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INVESTIGATION OF THE MOLECULAR STRUCTURE OF A FEW 1-OXA-2,6-DISILACYCLOHEXANE DERIVATIVES BY THE CALCULATION OF THEIR DIPOLE MOMENTS

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Summary

The molecular structure of 1-oxa-2,6-disilacyclohexane derivatives has been investigated. Each derivative has a chair configuration, substituents at 2,6 silicons are in *trans*-position, and ethoxy and triethylsiloxy groups in the same position exhibit free rotation. 1,3,5,7-tetramethyl-1,3:5,7-dipropanocyclotetrasiloxane has a conformation belonging to the S_4 point group.

It has been established that in organosilicons containing oxygen, there is a linear relationship between the cosine of the bond angle of Si—O—R (where R = C, Si) and the bond moment *m*(Si—O); the bond moment decreases with increasing bond angle.

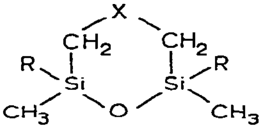
Introduction

Recently, considerable interest has been shown in siloxanes, particularly in their molecular and bond structure. However, few X-ray and electron diffraction investigations have been carried out, due to practical difficulties. Comparison of dipole moments can give good information on conformation and molecular or bond structure, especially when NMR and IR cannot be succesfully applied.

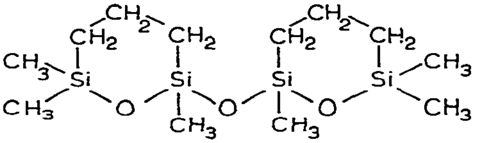
Since configuration, particularly in organosilicons, may be completely different in solid phase from that in dilute solution or that in vapour phase (where molecular interactions can be neglected) (e.g. octamethylcyclotetrasiloxane), the structure of free molecule is of as much interest as the solid state structure. Dipole moment studies are the most suitable for this.

Results and discussion

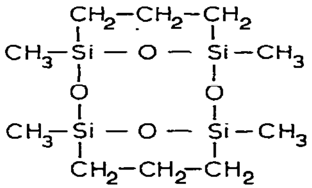
Investigations were carried out on 1-oxa-2,6-disilacyclohexane derivatives I - VIII to elucidate the molecular structure of the free molecule.



(I - VI)



(VII)



(VIII)

	X	R	name
I	CH_2	CH_3	2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane
II	CH_2	C_6H_5	2,6-dimethyl-2,6-diphenyl-1-oxa-2,6-disilacyclohexane
III	CH_2	OC_2H_5	2,6-dimethyl-2,6-diethoxy-1-oxa-2,6-disilacyclohexane
IV	CH_2	$OSi(C_2H_5)_3$	2,6-dimethyl-2,6-bis(triethylsiloxy)-1-oxa-2,6-disilacyclohexane
V	S	CH_3	2,2,6,6-tetramethyl-1-oxa-4-thia-2,6-disilacyclohexane
VI	NC_2H_5	CH_3	2,2,6,6-tetramethyl-4-ethyl-1-oxa-4-aza-2,6-disilacyclohexane
VII			2,2′-bis(2-methyl-6,6-dimethyl-1-oxa-2,6-disilacyclohexyl) ether
VIII			1,3,5,7-tetramethyl-1,3:5,7-dipropanocyclotetrasiloxane

Calculation methods

The dipole moments of the compounds I - VII have been determined by the method of Onsager [1], that of compound VIII according to Hedestrand [2] in the form of its solution in benzene. Calculations were carried out on the basis of the relationships discussed earlier [3,4]. Results are contained in Tables 1 and 2.

The dipole moment has been calculated in two different ways. According to one of the methods, atom and electron polarization have been taken into account by the known approximation ($R = 1.05\ MR_D$). The dipole moment obtained by this method has been denoted as μ_A.

In the other method, electron polarization has been determined on the basis of anomalous dispersion by extrapolation, while atom polarization was calculated through use of atom polarization increments [5,6]. The increments

