data of Rank, Saksena and Shull,[16] of Siebert, and of Lippincott and Tobin were used for all molecules but $Sn(CH_3)_4$. The previous tentative assignment of a band at 1250 cm.$^{-1}$ to ν_{17} in $Si(CH_3)_4$ is inconsistent with the trends shown here. A strong, infrared band has been observed[16] at 863 cm.$^{-1}$ for this molecule and we believe it is better assigned to ν_{17} as indicated in Fig. 5. The other methyl rocking frequency ν_7 is very weak in all the molecules of this series and has not been assigned with certainty in any of them.

It should be noted that the nature of the atomic motions in ν_{17} and ν_{18} change when the central atom becomes light. In $C(CH_3)_4$ skeletal stretching and methyl rocking motions take place in both ν_{17} and ν_{18}. However, the present evidence suggests that ν_{18} is more methyl rocking than skeletal stretching and *vice versa* for ν_{17}.

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(16) D. H. Rank, B. D. Saksena and E. R. Shull, *Disc. Faraday Soc.*, **9**, 187 (1950).

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The Molecular Structure of Trisilylamine $(SiH_3)_3N$[1,2]

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The structure of trisilylamine has been studied by electron diffraction in the gas phase. Assuming the molecule to have trigonal symmetry, the Si_3N skeleton is found to be coplanar. The parameter values and limits of error are Si–N = 1.738 ± 0.020 Å., Si. . .Si = 3.005 ± 0.020 Å., Si–H = 1.54 ± 0.05 Å., ∠Si–N–Si = 119.6° to within 1.0°, $2a_{Si..Si} = \overline{l^2}_{Si...Si} - \overline{l^2}_{Si-N} = 0.0030 \pm 0.0014$ Å.[2] It appears likely that the coplanar bonding around the nitrogen atom occurs with only about 50% delocalization of the odd electron pair.

Professor A. B. Burg has called to our attention the interesting substance trisilylamine, which is a very weak electron donor in comparison with its analog trimethylamine, and in place of the ordinary Lewis acid-base type reaction with electron acceptors frequently undergoes disproportionation and exchange.[3] An attractive possible explanation of this different behavior is that relatively stable, unfilled d orbitals on the silicon atoms are conjugated with the unshared pair of electrons on the nitrogen atom, making the electrons less available for coördination with acceptor reagents. This conjugation would also, presumably, give rise to an increased nitrogen bond angle and an abnormally short Si–N bond distance, two points which could be readily checked by an electron diffraction investigation of the structure.

Experimental.—A sample of essentially pure trisilylamine was kindly supplied by Mr. Earnest A. Kuljian. The photographs were made and interpreted in the ways described in past reports from this Laboratory[4]; the electron wave length and the camera distance were about 0.06 Å. and 11 cm., respectively.

Results.—The radial distribution curve (Fig. 1) shows two strong peaks at 1.735 and 3.00 Å. These peaks are due to the bonded Si–N and non-bonded Si . . . Si interactions, and correspond to an average bond angle of 120°, *i.e.*, to a coplanar Si_3N skeleton.

Theoretical intensity curves were calculated for trigonally symmetrical models over the shape parameter ranges $1.694 \leqslant$ Si . . . Si/Si–N $\leqslant 1.734$ (corresponding to ∠Si–N–Si = 115.6 to 120.2°[5]) and $1.102 \leqslant$ Si–N/Si–H $\leqslant 1.218$. In addition, the vibrational amplitude factor $\exp(-a_{ij}q^2)$ for the Si . . . Si interactions was studied over the range $0 \leqslant a_{Si\,...\,Si} \leqslant 0.0003$. In all models the coefficient a_{Si-H} was given the value 0.00022, which is a reasonable value in view of general experience in these Laboratories. The effective value 1.25 was used for Z_H. In most models terms were included for only the Si . . . Si and the bonded interactions; the effect of the N–H interaction was tested and found to be negligible. Of the curves shown (Fig. 1) A and H are unacceptable, D, E and F are acceptable but close to the limits of uncertainty, and B, C and G are in good agreement with the observed intensity. The usual detailed qualitative and quantitative (Table I is an example) procedures lead to parameter values corresponding closely to Model C except for $a_{Si\,...\,Si}$. These values and their limits of error are Si–N = 1.738 ± 0.020 Å., Si . . . Si = 3.005 to 0.020 Å., Si–H = 1.54 ± 0.05 Å., ∠Si–N–Si = 119.6° to within 1.0°, $2a_{Si\,...\,Si} = \overline{l^2}_{Si\,...\,Si} - \overline{l^2}_{Si-N}\ 0.0030 \pm 0.0014$ Å.[2]

Discussion.—The structure of trisilylamine provides a particularly satisfying explanation of its chemical behavior as a weak electron donor. The essentially coplanar Si_3N group and the short Si–N bond length[6] indicate that the odd electron pair is involved to a considerable extent in π-bonding instead of being localized in a nitrogen orbital as in ammonia or the aliphatic amines.

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(1) This work was supported by the Office of Naval Research under Contract N6onr-24423. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Presented at the XII International Congress of Pure and Applied Chemistry, September, 1951, New York City, and at the International Congress of Crystallography, Stockholm, July, 1951.

(3) See A. B. Burg, First, Second, and Third Annual Technical Reports, "Investigation of Water Reactive Compounds" N6onr-238-TO-I (1947, 1948, 1949).

(4) See, for example, K. Hedberg and A. J. Stosick, THIS JOURNAL, **74**, 954 (1952).

