)Si	\mathbf{H}_{3}
Peak		100 3 r ^a	$A_c b$	A_0 ^c	100 r	Ae	A_0	100 r	Ac	A_{0}
C-H	72	109	495	493	109	330	338	109	165	174
Si-H	90	148	95		148	189	111	148	283	285
Si-C	62	187	1350	1350	186	903	903	186	452	452
Si-He	106	245	513	374	245	343	252	245	171	171
C-H _{8i}	110	270	67	97	272	88	107	270	-67	74
C-C	102	308	351	343	308	117	128		• • •	
^a Dis	stance	in Å.	° 10	nZ_iZ_j	r_{ij} .	° Ob	serve	ed p	eak	area
relativ	e to un	derline	ed valı	ıe.						

The general quality of the radial distribution curves inspires confidence in the results independently of theoretical intensity checks, especially since M_1 , M_2 and M_3 differ only rather subtly from each other and the simple diatomic curve. A complete correlation analysis of our data would obviously allow some refinement of our final results as well as a quantitative estimate of the limits of er-

⁽¹⁸⁾ This validity of this assumption has been critically investigated for the fluoromethanes by Clare Thornton, Thesis. University of Michigan, 1952. For these compounds $U_{ij}(s)$ is nearly unity at values of s greater than 5.

ror. While such an analysis was not made in this investigation a few theoretical intensity curves were calculated for models based on the radial distribution l_{ii} and bond length values and a rather wide range of bond angle values. C3v local symmetry was assumed for Si in mono- and trimethylsilane and for CH3 throughout, while C2V local symmetry for Si and tetrahedral HSiH bond angle were assumed in dimethylsilane. The H-H terms and the H-C terms dependent on internal rotation were omitted. The omission of the rotation-dependent H-C terms probably has some effect on the radial distribution results, at least for trimethylsilane, since Sheehan and Schomaker concluded,³ for Si-(CH₃)₄, that "models with opposed methyl groups are unsatisfactory and it seems certain that the methyl groups are indeed predominately stag-gered." It may also be noted that the nodal displacements of the final (dashed) M_3 curve from the original curve are everywhere of the same sign, except only at s = 4.2 and beyond s = 8, as would be predicted from the differences between Sheehan and Schomaker's complete "staggered"-methyl $Si(CH_3)_4$ curve, here presumed to be indicative of what would be correct for (CH₃)₃SiH, and their curve from which the rotation dependent terms had been omitted.¹⁹ Insofar as this particular point is significant the original M_3 curve, unaffected as it is by assumptions as to details of the molecular structure, would of course be the more nearly correct one.

The models of this series for which curves were calculated are listed in Table III together with the average deviations, for the maxima and minima, of the s_{calcd}/s_{obsd} values (R_{I}) and of the M_{calcd}/M_{obsd} values (R_{II}) from their respective means. The curves (shown as J_3 , J_2 and J_1 for tri-, di- and monomethyl, respectively, in Fig. 1) based in each case on the angle values suggested by the radial distribution curve, are uniformly best in regard to R_{II} (which we believe to be the more important criterion), are very close to best in regard to R_{II}^{20} and are regarded by us as confirming the radial distribution values; for these curves a full comparison of s values is presented in Table IV.

Examination of the data in Table III reveals that the radial distribution values for the C-Si-C angle in trimethylsilane is supported in the variation of both $R_{\rm I}$ and $R_{\rm II}$, and that of the CSiH angle in tri- and dimethylsilane by the variation of $R_{\rm I}$. An angle greater than the radial distribution value is suggested by the variation of $R_{\rm I}$ and $R_{\rm II}$ for the C-Si-C angle in dimethylsilane and of $R_{\rm II}$ for the CSiH angle in di- and trimethylsilane and the CSiC angle in trimethylsilane. $R_{\rm I}$ and $R_{\rm II}$ variation for monomethylsilane indicates that the SiCH angle may be larger than the tetrahedral value while variation of the CSiH angle in monomethylsilane has opposite effects on $R_{\rm I}$ and $R_{\rm II}$.

Any conclusions drawn from Table III of course imply an extreme reliance on the *relative* values of

(19) Private communication from Verner Schomaker.