TABLE 1

DIPOLE MOMENTS OF I - VII OBTAINED BY THE METHOD OF ONSAGER AND DATA NECESSARY FOR CALCULATIONS

	I	II	III	IV	V	VI	VII
n_D^{25}	1.4238	1.5460	1.4214	1.4401	1.4706	1.4298	1.4403
d^{25} g/ml	0.8661	1.0414	0.9565	0.9236	0.9835	0.8731	0.9713
ϵ^{25}	2.681	3.031	3.652	2.504	3.093	2.803	2.942
$n_F - n_C$	0.00845	0.01669	0.00793	0.00835	0.01151	0.00945	0.00874
$MR_{D\ \mathrm{calc}}$ ml	51.336	90.976	62.220	116.156	54.904	60.334	91.532
$MR_{D\ \mathrm{measd}}$ ml	51.359	90.758	62.208	116.140	54.652	60.158	90.891
n_∞	1.4111	1.5208	1.4096	1.4275	1.4533	1.4156	1.4271
P_e	50.000	87.262	60.679	113.210	52.912	60.844	88.501
P_a	7.388	7.888	7.804	14.808	8.482	7.514	15.234
$MR_D \cdot 1.05$	53.927	95.296	65.319	121.947	57.384	63.166	95.436
$P_a + P_e$	57.388	95.150	68.483	128.018	61.394	68.358	103.735
μ_A D	0.977	1.027	1.698	1.128	1.108	1.129	1.457
μ_B D	0.865	1.030	1.629	0.978	1.000	0.994	1.276

TABLE 2

DIPOLE MOMENTS OF VIII, OBTAINED BY THE METHOD OF HEDESTRAND AND DATA NECESSARY FOR CALCULATION

Number of solution	1	2	3	4	5
x_2	0.00577	0.00782	0.00909	0.01213	0.01942
d^{25}	0.8779	0.8797	0.8801	0.8819	0.8867
ϵ^{25}	2.280	2.286	2.288	2.290	2.298
n_D^{25}	1.4967	1.4963	1.4961	1.4958	1.4945
P_e	25.510	25.586	25.654	25.842	26.210

$\alpha = \frac{d\epsilon}{dx_2} = 1.2133$

$\beta = \frac{d(d^{25})}{dx_2} = 0.6444$

$\gamma = \frac{dP_e}{dx_2} = 51.842$

$\epsilon_1 = 2.275$

$d_1 = 0.8742$

$P_\infty = 107.550$ ml

$P_e = 77.052$ ml

$P_a = 17.334$ ml

$P_e + P_a = 94.386$ ml

$\mu_A = 1.074$ D

$\mu_B = 0.803$ D

used are shown in Table 3. Dipole moments calculated in this way are denoted μ_B.

Measurements were carried out at 25.00 ± 0.02°C using an ultrathermostat. Densities (d^{25}) were determined with graduated-neck dilatometers, while the refractive index (n_D^{25}) and dispersion values (n_F-n_C) were determined with an Abbé Refractometer. The dielectric constant (ϵ^{25}) was measured with an instrument constructed in our laboratory [9] at a frequency of 10 kHz. Compounds investigated were prepared as described earlier [10 - 13], and a summary is given in the experimental section. Purity was checked by gas chromatography.

Investigation of the molecular structure

The stereostructure of the cyclic compounds listed under I to VIII is from several aspects of interest. Thus, what is the value of the bond angle Si—O—Si, and in what conformation does the given compound exist?

Hexamethylcyclotrisiloxane (D_3) and the cyclohexane derivatives, owing to their six-atomic ring structure, have an isostructural skeleton. Dipole moment measurements on D_3 also suggest a planar structure ($\mu = 0$ D [16], $\mu = 0.14$ D [17]). At the same time, chair conformation is characteristic of cyclohexane derivatives. It was expected that our case is more similar to the cyclohexane structure, than to that of D_3.

In the carbo-cyclosiloxanes investigated, the Si—O—Si bond is fixed. In these ring systems, stretching vibrations exhibited in the IR region are: $\nu(\text{Si—O—Si})_{as} = 990\ \text{cm}^{-1}$ [10,18], which means that the bond angle of the Si—O—Si bond is 120°, except in VI(110 - 115°) [18]. In VII and VIII there

TABLE 3

VALUES OF THE ATOMIC POLARIZATION BOND INCREMENTS

C—H	0.02 ml	Si—O_{cycl}	1.36 ml [8]	C—N	0.03 ml
C—C	0.03 ml	Si—C_{cycl}	0.80 ml [8]	C—S	0.65 ml [14]
Si—C_{al}	0.60 ml	Si—O—C	0.73 ml [7]	Si—C_6H_5	2.60 ml [15]

are two active $\nu(\mathrm{Si{-}O{-}Si})_{as}$ vibrations, for VII at 900 $\mathrm{cm^{-1}}$ and 1080 $\mathrm{cm^{-1}}$, while for VIII at 1006 $\mathrm{cm^{-1}}$ and 1067 $\mathrm{cm^{-1}}$, due to the stretching of the 6-member ring and of disiloxane or tetrasiloxane, respectively.

We therefore assumed for each 1-oxa-2,6-disilacyclohexane derivative an Si—O—Si angle of 120°, which was justified by later results.