(5) Trigonally symmetrical models with ∠Si–N–Si > 120° are of course not real; the curves are useful for interpolation, however.

(6) Two pairs of estimates for the SiN single- and double-bond lengths may be mentioned: (a) 1.80 Å. (1.17 + 0.74 − 0.09 | 3.0 − 1.8 |, V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941)) and 1.62 Å. (1.07 + 0.62 − 0.06 | 3.0 − 1.8 |, W. Gordy, *J. Chem. Phys.*, **15**, 81 (1947)), and (b) 1.87 and 1.67 Å. (L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, N. Y., 1940, p. 164).

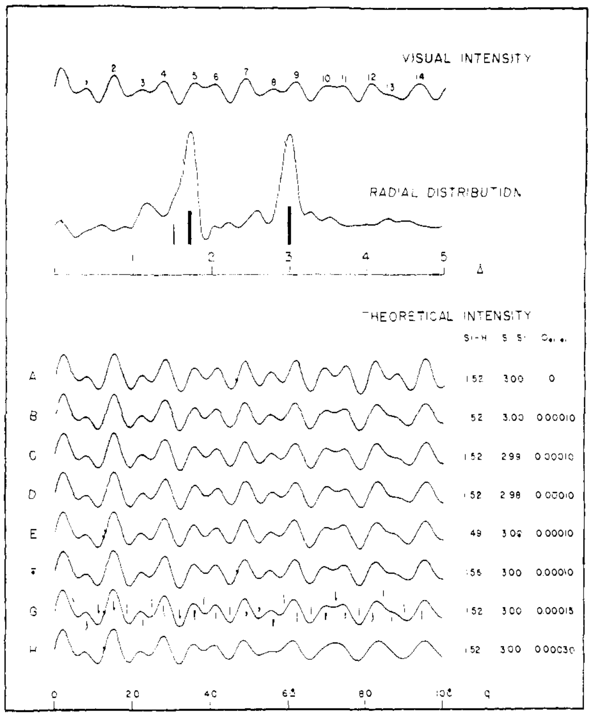

Fig. 1.—Trisilylamine: The positions of the vertical bars under the radial distribution curve give the more important interatomic distances for the best model; their heights are proportional to the weights of the terms. All the theoretical intensity curves are for Si–N = 1.73 Å. The best distance parameter values are close to those of curve C. The arrows on curve G show the measured positions of maxima and minima.

One might hope to estimate the amount of this π-bonding by using Pauling's equation[7] $R = R_1 - (R_1 - R_2)\ 3x/(2x + 1)$ to relate the actual Si–N bond length to standard single- and double-bond lengths and the fractional double-bond character x. However, the range of uncertainty in R_1 and R_2 is so wide (for example, the Pauling radius sums[6b] lead to $x = 0.39$, whereas the probably more reliable Schomaker–Stevenson and Gordy values[6a] lead to $x = 0.15$) that no definite conclusion can be reached. The odd pair would seem to be involved in π-bonding to the extent of about 50%, but 100% involvement cannot be excluded.

The result of 119.6° for the *average* Si–N–Si angle differs from the 120° corresponding to coplanarity by considerably less than the limit of error; yet the difference is probably less than a standard deviation and so may be significant. So far as the *equilibrium* angle is concerned, a range of values is doubtless compatible with the observed value. For example, an equilibrium value somewhat smaller than 119.6° would be perfectly compatible provided that the corresponding potential function for the out-of-plane Si_3N vibration had, with its two minima, an appropriate shape. But it seems most likely that the equilibrium angle is actually 120° and that the average angle is less merely in consequence of the out-of-plane vibration. Indeed, calculation shows that a normal vibration frequency in the reasonable range 175–350 $cm.^{-1}$ corresponds to an average angle in the range 119.3–119.8°, in more than adequate agreement with the observed value.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED POSITIONS OF MAXIMA AND MINIMA

Model G

	Max.		Min.	
No.	$q_{obsd.}$	$q/q_{obsd.}$	$q_{obsd.}$	$q/q_{obsd.}$
1	8.26	[0.956]	4.83	[1.222]
2	15.18	(.995)	11.22	0.980
3	22.56	(.971)	18.62	(1.020)
4	27.90	(1.003)	24.84	(0.978)
5	35.70	(0.994)	31.83	1.005
6	41.26	(.996)	38.23	1.007
7	48.91	.992	44.80	1.002
8	55.82	(.989)	52.33	(0.998)
9	61.78	(.992)	58.45	(.986)
10	69.15	(1.003)	65.53	.998
11	74.33	(0.995)	71.80	.996
12	81.42	(1.016)	77.94	1.003
13	86.38	(1.010)	84.19	(1.020)
14	94.16	(1.011)	89.62	(1.010)
15			98.06	(1.030)
	av. 26 features			1.001
	av. dev.			0.010
	av. 7 features			1.000
	av. dev.			0.004

Best model: Si–N = 1.73 × 1.005 = 1.738 Å.

Altogether, coplanar bonding without complete conjugation seems most likely in trisilylamine, as it does in such molecules as pyrrole,[8] urea[9] and the acid amides.[10] This is an interesting type of bonding situation for which the theory does not appear to have been much discussed.

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[7] Reference 6b, p. 175.

[8] W. S. Wilcox and J. H. Goldstein, *J. Chem. Phys.*, **20**, 1656 (1952).

[9] R. D. Waldron and R. M. Badger, *ibid.*, **18**, 566 (1950).

[10] J. E. Worsham, Jr., and M. E. Hobbs, THIS JOURNAL, **76**, 206 (1954).