(20) The M(obsd.) values are more sensitive than the s(obsd.) to errors in photographic calibration and drawing of the background lines. To make the R_{II} as significant as possible they were based on the limited region from max. 2 through max. 6, excluding max. 1 and min. 2 because of possible error in the fitting together of the 10 cm. and 25 cm. data and the outer features because the theoretical intensities were almost invariant among the curves calculated.

TABLE III

COMPARISON OF THEORETICAL AND EXPERIMENTAL IN-TENSITY CURVES

			(CH ₃):SiH	$(CH_3)_{2}$	SiH2	CH	3SiH3
Model	α^{0a}	<sich<sup>0</sich<sup>	R_{I}	R_{II}	R_{I}	$R_{\rm II}$	R_{I}	RII
J^b			34	100	18	57	42	95
Α	115	115	49	149	57	66	46	119
В	115	θt	60	111	29	46	69	134
С	115	105	74	143	84	104	99	221
D	θt	115	83	76	88	78	53	94
Е	θt	θt	43	93	39	72	43	119
F	θt	105	57	171	66	141	78	188
G	105	115	118	143	113	90	79	98
Η	105	θt	80	176	75	95	47	83
Ι	105	105	83	208	69	141	86	153
_			011	OTT	-00.0			1. 70

 $a_{\alpha} = \langle \text{CSiH} \text{ for CH}_3\text{SiH}_3, \langle \text{CSiC otherwise: } ^b\text{Best} \text{model: } 111^\circ, 109^\circ \text{ for (CH}_3)_3\text{SiH} \text{ and (CH}_3)_2\text{SiH}_2; 107^\circ, 109^\circ \text{ for CH}_3\text{SiH}_3 \cdot \theta t$: tetrahedral angle $109^\circ 28'$.

the radial distribution bond lengths. The actual reliability of these bond lengths could be determined only by the calculation of many additional theoretical curves in which not only the angle and bond length parameters but also the l_{ij} are varied. As a qualitative check of the effect of relative bond length variations in monomethylsilane eight additional theoretical curves were calculated covering the range 1.43 Å. \leq Si-H \leq 1.52 Å., 1.04 Å. \leq $C-H \leq 1.14$ Å. wth tetrahedral angles throughout and Si-C = 1.86 Å. All of these curves have higher R_{I} and R_{II} values than J_{1} and even though the difference is small for curves with C-H 1.14 Å. and Si-H 1.48 Å. or 1.52 Å. their over-all appearance is sufficiently different from the experimental curve in the region 10 < s < 50 to eliminate them as unsatisfactory models.

TABLE IV

Comparison of s₀ with Theoretical Curves from Radial Distribution Data

			LIGINI	DOILON	DAIA		
Mor	Min	Si(CI	H ₃) ₃ H	Si(C)	$H_3)_2H_2$	SiCI	H ₃ H ₃
wax.	win.	30	318/30	30	312/30	30	3 3 1 / 30
1		4 , 27	1.007	4.34	1.000	4.84	0.994
	2	5.65	1.006	5.87	1.000	6.28	1.010
2		7.70	1.000	7.79	0.996	7.76	1.004
	3	9.36	1.007	9.36	1.003	9.33	1.000
3		10.90	0.997	10.93	0.997	10.81	1.000
	4	12.32	1.000	12.41	1.000	12.47	0.992
4		14.20	0.996	14.20	0.996	14.07	1,000
	5	15.87	0.998	15.93	1.002	15.96	0.998
5		17.69	1.004	17.78	1.004	17.78	1.004
	6	19.42	1.007	19.54	1.002	19.57	1.002
6		20.92	1.000	21.05	1.000	21.17	0.999
	7	22.53	0.999	22.71	0.999	22.68	1.000
7		24.32	1.000	24.50	0.996	24.35	1.004
	8	26.08	0.999	26.17	1.002	26.33	0.994
8		27.77	0.998	27.87	1.000	28.12	.992
	9	29.22	1.003	29.53	1.000	29.85	.987
9		30.79	1.006	31.10	1.000	31.16	1.000
Avera	ıge		1.002		1.000		0.999
Avera	ige de	eviation	0.0035		0.0017		0.0042

The similarity of the M curves for the three compounds at large s values is virtually complete; it occurs, of course, because one term, Si–C, has the greatest weight nZ_iZ_j/r_{ij} by far and the least ampli-

tude, l_{ij} ,²¹ and it affords the simplest of three ways of deriving the Si–C lengths as summarized in Table V. It is interesting that CH₃SiH₃, with the smallest amount of Si–C scattering relative to C–H and Si–H (the other terms of comparatively small l_{ij} values), agrees least well with the diatomic curve as judged by the average deviations in Table V; (CH₃)₃SiH, which would be expected to agree best, is, however, intermediate.