Correlation of our data on measured and calculated dipole moments of compounds containing sulphur and nitrogen shows that only the chair conformation is possible. Details of calculation are as follows.

Verification of the structure is made by vectorial summation of the bond vectors of the various bonds, according to the procedure described in ref. 19.

Coordinate components belonging to the different conformations have to be determined in each case from published bond distances and bond angles. Distance vector components between the single points can then be calculated, and from these the unit vector components were constructed. These data give the direction of the single vectors. Next, in knowledge of the corresponding bond and group moment values, the components of the dipole moment vector of the given system can be established.

First the bond moment of the Si—O bond was computed from the experimental dipole moment value of compound I.

The Si—O—Si bond angle was assumed to be 120°, and all the other angles 110°. In addition, the following bond distances [20] and bond dipole moments [19] were used: $R(\mathrm{C{-}C}) = 1.54$ Å, $R(\mathrm{Si{-}C}) = 1.93$ Å, $R(\mathrm{Si{-}O}) = 1.634$ Å, $m(\mathrm{Si}\overset{\rightarrow}{-}\mathrm{C}) = 0.6$ D, $m(\mathrm{C}\overset{\leftarrow}{-}\mathrm{H}) = 0.4$ D, $m(\mathrm{Si}\overset{\rightarrow}{-}\mathrm{CH_3}) = 0.2$ D.

The numbering of the atoms of I is shown in Fig. 1; distance unit vector values needed for the calculations are summarized in Table 4.

From $m(\mathrm{Si{-}C})$ and $m(\mathrm{C{-}H})$, the experimental dipole moment value ($\mu_B = 0.865$ D), and based on the assumption of a chair conformation, the bond moment of the Si—O bond of I was found to be 1.04 D. The dipole moment thus calculated is $\vec{\mu} = 0.7321\,\vec{i} - 0.4720\,\vec{k}$, $\mu = 0.8711$ D. This value closely approaches the measured value of $\mu_B = 0.865$ D, and so an estimated Si—O—Si bond angle of 120° is realistic.

Bond distances, bond angles, unit vector coordinates, bond and group moments of II are the same as for I. The missing $m(\mathrm{Si{-}Ph})$ group moment is 0.448 D [21].

The three possible positions of the phenyl group are shown schematically in Fig. 2, and values of the dipole moment have been calculated for all three: II(a) $\vec{\mu} = 0.8923\,\vec{i} - 0.0208\,\vec{k}$, $\mu = 0.8925$ D; II(b) $\vec{\mu} = 0.8735\,\vec{i} - 0.7768\,\vec{k}$, $\mu = 1.1690$ D; II(c) $\vec{\mu} = 0.8829\,\vec{i} - 0.1191\,\vec{j} - 0.3988\,\vec{k}$, $\mu = 0.9760$ D.

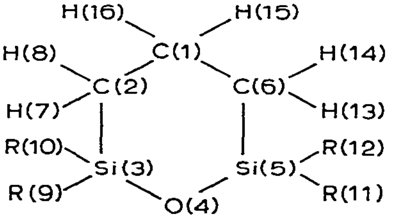
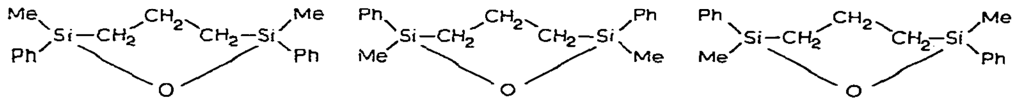


Fig. 1. Numbering of atoms I.



II(a) II(b) II(c)

Fig. 2. Possible positions of phenyl group.

TABLE 4

DISTANCE UNIT VECTOR COMPONENTS OF I

For numbering see Fig. 1.

$\vec{R}$	x	y	z
2,1	−0.2764	−0.8192	0.5025
3,2	−0.9968	−0.0795	0
3,4	0.4121	−0.8660	−0.2832
5,4	0.4121	0.8660	−0.2832
5,6	−0.9968	0.0795	0
6,1	−0.2764	0.8192	0.5025
15,1	−0.4158	0	−0.9094
16,1	0.9905	0	−0.1359
7,2	0.4078	−0.8116	−0.4181
8,2	0.3396	0.0441	0.9395
3,9	0.2850	0.7315	−0.6146
3,10	0.3233	0.2512	0.9096
5,11	0.2850	−0.7315	−0.6146
5,12	0.3233	−0.2512	0.9096
13,6	0.4078	0.8116	−0.4181
14,6	0.3396	−0.0441	0.9395

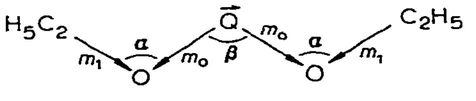
The experimental dipole moments $\mu_A = 1.027$ D, $\mu_B = 1.030$ D lie closest to the calculated value II(c), and therefore this steric position is the most probable. However, a mixture of the three conformations seems also possible, since their preparative isolation has not been undertaken.

