*Dipole Moments of Cyclic Siloxanes and Thiosiloxanes**

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Introduction

The molecular structures of cyclic siloxanes have been studied in various ways, especially by electron diffraction[1,2] and by X-ray study[3]. Although Sauer and Mead[4] calculated the dipole moments of several cyclosiloxanes from the dielectric measurements on pure liquids, they did not discuss the configuration in detail. The physicochemical studies of cyclothiosiloxanes have not yet been carried out extensively, but Yokoi and Nomura[5] have made electron diffraction studies on these compounds.

The measurement of the dipole moments of these compounds in nonpolar solvents seemed to be desirable to elucidate the geometrical configurations and atomic polarizations of these compounds as well as the polarity of Si-O and Si-S bonds. Hence we measured the dipole moments of hexamethyldisiloxane, two cyclosiloxanes, and two cyclothiosiloxanes in benzene solution.

Experimental

The materials used were kindly given to us by Mr. M. Yokoi of Nagoya University. They are:

I. Hexamethyldisiloxane. b.p. 98°.
II. Hexamethylcyclotrisiloxane. m.p. 64.5°, b.p. 135°.
III. Octamethyltetracyclosiloxane. m.p. 17.4°, b.p. 171°.

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* Read before the Annual Meeting of the Chemical Society of Japan held on April 4, 1953.

[1] E. H. Aggerwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).

[2] M. Yokoi, (to be published shortly).

[3] L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945).

[4] R. O. Sauer and D. J. Mead, *J. Am. Chem. Soc.*, **68**, 1794 (1946).

[5] M. Yokoi and T. Nomura, (to be published shortly).

IV. Tetramethylcyclodithiosiloxane*. m. p. 105.5°, b.p. 172–3°.

V. Hexamethylcyclotrithiosiloxane*. m. p. 17–8°, b.p. 151.5–3.5° (38 mm. Hg.)

The apparatus and the method of measurements were the same as given already in our previous paper[6]. For the calculation of $P_{2\infty}$, we used a modified Hedestrand's method[7]. The results are shown in Table I. The values of P_0+P_A of these compounds are not very large, and the calculated moments therefore depend sensitively upon the assumed values of P_A. The values in Table I are considered to be most reasonable, as will be discussed in the following.

TABLE I

DIPOLE MOMENTS OF CYCLOSILOXANES AND CYCLOTHIOSILOXANES IN BENZENE SOLUTION

	temp.	ε_1	d_1 (g./cc.)	α	(g./cc.)	$P_{2\infty}$ (cc.)	R_D	P_A	μ(D)
I	20°	2.2845	0.87610	0.13	−0.12	67.1	48.9	4.9=0.1R	0.80
II	30°	2.2632	0.86642	−0.070	0.047	66.7	55.8	10.9=0.2R	0.0
III	25°	2.2750	0.87114	0.11	0.082	98.1	74.5	14.5=0.2R	0.67
IV	30°	2.2652	0.86554	0.348	0.133	64.3	55.3	9.0	0.0
V	20°	2.2839	0.87635	0.804	0.162	116.0	82.9	10.9	1.03

The data found in the literature of the subject to be compared with the present results are that of the compound I 0.79D measured by Freiser, Eagle and Speier[8], which is in good agreement with ours. Sauer and Mead found the values 0.74D and 1.09D for the moment of I and III respectively. Their results, however, should not be compared directly with our results, since their measurements were carried out on pure liquids.

Discussion of the Results

Polarity of Si-O bond If we use ∠SiOSi =130°, evaluated from electron diffraction data of the experiment on I,[9] and the moment of 0.80D observed for I, the moment of Me_3SiO-group can be calculated as $0.80/(2\cos 65°)=0.95$D**, which is identical with the value estimated by Freiser and others. It is only half as great as the value, 2.2D estimated by Sauer and Mead[4]. On the assumption that the bond moment of O–H is equal to 1.5D and the valency angle SiOH to 110°, the moment of trimethylsilanol is calculated to be 1.5D or 2.2D, according to the value of Me_3SiO-group moment of 0.95D or 2.2D. If we compare these values with the observed moment of Et_3SiOH[10], 1.50D, it may be concluded that the Me_3SiO-group moment estimated by us is more proper than that of Sauer and Mead***. Subtracting the bond moment of Si-C (1.0D) and H-C (0.4D) algebraically from the Me_3SiO-moment (0.95D), we obtain the Si-O bond moment as 1.55D.

