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# The Structure of Hexamethylcyclotrisiloxane as Determined by the Diffraction of Electrons on the Vapor

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Hexamethylcyclotrisiloxane vapor has been shown to have a structure incorporating a planar ring with larger oxygen valence angles ( $125 \pm 5^\circ$ ) than silicon valence angles ( $115 \pm 5^\circ$ ); the methyl groups extend above and below the plane of the ring, their equilibrium bond positions making a probable angle of  $112 \pm 6^\circ$  with silicon, the temperature motion of the methyl groups allowing an average change in the interatomic distances involved of about 0.09Å, as compared with the normal temperature motion change of about 0.03Å. The Si—O distances are  $1.66 \pm 0.04$ Å and the Si—C distances are  $1.88 \pm 0.04$ Å.

The shortness of the Si—O distance suggests a larger ionic character of the bond than that indicated by the electronegativity table.

**H**EXAMETHYLCYCLOTRISILOXANE  $[(CH_3)_2SiO]_3$ , is the lowest isolated member of the polymeric cyclic siloxanes. Frevel and Hunter<sup>1</sup> reported preliminary x-ray diffraction work on several members of this series. They suggested that the structure of the trimer is similar to that found in benitoite,<sup>2</sup> where alternate oxygen and silicon atoms are arranged in a planar six-membered ring, and each silicon is surrounded by four oxygen atoms situated approximately at the corners of a tetrahedron. The octamer and probably all other polymers in this series have puckered rings. X-ray studies by Roth<sup>3</sup> on spiro-siloxane [octamethylspiro (5,5) pentasiloxane] revealed that each molecule consists of two planar six-membered rings linked at  $90^\circ$  through a silicon atom. The interatomic distances and bond angles cited are:

Si—O  $1.64 \pm 0.03$ Å      Si—C  $1.88 \pm 0.03$ Å  
 $\angle CSiC$   $109 \pm 4^\circ$      $\angle OSiO$   $109 \pm 4^\circ$      $\angle SiOSi$   $130 \pm 4^\circ$ .

The diffraction data reported below confirm the planar six-membered ring structure for the trimeric siloxane as well as the interatomic distances quoted by Roth and Harker,<sup>3(b)</sup> as being typical.

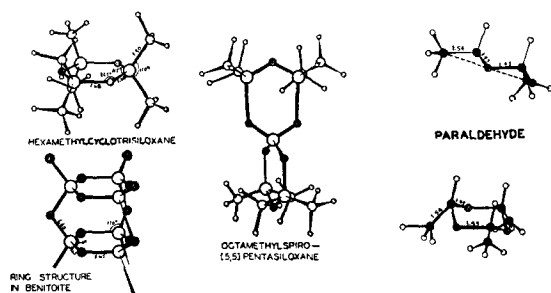


FIG. 1. Structures of hexamethylcyclotrisiloxane and related compounds. Please note that the values given in the drawing for the interatomic distances are not the "best" values quoted in the conclusion of this paper.

<sup>1</sup> L. K. Frevel and M. J. Hunter, J. Am. Chem. Soc. **67**, 2275 (1945).

<sup>2</sup> *Strukturberichte*, II (1937), p. 128.

<sup>3</sup> (a) W. L. Roth, J. Am. Chem. Soc. **69**, 474 (1937). (b) W. L. Roth and D. Harker, Acta Krist. **1**, 34 (1948).

Before proceeding with details of the analysis, it will prove interesting to compare the structure and some of the properties of hexamethylcyclotrisiloxane with those of comparable carbon compounds, trioxane and paraldehyde. Their respective geometries are illustrated in Fig. 1. Whereas the silicon analog of trioxane has yet to be prepared, the one directly analogous to paraldehyde, trimethylcyclotrisiloxane, has been synthesized.<sup>4</sup> From both x-ray and spectroscopic evidence<sup>5</sup> the carbon-oxygen compounds have puckered rings, with the chair form predominating as in cyclohexane in contrast to the planar (Si—O)<sub>3</sub> rings. Paraldehyde consists of an equilibrium mixture of the *cis*- and *trans*-forms, with the former predominating; the carbon atoms of the methyl groups are roughly coplanar with the oxygen atoms in the ring. Electron diffraction data on this compound indicate<sup>6</sup> that all the bond angles are tetrahedral, and that C—O is  $1.43 \pm 0.02$ Å, while C—C is  $1.54 \pm 0.02$ Å. The dipole moment of trioxane, 2.18D, is very close to the computed value for the pure chair form, 2.3D, as compared to the estimated value for the cradle form, 0.6D.<sup>7</sup> On the other hand, the dipole moment of the siloxane trimer is expected to be zero. In general, the carbon analogs are less stable to chemical attack, are more dense, and have higher electric moments. The melting and boiling points are comparable.

One can but speculate at present regarding the structure of hexamethylcyclotrisilazane  $[(CH_3)_2SiNH]_3$ , the preparation of which has recently been reported,<sup>8</sup> along with that of higher linear and cyclic members. It is probable that the valence angle of the nitrogens is not as large as that of the oxygen atoms, due to the smaller ionic character of the Si—N bonds; if so, the (Si—N)<sub>3</sub> rings may prove to be somewhat puckered.

<sup>4</sup> S. D. Brewer, J. Am. Chem. Soc. **70**, 3962 (1948).

<sup>5</sup> N. F. Moerman, Rec. Trav. Chim. **56**, 161 (1937); H. Gerding and J. Lecomte, Rec. Trav. Chim. **58**, 614 (1939); D. A. Ramsay, Trans. Faraday Soc. **44**, 289 (1948).

<sup>6</sup> D. C. Carpenter and L. O. Brockway, J. Am. Chem. Soc. **58**, 1270 (1936).

<sup>7</sup> A. A. Maryott and S. F. Acree, J. Research Nat. Bur. Stand. **33**, 71 (1944).

<sup>8</sup> S. D. Brewer and C. P. Haber, J. Am. Chem. Soc. **70**, 388 (1948).