TABLE V

Comparison of s_0 with Diatomic Curve. Summary of Si-C Values

Max.	Min.	1.86 Å.	Si(CH ₈) ₈ H Sc/S0	Si(CH ₈) ₂ H ₂ s _c /s ₀	SiCH ₂ H ₃ sc/so
	7	22.78	1.011	1.003	1.004
7		24.47	1.007	0.999	1.008
	8	26.17	1.004	1.000	0.994
8		27.87	1.003	1.000	.991
	9	29.56	1.012	1.001	.991
9		31.23	1.014	1.004	1.002
Aver	age		1.007	1.001	0.998
Aver	age devia	tion	0.004	0.002	0.006
Si-C, 1.86 \times s _c /s ₀			1.877	1.862	1.856
Si-C from Table IV			1.873	1.860	1.857
Si-C radial distribution			1.872	1.860	1.857

TABLE VI

SUMMARY OF BOND LENGTHS AND BOND ANGLES

	Si(CH ₂) ₂ H	Si(CH ₃) ₂ H ₂	SiCH ₂ H ₂
Si-C, Å.	1.873 ± 0.006	1.860 ± 0.004	1.857 ± 0.007
С-н, Å.	$1.09 \pm .02$	$1.09 \pm .02$	$1.09 \pm .02$
SiH, Å.	$1.48 \pm .02$	$1.48 \pm .02$	$1.48 \pm .02$
<c-si-c< td=""><td>$110 \pm 2^{\circ}$</td><td>$110 \pm 3^{\circ}$</td><td> <i></i></td></c-si-c<>	$110 \pm 2^{\circ}$	$110 \pm 3^{\circ}$	<i></i>
<si−c−h< td=""><td>$109 \pm 2^{\circ}$</td><td>$109.5 \pm 2^{\circ}$</td><td>$109.5 \pm 2^{\circ}$</td></si−c−h<>	$109 \pm 2^{\circ}$	$109.5 \pm 2^{\circ}$	$109.5 \pm 2^{\circ}$
<c-si-h< td=""><td></td><td>· · · · · · · · · · · · · · · ·</td><td>$107 \pm 2^{\circ}$</td></c-si-h<>		· · · · · · · · · · · · · · · ·	$107 \pm 2^{\circ}$

Discussion of Results

The smooth increase in Si–C bond length, from 1.857 Å. in CH₃SiH₃ to 1.888 in (CH₃)₄Si, on adding further CH₃ groups in the methylsilanes, is interesting and doubtless significant, but suitable experi-

(21) The l_{ij} values are plausible, least for Si-C and less for all the bonds than for any distances which depend both on bond stretching and bond-angle coupling, but of course need to be correlated in detail with relevant spectroscopic information. The value 0.062 Å. for l_{Si-C} , for example, may well be as much as a third too large (private communication from Verner Schomaker).

mental results for comparative discussion of other carbon bond lengths seem to be lacking. The other reported Si–C bond lengths appear to be too imprecise, and require reinvestigation; and similar series of molecules, such as ethane, propane, isobutane and neopentane, have shown no trend in bond length at all, although here again precise sector-microphotometer determinations might well be very profitable. The substitution of a further halogen atom for methyl or hydrogen, however, seems almost uniformly to decrease the halogen bond length.^{18,22}

The 1.48 Å. value found for the Si-H distance in this investigation is in fair agreement with the previously reported values—1.47 \pm 0.03 Å. in disilane,²³ 1.46 Å. calculated by Badger's rule,²⁴ and 1.45₆ Å. which Herzberg²⁵ calculates on the basis of Tindal, Straley and Nielson's^{26,27} infrared spectra work on silane. The prominence of the Si-H peak in the radial distribution curve for monomethylsilane suggests that a sector-microphotometer determination of SiH₄ might lead to a more precise value for this bond length.

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