The three possible positions of the ethoxy group in compound III are shown in Fig. 3. Owing to the rotation of the ethoxy group, the resultant dipole moment has been separated into two components: $\vec{\mu} = \vec{\mu}_{\text{trunk}} + \vec{\mu}_{\text{rot}}$. In calculations on III(c) the angle β between the two O—Si vectors has been calculated with the aid of the unit vectors, on the basis of Eyring's relationship [7]:

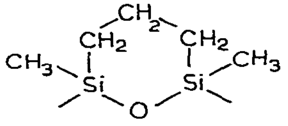
$$\mu_{\text{rot}}^2 = 2m_0^2(1 + \cos\beta) + 2m_1^2(1 + \cos^2\alpha\cos\beta) + 4m_0 m_1 \cos\alpha(1 + \cos\beta)$$

where

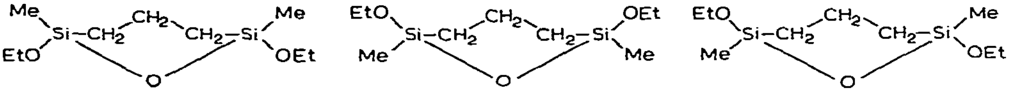
$\alpha = 113°$, m(Si—C) = 1.22 D, and $m(\text{O—C}_2\text{H}_5)$ = 1.12 D [22].



where Q is



The following results were obtained: $\mu_{\text{rot}} = 1.5979$ D; $\vec{\mu} = 1.5837\vec{i} - 0.6724\vec{j} - 0.0590\vec{k}$; $\mu = 1.7215$ D. Similar calculations on configuration III(b) give the dipole moment values: $\mu_{\text{rot}} = 2.1009$ D; $\vec{\mu} = 1.0605\vec{i} + 2.9646\vec{k}$; $\mu = 3.5542$ D.



III(a) III(b) III(c)

Fig. 3. Possible positions of ethoxy group in III.

It can be seen that configuration III(a) gives similar values. μ_A is 1.698 D, and μ_B 1.630 D. It follows from this that configuration III(c) is realistic, and the two ethoxy groups rotate freely.

Calculations for IV were analogous to those on III. The dipole moment value of the *trans*-conformation IV(c), shown in Fig. 4, has been calculated. On the basis of a relationship discussed earlier, where $\alpha = 130°$ [20], $m_0 = 0.77$ D [7], $m_1 = 0.75$ D [7], the following results were obtained: $\mu_{rot} = 0.8475$ D; $\vec{\mu} = 1.1275\vec{i} - 0.3122\vec{j} - 0.2802\vec{k}$; $\mu = 1.2030$ D. These values are in good agreement with the experimental dipole moment values: $\mu_A = 1.128$ D, $\mu_B = 0.978$ D. Since larger dipole moments than these were obtained for the other two configurations, only IV(c) can exist, in which the rotation of the two siloxy groups is either completely free, or only slightly hindered.

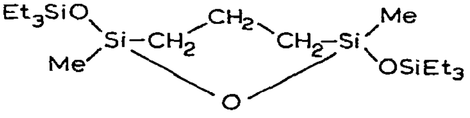
For V, the length of the C—S bond and the value of the bond moment *m*(C—S) were needed in addition to the bond moment values and bond distance values used so far. *m*(C—S) was calculated from the dipole moment of $(CH_3)_2S$ [14] ($\mu = 1.5$ D), from its bond angle [20] ($\theta = 105°$) and from the bond moment *m*(C—H) = 0.4 D, yielding a value of *m* (C—S) = 0.33 D. The bond distance C—S is 1.81 Å [20].

First the Si—O—Si bond angle was assumed to be 120°, the C—S—C angle 99° [20] and the other angles 110°: this gives a dipole moment of 0.817 D. As the sulphur atom in the ring may modify the Si—O—Si bond angle slightly, calculations were also carried out with angles differing from 120°. As a result, the Si—O—Si bond angle was taken as 123°.

The three views of compound V and the numbering of its atoms are shown in Fig. 5, and distance unit vector components needed for the calculations are contained in Table 5.

The dipole moment calculated on the basis of these data is: $\vec{\mu} = -0.1226\vec{i} + 0.9192\vec{k}$; $\mu = 0.927$ D, which is in good agreement with the experimental dipole moments $\mu_A = 1.108$ D, $\mu_B = 1.000$ D.