## EXPERIMENTAL PROCEDURE

The cyclic trimer used in this study was obtained from Dr. Robert O. Sauer of the General Electric Company, to whom we express our sincere thanks. This sample melts at 65°C, and its vapor pressure at 53°C is 30 mm. At this temperature ( $dp/dt$ ) is 2 mm/°C. An evacuated vial containing the sample was sealed by means of a magnetic breaker joint to a metal high temperature nozzle in the electron diffraction apparatus. The sample was kept at various temperatures between 49° and 66°C during the runs. Electron diffraction pictures, with and without a sector, were taken. The experimental procedure and method of reduction of the photographs has been described by Hastings and Bauer.<sup>9</sup>

A visual intensity curve, showing intensity as a function of scattering angle, was drawn from visual estimation of the ring diameters and relative intensities of maxima and minima for both the sector and non-sector pictures (see Table I and Fig. 2). The sectors microdensitometer tracings showed structure only out to about  $s=15$ , whereas rings out to an  $s$  value of almost 32 could be seen on the non-sector films.

## ANALYSIS OF DATA

A radial distribution curve was computed following the method of Walter and Beach,<sup>10</sup> using the observed intensities above and below a decreasing background as deduced from the non-sector photographs (see Fig. 3—R.D.). Significant peaks in the radial distribution function appear at values of  $r$  (interatomic distance), summarized in Table II; also included are the interatomic distances with which they have been identified.

The radial distribution curve enables us to eliminate the puckered ring models and also many of the planar structures. We found no acceptable puckered ring models with interatomic distances corresponding completely to those indicated by the radial distribution curve, as can be seen by comparing the "synthetic"  $\alpha_2$ -curve with the observed radial distribution curve in Fig. 3. Thus, in model  $\alpha_2$ , the heavily weighted C—Si distance across the ring was split up into a number of rather lightly weighted distances because of the dissymmetry introduced by the puckered ring. Furthermore, there is no important distance corresponding to the radial distribution peak at 4.27Å. With respect to the planar ring models, it is clear that the Si—O distance is shorter than expected, being in the neighborhood of 1.62Å rather than 1.76Å. Shortening the Si—O bond also alters the important C—Si distance across the ring. Models incorporating oxygen valence angles outside the range 110°–130° are immediately eliminated because then the important Si/O and C/Si distances across the ring cannot be made to agree with the curve. The models which best fit the radial distribution curve

<sup>9</sup> J. M. Hastings and S. H. Bauer, J. Chem. Phys. 18, 13 (1950).

<sup>10</sup> J. Walter and J. Y. Beach, J. Chem. Phys. 8, 601 (1940).

TABLE I.

Max.	Min.	Visually estimated $s_0$ (non-sector)	Visually estimated relative intensity	Visually estimated $s_0$ (sector)	Microphotometer intensities (relative to unit background)
1		(1.77)	(10)	(1.99)	—
		2.28	-10	2.27	—
2	1	3.20	10	3.24	—
		3.95	-20	3.91	-0.109
3	2	4.84	20	4.79	0.256
		5.98	-15	5.84	-0.164
4	3	6.98	6.5	6.66	—
		7.40	5	7.35	—
5	4	7.96	8	7.85	0.043
		8.56	5	8.44	—
6	5	9.20	7	9.07	—
		10.09	-10	9.96	-0.047
7	6	11.18	7	11.19	0.035
		12.61	3	12.62	—
8	7	13.62	6	13.54	(0.003)
		14.49	-5	14.29	(-0.018)
9	8	15.42	4	14.95	—
		16.79	2		
10	9	17.78	4		
		18.81	-3		
11	10	19.64	3		
		20.80	2		
12	11	21.68	3		
		22.85	-2.5		
13	12	23.97	2		
		25.96	-1		
14	13	26.56	2		
		29.58	-0.5		
15	14	31.61	1		

are  $\gamma_4$  and  $\zeta_3$ ; the first has an oxygen valence angle of 130°, a silicon valence angle of 110°, and the Si—O distance 1.62Å, while the second has an oxygen valence angle of 125°, a silicon valence angle of 115°, and the Si—O distance 1.68Å. The synthetic curves are based on empirical shapes observed in many radial distribution curves.

Diffraction patterns expected for various models were computed and compared with the visual and microphotometer curves. The equation for calculating the scattered intensity as a function of angle is:

$$\left[ \frac{I(s)}{I_0} \right]_{\text{sector}} = \left[ \frac{8\pi^2 m e^2}{h^2} \right]^2 \frac{N}{R^2} \times \left[ 1 + \frac{\sum_i' \sum_j' f_i f_j \sin sr_{ij}}{\sum_i (f_i^2 + g_i) sr_{ij}} \exp(-a_{ij} s^2) \right]. \quad (1)$$

As a preliminary approximation, some of the theoretical curves were computed using the simplified equation

$$I(s) = \sum_i' \sum_j' Z_i Z_j \frac{\sin sr_{ij}}{sr_{ij}}. \quad (2)$$

Three important parameters determine the structure of this compound; these are the oxygen valence angle, the ratio of the distances C—Si/Si—O, and the C—Si—C angle. The motion of the  $\text{Si}(\text{CH}_3)_2$  groups relative to one another might be taken as a fourth parameter. The effect on the total curve of changing the C—Si—C angle is small, however, when restricted to the reasonable range 108°–118°, whereas the effect of temperature motion of the  $\text{Si}(\text{CH}_3)_2$  groups is to smooth out the sharper features of the pattern, and hence the latter can readily be predicted. Consequently, the essential