If we take into consideration the contribution of the ionic structure $Si^+—O^-$ only, the Si-O moment is calculated to be 3.2D, twice as large as the observed value. This discrepancy is explained as follows. It has generally been acknowledged by many authors that silicon has an ability to expand the valency shell beyond octet and to from multiple bonds. Therefore the $Si^-=O^+$ double bond structure contributes to the normal state in such a manner as to cancel the moment of $Si^+—O^-$ structure partly. Pauling[11] presented an elaborate method of calculating the percentage character of the polar and the double bond structure in oxygen acid, such as silicate ion. If we apply his method to the bond of siloxane, the ionic character of $Si^+—O^-$ is estimated to be 41%, the double bond character of $Si^-=O^+$ to be 27% and the Si-O bond length to be 1.63A. From these values, SiO moment is calculated to be 1.1D, which agrees fairly well with the observed value of 1.55D, considering the approximations made in the calculation.

Atomic Polarization of Cyclotrisiloxane and Cyclodithiosiloxane From an electron diffraction study of hexamethylcyclotrisiloxane II, Aggerwal and Bauer[1] concluded that it has a planar structure. Frevel and Hunter[3] reached the same conclusion from an X-ray investigation on it. Accordingly it is reasonable to assume that it has a planar structure with no permanent moment even in

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* T. Nomura, M. Yokoi and K. Yamasaki, *Proc. Japan Acad.*, **29**, 342 (1953).

[6] Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951).

[7] Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **26**, 242 (1951).

[8] H. Freiser, M. V. Eagle and J. Speier, *J. Am. Chem. Soc.*, **75**, 2824 (1953).

** If we use the value of ∠SiOSi=137° cited in *Ann. Rev. Phys. Chem.*, **2**, 224 (1951) instead of 130°, the moment of Me_3SiO-group is calculated as 1.09D.

*** From the constancy of the moments per monomeric units of dimethylsiloxane polymers greater than tetramers, they concluded that −0=160° and that the group moment of Me_3SiO is equal to 2.2D. However, the observed moments can be explained adequately with our value for the bond moment, if a slight hindrance of rotation about Si-O bond is assumed to be present.

[9] K. Yamasaki, A. Kotera and M. Yokoi, *J. Chem. Phys.*, **18**, 1414 (1950).

[10] M. Pizotti, *Gazz. Chim. Ital.*, **73**, 143 (1943).

[11] L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

solution. Then we are led to the conclusion that II has the atomic polarization of 10.9 cc., amounting to 20% of the electronic polarization. It is not an unreasonable value as compared with the large atomic polarization of compounds with a similar ring structure, such as paraldehyde (11.4 cc.) and trioxane[12] (13 cc.). Baker et al.[13] obtained large atomic polarizations for linear polysiloxanes.

In the molecule IV, the distortion of the valency angle of SiSSi and SSiS and the repulsion between methyl groups across the ring are minimum for the planar configuration. This supposition was confirmed by Yokoi and Nomura[5] with an electron diffraction study. Hence it can be assumed that IV has a planar structure with no permanent dipole moment. Then the atomic polarization is estimated as $P—R_D=9$ cc.

These results will be used later for the estimation of the atomic polarizations of III and V.

Configuration of Octamethylcyclotetrasiloxane If the atomic polarization of III is assumed, from analogy to II, to be 14.5 cc. or 20% or R_D, the moment of III is calculated to be 0.67D. From the electron diffraction study Yokoi[2] determined the valency angles of O and Si and bond lengths, but he failed to draw a definite conclusion concerning the configuration of the molecule. Among the possible symmetrical configurations, only the crown form has a finite moment (1.7D)*, while the cradle and tub forms have no moment. The possible explanation of the observed moment (0.67D) is that III exists either as mixture of these symmetrical forms or as a certain less symmetrical form intermediate between these symmetrical forms. For example, D-form has a moment of 0.6–0.7D.