For the determination of the dipole moment of VI *m*(C—N) had to be calculated from the dipole moment [14] of $(CH_3)_3N$ ($\mu = 0.61$ D), from the



IV (c)

Fig. 4. The *trans*-conformation of IV.

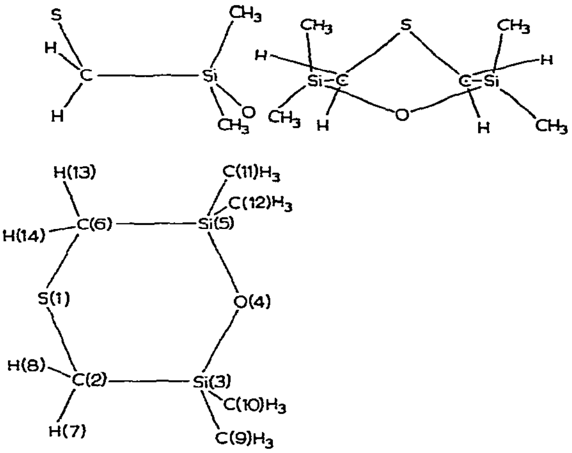


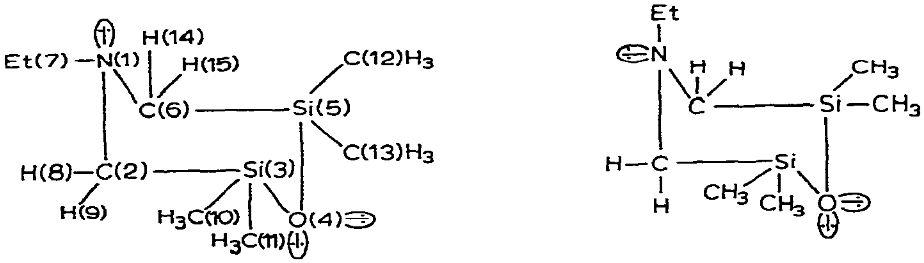
Fig. 5. Three projections, and the numbering of V.

TABLE 5

DISTANCE UNIT VECTOR COMPONENTS OF V

For numbering see Fig. 5.

$\vec{R}$	x	y	z
2,1	−0.3186	−0.7604	0.5659
3,2	−0.9995	−0.0309	0
3,4	0.3693	−0.8788	−0.3021
5,4	0.3693	0.8788	−0.3021
5,6	−0.9995	0.0309	0
6,1	−0.3186	0.7604	0.5659
7,2	0.3688	−0.8624	−0.3469
8,2	0.3389	0.1042	0.9351
3,9	0.3796	0.7308	−0.6028
3,10	0.3356	0.2149	0.9172
5,11	0.3796	−0.7308	−0.6028
5,12	0.3356	−0.2149	0.9172
13,6	0.3688	0.8624	−0.3469
14,6	0.3389	−0.1042	0.9351



VI(a) VI(b)

Fig. 6. Two configurations and the numbering of the atoms in VI.

TABLE 6

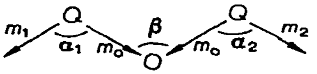
DISTANCE UNIT VECTOR COMPONENT OF VI.
For numbering see Fig. 6.

$\vec{R}$	x	y	z
2,1	−0.2401	−0.8039	0.5441
3,2	−0.9916	−0.1292	0
3,4	0.4577	−0.8660	−0.2013
5,4	0.4577	0.8660	−0.2013
5,6	−0.9916	0.1292	0
6,1	−0.2401	0.8039	0.5441
7a,1	−0.9952	0	−0.0982
7b,1	0.5982	0	−0.8014
8,2	0.4346	−0.6885	−0.5805
9,2	0.3082	0.2818	0.9087
3,10	0.2622	0.6343	0.7273
3,11	0.3102	0.2659	−0.9127
5,12	0.2622	−0.6343	0.7273
5,13	0.3102	−0.2659	−0.9127
14,6	0.4346	0.6885	−0.5805
15,6	0.3082	−0.2818	0.9087

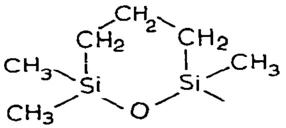
C—N bond distance [20] (R(C—N) = 1.45 Å) and from the C—N—C bond angle (= 107° [20]): A value of m(C—N) = 0.15 D was obtained. Calculations were carried out for the two configurations shown in Fig. 6, and the distance unit vector components needed for the calculations are summarized in Table 6. The following dipole moment values were obtained for the two configurations: VI(a): $\vec{\mu} = -0.0317\,\vec{i} - 0.1202\,\vec{k}$; $\mu = 0.1565$ D. VI(b): $\vec{\mu} = 0.8399\,\vec{i} - 0.5048\,\vec{k}$; $\mu = 0.9799$ D. Since μ_A is 1.129 D and μ_B 0.994 D, the conclusion can be drawn that only configuration VI(b) exists. This is consistent with the known fact that lone electron pairs, owing to repulsive potentials, tend to occupy positions as fas as possible from each other (e.g. as in hydrazine [25]).