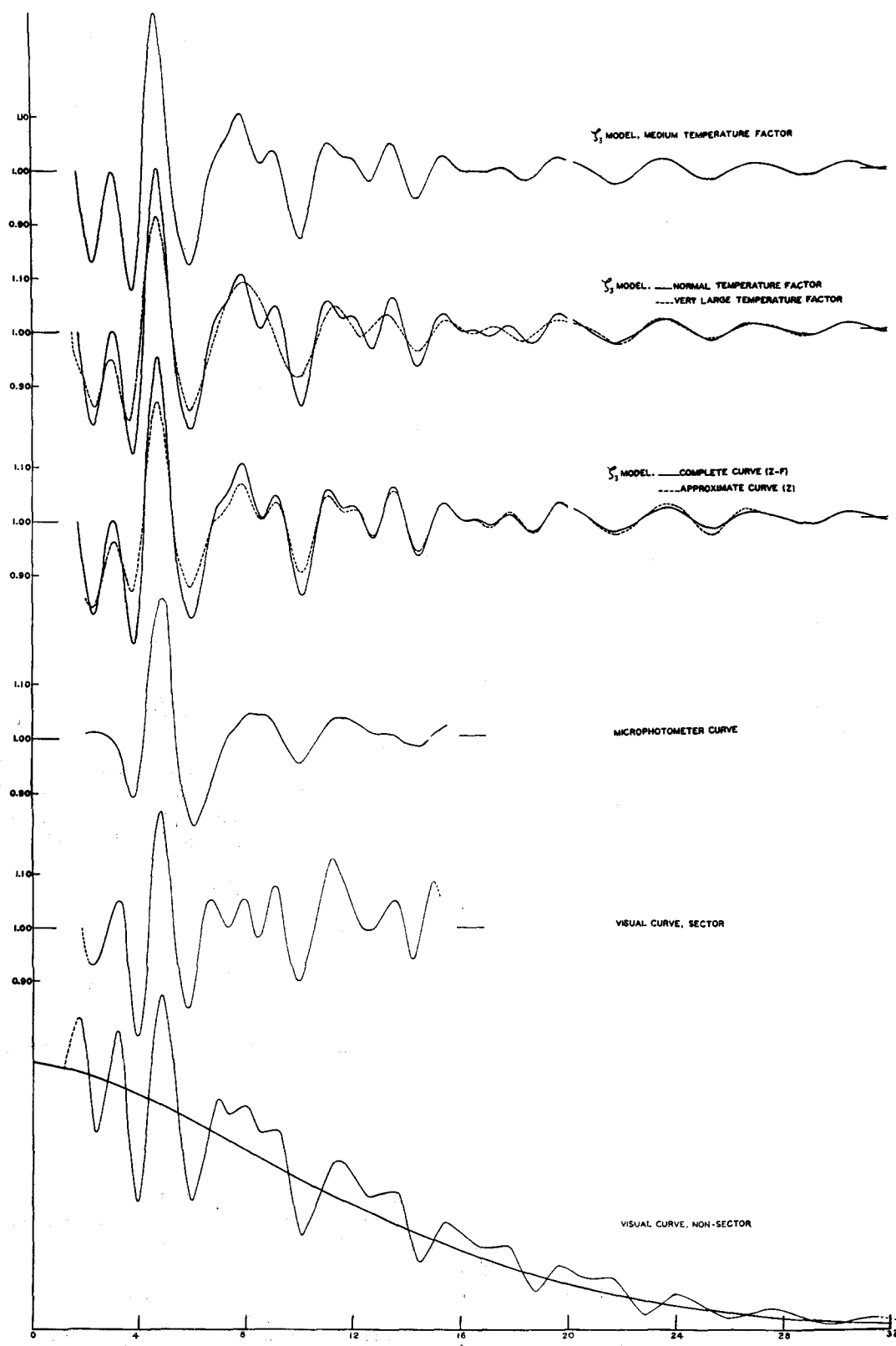


Fig. 2. Theoretical curves based on  $\zeta_3$ -model:  $\angle \text{Si}-\text{O}-\text{Si} = 125^\circ$ ,  $\angle \text{O}-\text{Si}-\text{O} = 115^\circ$ ;  $\text{C}-\text{Si} = 1.90\text{\AA}$ ,  $\text{Si}-\text{O} = 1.68\text{\AA}$ . (1)  $\zeta_3$ -model, medium temperature factor (0.0050), (2)  $\zeta_3$ -model, normal temperature factor (0.0020), (3)  $\zeta_3$ -model, large temperature factor (0.0261). (3)  $\zeta_3$ -model, "complete" curve, calculated from Eq. (1).  $\zeta_3$ -model, "approximate" curve, calculated from Eq. (3). (Note: The break in each of the theoretical curves appearing here and in Figs. 5 and 6, is caused by the fact that the tabulated values of the function  $\sin sr/sr$  were available, beyond  $s = 20$ , only up to the value of  $r = 3.99$ . The interatomic distances exceeding this value were therefore not included in the sum beyond  $s = 20$ . The difference in most cases is not large.)

FIG. 3. "Synthetic" radial distribution curves (SRD):

$\alpha_2$ —puckered ring (chair form)  
model: all angles tetrahedral,  
C—Si=1.90Å,  
Si—O=1.68Å.

$\xi_3$ —planar ring model:  
 $\angle$ Si—O—Si=125°;  
 $\angle$ O—Si—O=115°;  
C—Si=1.90Å,  
Si—O=1.68Å.

$\epsilon_2$ —planar ring model:  
 $\angle$ Si—O—Si=120°;  
 $\angle$ O—Si—O=120°;  
C—Si=1.90Å,  
Si—O=1.68Å.

$\gamma_4$ —planar ring model:  
 $\angle$ Si—O—Si=130°;  
 $\angle$ O—Si—O=110°;  
C—Si=1.90Å,  
Si—O=1.62Å.

RD—computed radial distribution curve.