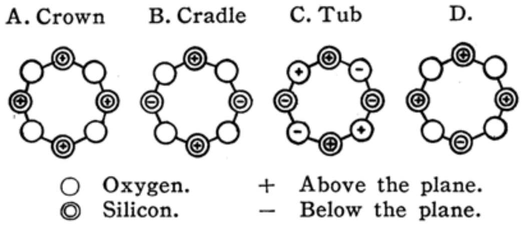

Fig. 1

Configuration of Hexamethylcyclotrithiosiloxane V has a moment of 1.03D, even if it has an atomic polarization 10.9 cc., the same value in magnitude as that of the corresponding oxygen compound II. The large of 1.03D for V rules out the planar symmetrical model similar to that in II.

The theoretical values for the chair and the boat configurations were calculated as follows. The moment of the chair form is given by $\mu=3\sin\theta\mu_{\text{SSiS}}$. In this expression, θ, the angle between the SSS plane and the SSiS plane, is calculated from the relation,

$$\cos\theta=(2\sin\alpha/2-\sin\beta/2)(\sqrt{3}\cos\beta/2),$$

where α is the valency angle of SiSSi and β the valency angle of SSiS. Assuming the bond moment of Si-S**, Si-C and H-C to be equal to 1.0D, 1.0D and 0.4D, respectively, and the valency angle of Si to be tetrahedral, the SSi(Me$_2$)S group moment, μ_{SSiS}, is calculated as 0.62D. On these assumptions, the resultant moment of the chair form is calculated to be 1.06±0.14D for the value of α equal to 110±5°, obtained from the electron diffraction by Yokoi and Nomura[5]. The moment of the boat form is calculated to be equal to about one third of that of the chair form. From the comparison of these values with the observed one, V appears to have predominantly the chair configuration. As the moment of the boat form is relatively smaller than that of the chair form, the existence of a small amount of the former does not affect appreciably the theoretical value of the moment of the mixture. When $\alpha=110°$, a mixture composed of 94% of the chair form and 6% of the boat form gives exactly the observed value, 1.03D. When $\alpha=105°$, the composition is 73%–27%. Hence the apparent agreement between the observed and the calculated moments does not preclude the existence of the boat form definitely. On the other hand, it is expected also from the consideration of the moleular model that the boat form of V is not significantly unstable compared with the chair form since the large Si-S distance will decrease steric repulsions. It is desirable to study the possibility of the existence of the boat form.

Summary

The dipole moments of several cyclosiloxanes and cyclothiosiloxanes were measured in benzene solution. The values obtained are: Hexamethyldisiloxane (I), 0.80D; octamethylcyclotetrasiloxane (III), 0.67D; hexamethylcyclotrithiosiloxane (V),

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[12] R. J. W. Le Fèvre, J. W. Mully and B. M. Smyth, *J. Chem. Soc.*, **1950**, 290.

[13] E. B. Baker, A. J. Barry and M. J. Hunter, *Ind. Eng. Chem.*, **38**, 1117 (19.6).

* In obtaining this value, we used the following values ∠SiOSi=140°, ∠OSiO=115° evaluated from electron diffraction study by Yokoi and H−C=0.4D, Si−C=1.0D and Si-O =1.55D estimated above.

** The ionic character of the Si—S bond is estimated to be equal to 11% from the electronegativity difference of Si and S. Then the Si—S moment may be taken as 1.0D, using 2.14 Å as the Si—S distance.

1.03D. The atomic polarizations obtained are: hexamethylcyclotrisiloxane (II), 10.9 cc.; tetramethylcyclodithiosiloxane (IV), 9.0 cc. The unexpectedly small bond moment of Si-O (1.55D) can be explained by the double bond character of the bond. For the configuration of (III) and (V), it is impossible to draw any definite conclusion from the study of the dipole moment alone.

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