In VII, the two rings are linked by a siloxane bond. The two identical rings are shown schematically in Fig. 7. Owing to the different linkage of the rings, the 4-2 or 4-1 rotational conformations may exist. In these cases the following general rotational formula must be used for the calculations:

$$\mu^2_{\text{rot}} = m_1^2 + m_2^2 + 2m_0^2(1 + \cos\beta) + 2m_1 m_0 \cos\alpha_1 (1 + \cos\beta) + 2m_2 m_0 \cos\alpha_2 (1 + \cos\beta) + 2m_1 m_2 \cos\alpha_1 \cos\alpha_2 \cos\beta$$



where Q is



where m_1 and m_2 are the group moment vectors of the rings and β = 130° [20]. Results of our calculations for steric position 4-1: m_1 = 0.9611 D; m_2 = 0.7984 D; $\cos\alpha_1 = -0.4174$; $\cos\alpha_2 = -0.3937$; m_0 = 0.97 D; $\cos\beta = -0.6428$; μ = 1.2551 D. Results for steric positions 4-2: $m_1 = m_2$ = 0.9611 D; m_0 = 0.97 D; $\cos\alpha_1 = \cos\alpha_2 = -0.4174$; $\cos\beta = -0.6428$; μ = 1.2067 D.

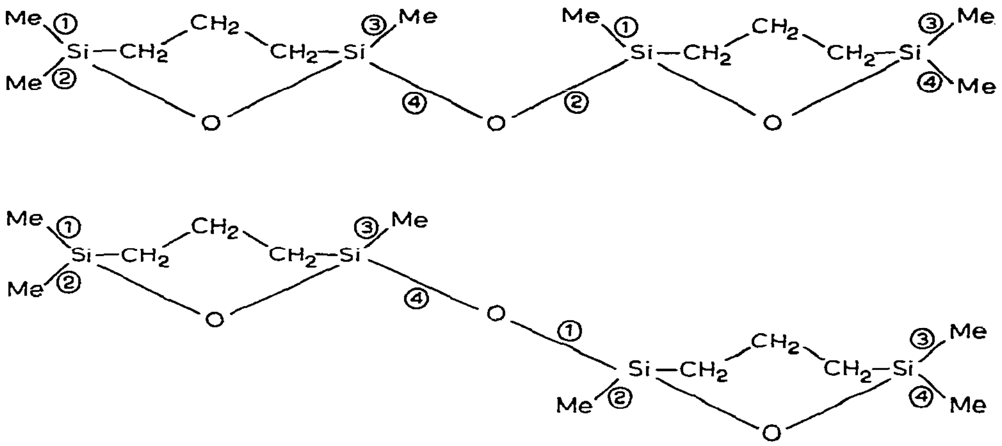


Fig. 7. Possible positions of two rings of compound VII.

The value of the experimental μ_B is 1.276 D. It follows from a comparison of the results that both cases are possible, but the 4-1 rotational conformation is the more probable.

The three views of VIII and the numbering of its atoms are shown in Fig. 8. Calculation has been made on the steric configuration in which the four silicon