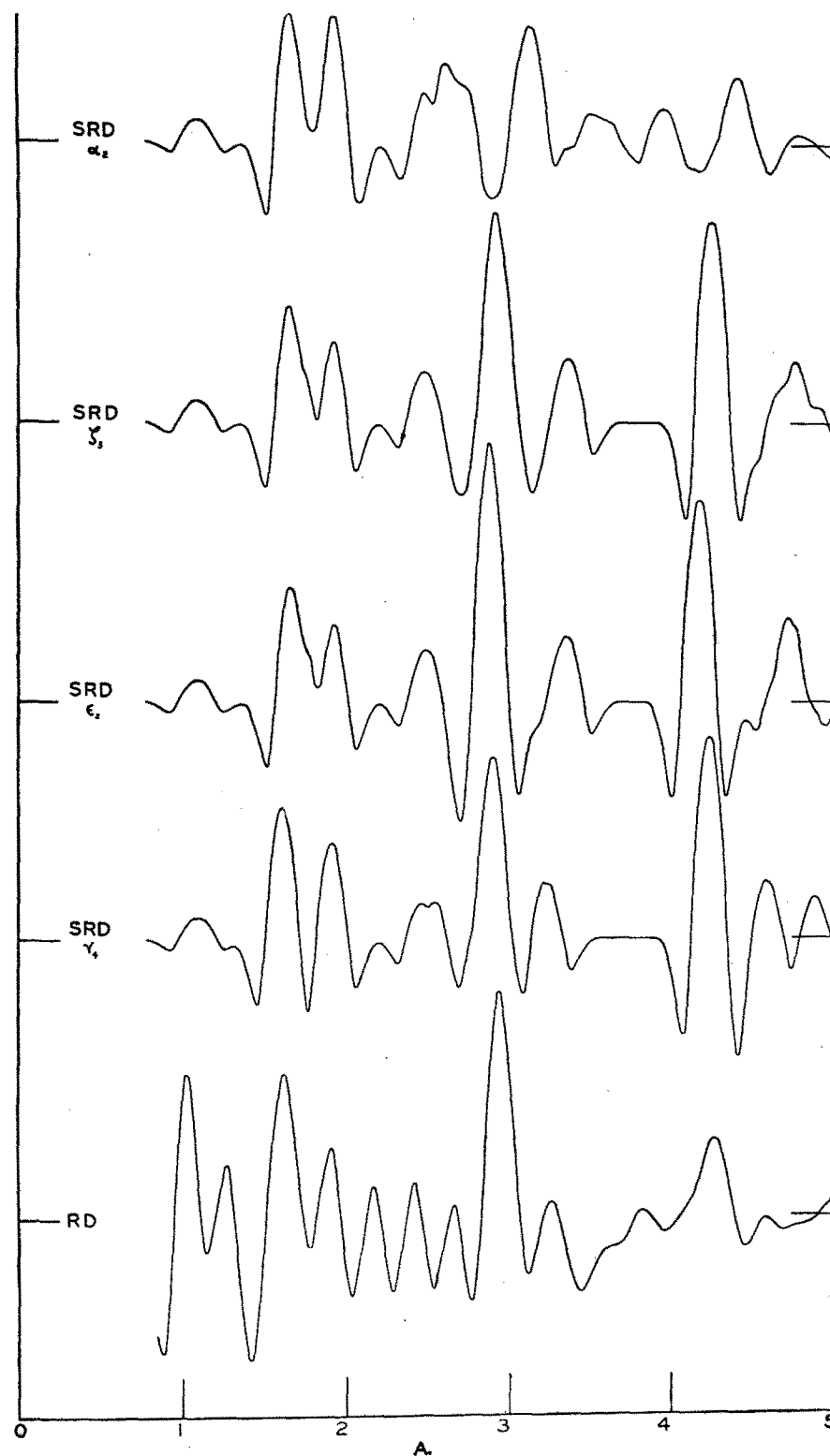









TABLE II.

Radial distribution maxima	Relative intensity	Interatomic distance identified	Distance in best model	Weight	Angle assumed	Distance expected*
1.03A	6	C—H	1.09A	108		1.10
1.27	2	?				
1.62	6	Si—O	1.66	672		1.76
1.91	3	C—Si	1.88	504		1.88
2.17	1		2.49	252	110°	
2.42	1					
2.66	$\frac{1}{2}$		2.84	192	115°	
2.94	10		2.98	588	125°	
			3.12	108	110°	
			2.90	576		
3.27	$\frac{1}{2}$		3.36	336	planar	
4.27	3		4.26	1008		

\* Distances calculated by method of Schomaker and Stevenson; see reference 12.

features of the pattern must be fitted by adjusting the first two parameters listed. The particular models computed are indicated in the field of Fig. 4. For these the angle C—Si—C was assumed to be tetrahedral (with the oxygen valence angle as ordinate and the C—Si/Si—O ratio as abscissa. Puckered ring models, in which all angles were assumed tetrahedral, are not included.

Some of the best theoretical intensity curves are reproduced in Figs. 5 and 6. Comparison of the theoretical curves with the curves drawn from visual and microphotometer data give added evidence for discarding those models which were believed incorrect on the basis of the radial distribution curve. In making these comparisons we must interpret the general impression which our eye receives in terms of our experience, which is based on the observation of many photographs of compounds of known structure. Since the eye accentuates various features in the density curve, we feel that the correct curve may be interpolated between the microphotometer curve which does not show all the necessary resolution and the visual impression of the sector pictures which shows accentuated features. With this in mind, let us now examine the theoretical intensity curves.

The puckered ring models bear little resemblance to the experimental curves, the relative heights and positions of the maxima and minima being incorrect in many instances. These are not shown in the figures.

There are several series of intensity curves in which the ratio C—Si/Si—O is varied but the oxygen valence