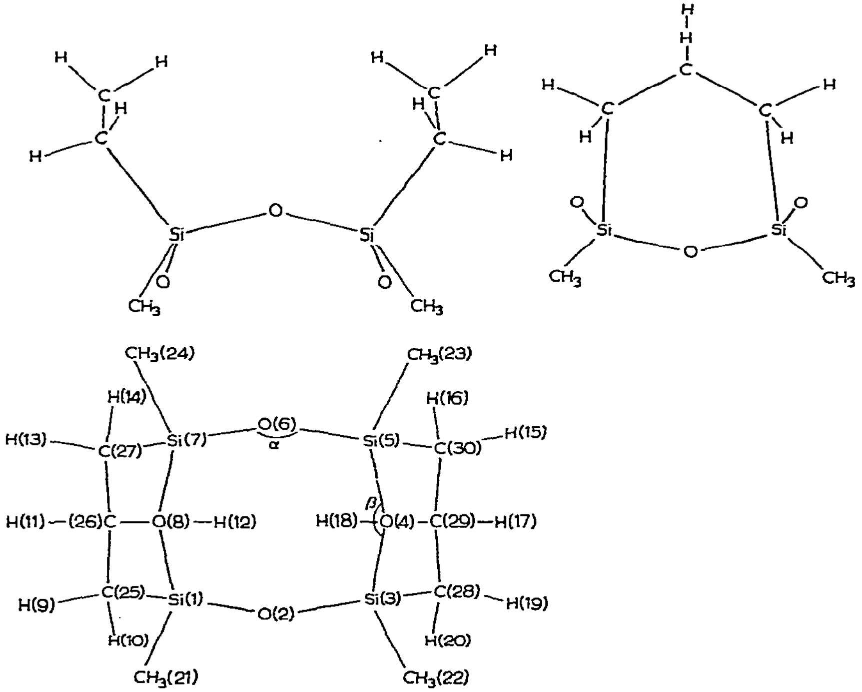


Fig. 8. Three projections and the numbering of VIII.

atoms lie in the same plane, and one of the opposing oxygen pairs is above this plane, and the other below it. Bond distances, bond angles and bond moments used were the following: R(C—C) = 1.5 Å, R(Si—C) = 1.93 Å, R(Si—O) = 1.634 Å, R(C—H) = 1.09 Å; α = 142° [20], β = 120°; m(1—2) = 0.97 D [7], m(3—4) = 1.04 D.

The distance unit vector components of the compound are summarized in Table 7. The calculations produce $\vec{\mu}$ as $-0.7300\,\vec{k}$, and μ as 0.7300 D, compared with values of μ_A of 1.074 D and μ_B of 0.803 D.

According to Bokij and Struchkov [23], in the case of cyclotetrasiloxane, configurations belonging to the point groups C_i, S_4, C_{4v} are possible. In the case of octamethylcyclotetrasiloxane, the structure C_i exists at low temperatures, S_4 at higher temperatures, in the crystalline phase, while in solution and vapour phase the structure C_{4v} is present. Assuming the structure C_{4v} for VIII (which means that all the oxygen atoms are in one plane), the computed dipole moment is 2.38 D. But since the dipole moment measured is much closer to the first calculated values, the structure shown in the figure is correct.

Investigation of the relationship between the dipole moment of the Si—O bond and the siloxane bond angle

It was found that the dipole moment of the Si—O bond depends on the

TABLE 7

DISTANCE UNIT VECTOR COMPONENTS OF VIII

For numbering see Fig. 8.

$\vec{R}$	x	y	z
1,2	0.9455	0.1803	0.2712
3,2	−0.9455	0.1803	0.2712
3,4	0.1969	−0.8660	−0.4595
5,4	0.1969	0.8660	−0.4595
5,6	−0.9455	−0.1803	0.2712
6,7	0.9455	−0.1803	0.2712
7,8	−0.1969	0.8660	−0.4595
1,8	−0.1969	−0.8660	−0.4595
1,21	−0.3338	0.7372	−0.5874
3,22	0.3338	0.7372	−0.5874
5,23	0.3338	−0.7372	−0.5874
2,24	−0.3338	−0.7372	−0.5874
1,25	−0.5793	−0.0796	0.8115
3,28	0.5793	−0.0796	0.8115
5,30	0.5793	0.0796	0.8115
7,27	−0.5793	0.0796	0.8115
26,27	−0.0466	−0.8192	−0.5716
26,25	−0.0466	0.8192	−0.5716
29,28	0.0466	0.8192	−0.5716
29,30	0.0466	−0.8192	−0.5716
9,25	0.9514	−0.1970	0.2383
10,25	−0.0915	−0.8183	−0.5671
19,28	−0.9514	−0.1970	0.2383
20,28	0.0915	−0.8183	−0.5671
13,27	0.9514	0.1970	0.2383
14,27	−0.0915	0.8183	−0.5671
15,30	−0.9514	0.1970	0.2383
16,30	0.0915	0.8183	−0.5671
11,26	0.7514	0	−0.6598
12,26	−0.8484	0	−0.5293
17,29	−0.7514	0	−0.6598
18,29	0.8484	0	−0.5293

TABLE 8

Si—O—C AND Si—O—Si BOND ANGLES OF SOME OXYGEN-CONTAINING ORGANOSILICONS, COSINES OF THE BOND ANGLES AND THE m(Si—O) BOND MOMENT