angle is constant. In the series  $\zeta_2$ ,  $\zeta_3$ ,  $\zeta_4$  (see Fig. 5), the oxygen angle is 125° and the Si—O distance varies from 1.72 to 1.64A.  $\zeta_2$  is excluded because although the fit is fairly good at low  $s$  values, at intermediate  $s$  the maxima and minima are shifted, and the structure in the region of  $s=15$  and beyond is poor.  $\zeta_3$  gives a good fit with the experimental data over the whole  $s$  range, with the exception of the eleventh and twelfth maxima in the region  $s=20-23$ .  $\zeta_4$  cannot be excluded, for although the relative intensities of the seventh and eighth maxima are not as good as in the  $\zeta_3$ -model, and the structure in the region  $s=20-23$  is not good, the essential features of the curve are not much altered. In the series  $\gamma_3$ ,  $\epsilon_4$ , and  $\epsilon_2$  (see Fig. 6), the oxygen valence angle is 120° and the Si—O distance varies from 1.76 to 1.68A. The  $\gamma_3$ -model is excluded because the match over the whole  $s$  range is not good, and there are scarcely any features which the computed and observed curves have in common beyond  $s=15$ .  $\epsilon_4$  is much better, and cannot be excluded on the basis of this comparison with the visual data. All the essential features of the visual curve are present, but the match is not good in the region of the eleventh maximum to the twelfth minimum, from  $s=19-23$ ; beyond this also the match is not as good as in the case of  $\zeta_3$ .  $\epsilon_2$  lies at the limit of acceptable models, the match with the visual curve being poor in the region from  $s=18$  to the end. The last series with constant oxygen valence angle of 130°, and Si—O distances 1.72, 1.68, and 1.62A, are Models  $\delta_4$ ,  $\delta_3$ , and  $\gamma_4$  (see Fig. 6). The  $\delta_4$ -model is definitely excluded, for it shows a very poor match throughout the entire  $s$  range. Even at low  $s$  values the theoretical structure fails to match the observed structure closely, and the fit becomes very poor at larger  $s$  values. The  $\delta_3$ -model, while close to the limit of acceptable models, cannot be ex-

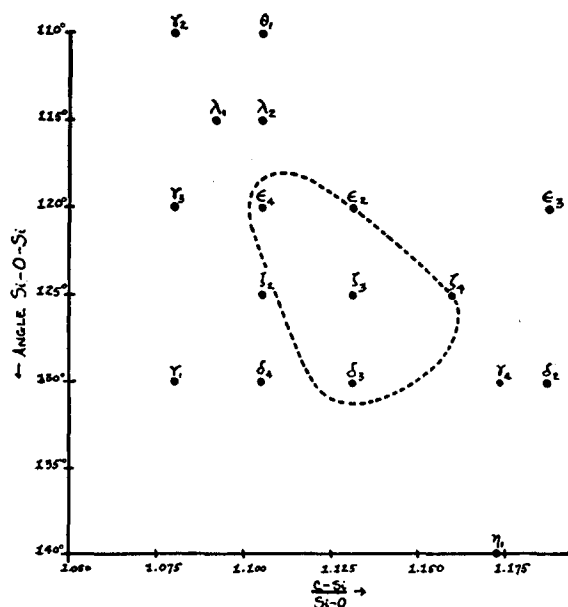


FIG. 4. Field of some of the planar ring models investigated.

cluded, for most of the important features of the observed curve are present, although the relative intensities of the seventh and eighth maxima in the region  $s=11-14$  are incorrect, and the match is not particularly good in the region  $s=16-22$ . The  $\gamma_4$ -model is excluded because of the incorrect relative intensities of the maxima and minima over the region  $s=11-20$ . The positions of these structural features also are not in good agreement.

Let us now examine the series having constant ratio C—Si/Si—O and varying oxygen valence angle. The members of the series  $\epsilon_2$ ,  $\zeta_3$ , and  $\delta_3$ , with distance Si—O=1.68Å, and oxygen angle varying from  $120^\circ$  to  $130^\circ$ , have already been discussed separately;  $\zeta_3$  is the best model in the series, but neither  $\epsilon_2$  nor  $\delta_3$  is definitely excluded. The series,  $\zeta_2$ ,  $\epsilon_4$ , and  $\lambda_2$ , has constant Si—O distance 1.72Å and oxygen angles varying from  $125^\circ$  to  $115^\circ$ .  $\zeta_2$  and  $\epsilon_4$  have been discussed separately;  $\zeta_2$  is not

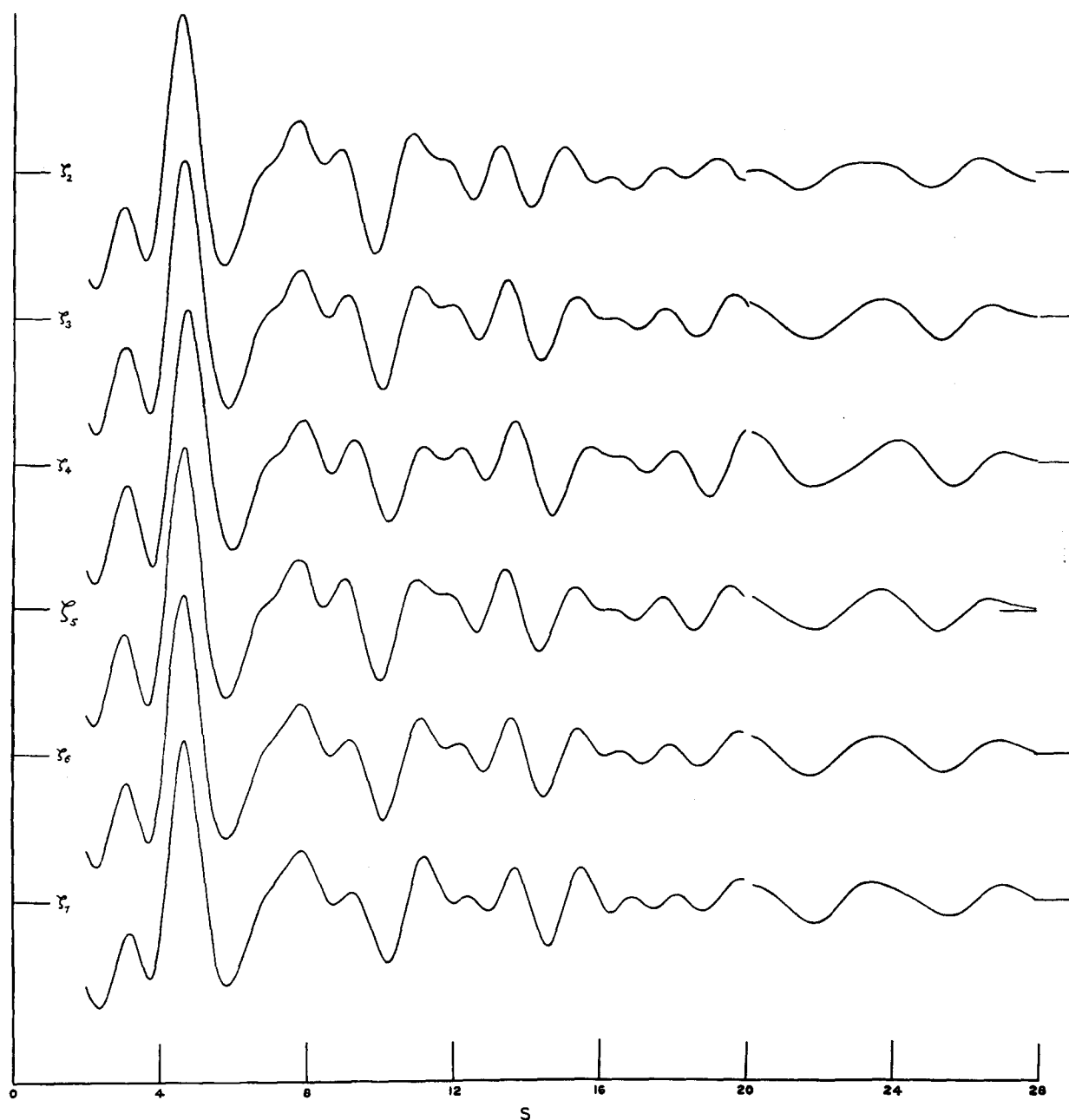


FIG. 5. Theoretical intensity curves.

Model	$\zeta_2$	$\zeta_3$	$\zeta_4$	$\zeta_5$	$\zeta_6$	$\zeta_7$
Si—O	1.72	1.68	1.64	1.68	1.68	1.68Å
$\angle$ CSiC	$110^\circ$	$110^\circ$	$110^\circ$	$108^\circ$	$115^\circ$	$120^\circ$

All C—Si 1.90Å, all  $\angle$ SiOSi  $125^\circ$ , all  $\angle$ OSiO  $115^\circ$ .

admissible, but  $\epsilon_4$  is not excluded. The relative intensities of structural features in the  $\lambda_2$ -model are not very good even at low  $s$  values, and the match in the region  $s=20$  and beyond is poor, so that this model may also be excluded.

The carbon-silicon-carbon angle is also an important parameter in this molecule. In all the models mentioned above, this angle has been assumed to be  $110^\circ$ . The effect of varying this angle while keeping the other structure of the molecule constant has also been in-

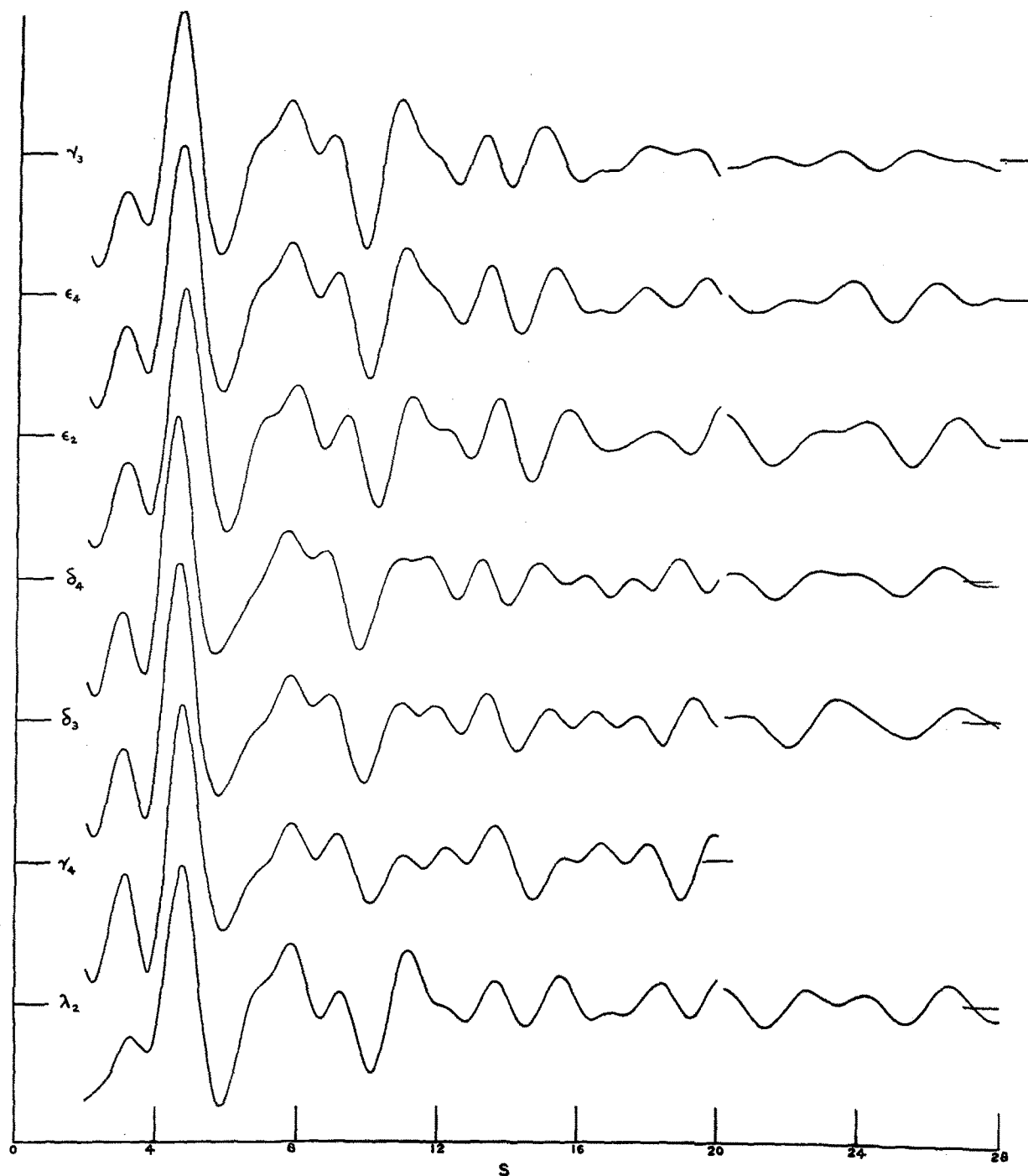


FIG. 6. Theoretical intensity curves.