Compound	$\theta°$	m(Si—O)	$-\cos\theta$
Alkoxysilanes	113	1.22	0.3907
1-Oxa-2,6-disilacyclohexanes	120	1.04	0.5000
Hexamethyldisiloxane	130	0.97	0.6428
Octamethylcyclotetrasiloxane	142.5	0.70	0.7880

bond angle: The higher is the bond angle, the lower is the dipole moment of the Si—O bond. For various oxygen-containing organosilicons values for Si—O—C bond angle and m(Si—O) are: Alkoxysilanes [22] 113°, 1.22 D. 1-Oxa-2,6-disilacyclohexanes 120°, 1.04 D. Hexamethyldisiloxane 130 ± 10°. 0.97 D. Octamethylcyclotetrasiloxane [24] 142.5°, and $\mu = 1.09$ D, from which m(Si—O) = 0.7 D. In Table 8, these data and the cosines of the θ bond angles have been summarized, and the Si—O bond moments have been plotted as a function of $-\cos\theta$ (Fig. 9).

Thus the Si—O bond moment can be calculated when the siloxane bond angle is known, and vice versa. Using this result, more accurate calculations for VIII have been carried out. Instead of m(Si—O) = 0.97 D, m(Si—O) = 0.7 D has been selected at a bond angle of 142.5°. In this case, as resultant dipole moment for configuration S_4 a value of $\mu = 1.02$ D was obtained, which lies closer to the experimental value of $\mu_A = 1.074$ D. At the same time, the dipole moment for C_{4v} configuration has also been calculated, and this too resulted in a much higher value ($\mu = 2.0812$ D).

Experimental

I has been prepared by the hydrolysis of $C_2H_5O(CH_3)_2Si(CH_2)_3$-$Si(CH_3)_2Cl$ [10]. B.p.: 146°.

II has been prepared by the hydrolysis of $Cl(CH_3)(C_6H_5)Si(CH_2)_3Si(C_6H_5)$-$(CH_3)Cl$ [11]. B.p. 181 - 185°/7 mmHg.

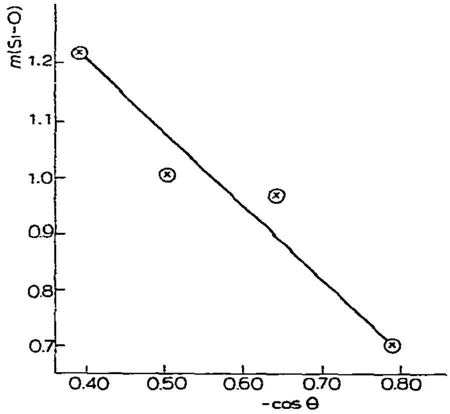


Fig. 9. Plot of bond moment against the cosine of bond angle.

III has been prepared by the hydrolysis of $Cl(C_2H_5O)(CH_3)Si(CH_2)_3Si(CH_3)(OC_2H_5)Cl$ with a calculated quantity of water at −5 to 0°, in the presence of $N(C_2H_5)_3$ [11]. B.p.: 92 - 96°/17 mmHg. Yield: 45%.

Preparation of IV: 68 g (0.51 mole) of $(C_2H_5)_3SiOH$ and 40 g (0.51 mole) of pyridine was dissolved in 120 ml of benzene, and under stirring, a solution of 31.4 g (0.11 mole) of $Cl_2(CH_3)Si(CH_2)_3Si(CH_3)Cl_2$ in 80 ml of benzene was added drop by drop. The mixture was boiled for 5 hours, washed with water and dried with Na_2SO_4. By fractionation 12.7 g of compound IV was obtained. B.p.: 120 - 125°/1 mmHg. Yield 28.5% and 18.6 g of $[(C_2H_5)_3SiO]_2(CH_3)Si(CH_2)_3Si(CH_3)[OSi(C_2H_5)_3]_2$. B.p.: 205 - 210°/1 mmHg.

V was prepared by the reaction of bis(chloromethyl)tetramethyldisiloxane with H_2S and KOH [12]. B.p. 72 - 72.5°/19 mmHg. Yield: 55%.

Preparation of VI: 20 g of bis(chloromethyl)tetramethyldisiloxane and 36 g of ethylamine were stirred in a closed flask for 30 minutes, during which the temperature of the reaction mixture strongly increased. The flask was left overnight, and the precipitate which formed was then filtered off, and VI was obtained by distillation. B.p.: 61.5°/17 mmHg. Yield: 75%.

VII was obtained by the hydrolysis of $Cl(CH_3)_2Si(CH_2)_3Si(CH_3)Cl_2$ [10]. B.p.: 116 - 117°/8 mmHg. Yield: 75%.

VIII was prepared by the hydrolysis of $Cl_2(CH_3)Si(CH_2)_3Si(CH_3)Cl_2$ [11]. B.p.: 105 - 106°/1 mmHg. M.p.: 100°C.

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