Model	$\gamma_3$	$\epsilon_4$	$\epsilon_2$	$\delta_4$	$\delta_3$	$\gamma_4$	$\lambda_2$
Si-O	1.76	1.72	1.68	1.72	1.68	1.62	1.72A
$\angle \text{OSiO}$	$120^\circ$	$120^\circ$	$120^\circ$	$110^\circ$	$110^\circ$	$110^\circ$	$125^\circ$
$\angle \text{SiOSi}$	$120^\circ$	$120^\circ$	$120^\circ$	$130^\circ$	$130^\circ$	$130^\circ$	$115^\circ$

All  $\angle \text{CSiC } 110^\circ$ .



vestigated. The best model of those listed is obviously  $\zeta_3$ , so the distances and angles found in that model were used and kept constant, while the angle C—Si—C was varied from  $108^\circ$  ( $\zeta_5$ ) to  $115^\circ$  ( $\zeta_6$ ) and  $120^\circ$  ( $\zeta_7$ );  $\zeta_5$  shows most of the structural features of the visual curve, but the relative intensities of the seventh and eighth maxima are incorrect, and the match at fairly large  $s$  values is not very good. The  $\zeta_6$ -curve shows a very good match over most of the  $s$  range, as do also the  $\zeta_3$ - and  $\zeta_7$ -curves. No quantitative information may be gained from this particular series, since the structural changes in the intensity curves are not large, but we may say that the most probable C—Si—C angle is  $112^\circ$ , with a possible variation of  $\pm 6^\circ$ . The preferred structure on the basis of these curves is the planar ring model with oxygen valence angles  $125^\circ$ , silicon valence angles  $115^\circ$ , and the methyl groups extending above and below the plane of the ring, with C—Si—C angles  $112 \pm 6^\circ$ .

Roth<sup>3(a)</sup> found it necessary to assume that the motion of the methyl groups swept out a cone of large volume around the silicon atoms; accordingly, we have calculated, using Eq. (1), an intensity curve corresponding to  $30^\circ$  oscillation of the methyl groups from their equilibrium positions, by adjusting the value of the temperature factor,  $\exp(-a_{ij}^2 s^2)$ , to allow for such departures from equilibrium. Various other curves assuming different temperature factors were calculated, and compared with the visual and microphotometer curves (see Fig. 2). As would be expected, the greater the temperature factor, the less prominent the features of the pattern become. Interpolations of the absolute intensities of the maxima and minima of the observed microphotometer curve between the complete  $\zeta_3$ -curves with varying temperature factors were made, in order to estimate the average temperature factor and from this obtain the average departure of the methyl groups from equilibrium position. Because of the inaccuracies inherent in the determination of intensities, we can only be certain of the indication of a large temperature factor, but the value quoted has no real quantitative significance. An average temperature factor between 0.0050 and 0.0261 gives the closest fit; perhaps a value closer to 0.0050 may be assumed. The normal average temperature factor (0.0020) corresponds to a root-mean-square departure of 0.03Å from equilibrium interatomic distance, whereas the medium (0.0050) temperature factor corresponds to a departure of 0.05Å and the very large one (0.0261) to an average departure of 0.11Å. Our interpolated value of 0.0150 corresponds to a root-mean-square motion of 0.09Å.

In Table III are listed for comparison the positions, and intensities, for the chief maxima and minima of the microphotometer curve and the best theoretical curve,  $\zeta_3$ , with normal temperature factor. The subscript  $m$  refers to the microphotometer curve, and the subscript  $c$  to the computed curve. The positions of the maxima and minima check reasonably well, but in all cases the intensities recorded by the microphotometer are less in

TABLE III.

Max.	Min.	Positions		Intensities (relative to unit background)	
		$s_m$	$s_c$	$I_m$	$I_c$
3	2	3.80	3.78	-0.109	-0.225
		4.91	4.68	0.256	0.303
	3	6.06	5.92	-0.163	-0.178
4		8.18	7.82	0.043	0.106
	4	10.04	10.08	-0.047	-0.137

absolute value than those of the computed curve.<sup>11</sup> Since in cases of other molecules treated in this way, there is much better agreement between the observed and computed intensities, and the resolution is close to unity, the lack of agreement in this case is interpreted as additional evidence for extensive relative motion of the  $\text{Si}(\text{CH}_3)_2$  groups. Large fluctuations in the equilibrium interatomic distances would produce broader peaks and decrease the deviation from unit background.

In summary, the quantitative comparison of the computed with the observed data is given in Table IV;  $\zeta_3$  is the best computed model, the subscript  $c$  refers to the computed data, the subscript  $O$  refers to observed data, and  $a$  and  $b$  refer to the data for  $\zeta_3$  with normal and large temperature factors, respectively. The average deviation is acceptable. This indicates that the assumed model is satisfactory.

## DISCUSSION OF RESULTS

If the bonds between silicon and oxygen and silicon and carbon were completely covalent in character, we should expect, using the covalent bond radii as given by Schomaker and Stevenson,<sup>12</sup> that the silicon-carbon bond distance would be 1.88Å, and the silicon-oxygen bond distance 1.76Å. It has been found that the silicon-carbon bond is 1.88Å, in agreement with the distance predicted, and with the values  $1.88 \pm 0.04$ Å in neopentyl chloride<sup>9</sup> and  $1.93 \pm 0.03$ Å in  $\text{Si}(\text{CH}_3)_4$ .<sup>13</sup> However, the silicon-oxygen distance is 1.66Å, which agrees with the values 1.60Å and 1.65Å reported for benitoite.<sup>2</sup> These results indicate the presence of one or both of the following: (1) partial double-bond character arising from resonance, and (2) larger ionic character of the bond than is suggested by the electronegativity table. It is more likely that the ionic contribution is the more important one, in view of the physical and chemical evidence against multiple bonding which will be cited.

Infra-red absorption spectra have been obtained by Wright and Hunter of both the linear and cyclic siloxane

<sup>11</sup> For a discussion of the inherent limitations of electron diffraction as a technic for structure determinations, and a listing of the sources of error, see Hastings and Bauer, reference 9.

<sup>12</sup> V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941), and unpublished discussions from a conference on the electron diffraction of gases at Cornell University, August, 1947.

<sup>13</sup> L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc. **60**, 1836 (1938).

TABLE IV.

Max.	Min.	Average $s_0$	$s_0$ for $\zeta_1$ $a$ $b$		$s_0/s_0$ $a$ $b$	
2	1	2.28	2.27	2.36	0.996	1.035
		3.22	3.00	2.97	0.932	0.922
	2	3.93	3.78	3.66	0.962	0.931
3		4.82	4.68	4.67	0.971	0.969
	3	5.91	5.92	5.91	1.002	1.000
4		6.82	[7.05]	—	—	—
	4	7.37	[7.33]	—	—	—
5		7.90	7.82	7.92	0.990	1.003
	5	8.50	8.59	—	1.011	—
6		9.13	9.09	—	0.996	—
	6	10.02	10.08	9.97	1.006	0.995
7		11.18	11.06	—	0.989	—
	7	12.62	12.71	12.28	1.007	0.973
8		13.58	13.49	13.22	0.993	0.973
	8	14.39	14.41	14.42	1.001	1.002
9		15.20	15.38	15.43	1.012	1.015
	9	16.79	17.07	16.42	1.017	0.978
10		17.78	17.80	17.30	1.001	0.973
	10	18.81	18.70	18.32	0.994	0.974
11		19.64	19.72	19.72	1.004	1.004
	11	20.80	—	—	—	—
12		21.68	—	—	—	—
	12	22.85	21.77	21.90	0.953	0.958
13		23.97	23.75	23.58	0.991	0.984
	13	25.96	25.43	25.46	0.980	0.981
14		26.56	26.90	27.20	1.013	1.024
	14	29.58	29.20	29.00	0.987	0.980
15		31.61	30.57	30.57	0.967	0.967
Average					0.991	0.983
Average deviation					0.015	0.021

## Final values

$$\text{Si-O} = (0.991)(1.68) = 1.66 \pm 0.04\text{\AA}$$

$$\text{Si-C} = (0.991)(1.90) = 1.88 \pm 0.04\text{\AA}$$

series.<sup>14</sup> These records cover the range 2–14 $\mu$  and show many lines, several of them quite strong. The unusual weakness of the C–H bands has been attributed to rather free angular motion of the –CH<sub>3</sub> groups around silicon, which decreases the dipole moment of C–H; also the methyl rocking vibration is much stronger in these compounds than in hydrocarbons. This is in agreement with the assumption proposed by Roth<sup>3</sup> that the –CH<sub>3</sub> groups in the spiro compound liberate very freely about the Si–C bond position. Indeed, in order to obtain good checks between the observed and calculated x-ray intensities, he had to assume a radius of precession equal to 0.6 $\text{\AA}$ . Lack of any evidence of an

<sup>14</sup> Wright and Hunter, *J. Am. Chem. Soc.* **69**, 803 (1947); C. W. Young *et al.*, *J. Am. Chem. Soc.* **70**, 3758 (1948).

absorption band due to Si=O at about 6.5 $\mu$  confirms the chemical evidence<sup>15</sup> that double bonding in the siloxanes does not exist. The strong band at 9.5 $\mu$  has been assigned to the Si–O stretching vibration.<sup>16</sup>

The spectrograms of the cyclic trimer and linear dimer, first of their respective series, differ more from other members of each series than do subsequent members. The two series approach congruence at large polymer size. This difference of the trimer confirms the suggestion already made by Scott<sup>17</sup> that cyclic methylpolysiloxanes above the trimer are probably strain-free, but that the trimer might have slight strain, since the equilibrium constants for a series of reactions involving this cyclic series varied in regular manner with number of units four or more.

From data on dipole moments of linear and cyclic dimethylpolysiloxanes, Sauer and Mead<sup>18</sup> have computed a Si–O–Si angle of  $160 \pm 15^\circ$ . Although the validity of the conclusions reached by these authors regarding the large oxygen valence angle is seriously questioned by their neglect of the atomic polarization term (as pointed out by Baker, Barry, and Hunter<sup>19</sup>); the dielectric constant data nevertheless suggest that the oxygen valence angle is comparatively large, and the force constant for its deformation comparatively small.

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<sup>15</sup> Kipping investigated the possible existence of ketone-like structures such as  $\text{R}_2\text{Si}=\text{O}$  [*J. Chem. Soc.* **79**, 455–6 (1901); **91**, 218 (1907); **93**, 442–4 (1908); **95**, 313 (1909); **101**, 2106 (1912)], but could not confirm their existence. Diols or linear and cyclic polymeric compounds always formed instead of the multiply bonded structures. [*J. Chem. Soc.* **105**, 484 (1914)]. He finally concluded that double bonding between Si and itself or other atoms never occurred [*J. Chem. Soc.* **1927**, 104 (1927); **1929**, 1180 (1929)]. See also Hunter, Hyde, Warrick, and Fletcher, *J. Am. Chem. Soc.* **68**, 671 (1946).

<sup>16</sup> The method used by Wright and Hunter (reference 14) for evaluating the ionic character of the Si–O bond from the intensity of the stretching frequency, is highly questionable.

<sup>17</sup> D. W. Scott, *J. Am. Chem. Soc.* **68**, 2294 (1946).

<sup>18</sup> R. O. Sauer and D. J. Mead, *J. Am. Chem. Soc.* **68**, 1794 (1946).

<sup>19</sup> Baker, Barry, and Hunter, *Ind. Eng. Chem.* **38**, 1117 (1946).