weak infrared band at 518 cm.$^{-1}$ is assigned to the ν_4 vibration; this value agrees fairly well with the value of 533 cm.$^{-1}$ from the Raman data. The lack of any significant infrared adsorption in the vicinity of 754 cm.$^{-1}$ confirms the assignment of this Raman band as ν_1.

The strong band at 598 cm.$^{-1}$ can be assigned with reasonable assurance to one of the oxygen–hydrogen torsional modes. It is possible that the band at 1310 cm.$^{-1}$ is the other torsional mode, since this is about the frequency which could be expected. It also could result from the overtone $\nu_1 + \nu_4$ although the value of 1310 cm.$^{-1}$ seems somewhat high; such an overtone is not unexpected, however, since it appears in the infrared spectra of the solid fluoborates.[13,14] It does not seem possible at present to give a satisfactory assignment to the weak band at 867 cm.$^{-1}$.

Discussion

As a check on the Raman spectrum of the borate ion, calculations based on the Heath–Linnett[17] potential function for tetrahedral structures were carried out. Using our values for ν_1, ν_3 and ν_4 to evaluate the three constants, the value of ν_2 was then calculated to be 382.7 cm.$^{-1}$. This value is in good agreement with the observed value of 379 cm.$^{-1}$.[18]

In all of the foregoing material, it was assumed that the borate ion is monomeric in aqueous solution. Such is not necessarily the case, but there is no good evidence that polymers do exist in large percentage in aqueous solution. For example, cryoscopic data on sodium borate solutions up to two molar concentration do not show any deviations attributable to polymerization.[19] It is also worth noting that the multiplicity of lines which should occur in the Raman data if polymerization were taking place are certainly not present, and that the ν_1 line is the predominant Raman line in all borate solutions from 0.18 molar up to saturated solutions of the potassium salt. For these reasons, the assumption that the borate ion is monomeric in aqueous solution seems justified.

The combination of results obtained in this investigation plus those from previous studies lead to the conclusion that the structure of the aqueous borate ion has tetrahedral symmetry. In all likelihood, therefore, it is $B(OH)_4^-$.

Acknowledgments.—The authors are indebted to D. F. Hornig and P. N. Schatz for many helpful discussions, and to C. C. Ferriso for carrying out the infrared measurements.

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[18] A similar calculation for the fluoborate ion using the values ν_1 = 772 cm.$^{-1}$, ν_3 = 1030 cm.$^{-1}$ and ν_4 = 520 cm.$^{-1}$ from the infrared data[13,14] gave ν_2 = 366 cm.$^{-1}$. This value agrees well with our value of 369 cm.$^{-1}$ and less well with the value of 353 cm.$^{-1}$ of Goubeau and Bues.[10]

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric Properties and Molecular Structure of Hexamethyldisiloxane[1,2]

BY RUSSELL S. HOLLAND[3] AND CHARLES P. SMYTH

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The dielectric constant and loss of hexamethyldisiloxane have been measured over a wide temperature range. From the data, a dipole moment of 0.46 in the pure liquid, and 0.66 in the vapor phase have been calculated; the atomic polarization was determined as 7.9 cc. These values are shown to be consistent with the wide Si–O–Si valence angle and its unusual flexibility. The unusually low critical wave length, about 0.1 cm., calculated from the losses are attributed to the considerable symmetry of the molecule and the low viscosity of the liquid.

Because of the importance of the silicones, the relatively simple molecule of hexamethyldisiloxane has been extensively investigated. From measurements on the pure liquid, Sauer and Mead[4] obtained a dipole moment value 0.74×10^{-18} for the molecule, while Baker, Barry and Hunter[5] obtained 0.43. From measurements in benzene solution, Freiser, Eagle and Speier[6] obtained 0.79. Unpublished measurements by Dr. A. Di Giacomo in this Laboratory gave polarization values for the vapor which showed no regular variation with temperature, the observed fluctuations in value being within the possible experimental error. The vapor results indicated zero dipole moment with a large atomic polarization, which could not be determined in the liquid measurements. These apparently discordant results were reconcilable if the dipole moment was actually zero and the atomic polarization, necessarily neglected in the liquid measurements, had a high value of 13 cc. A large atomic polarization seemed entirely reasonable in view of the softness[7,8] of the silicon–oxygen bond, likened to a ball-and-socket joint, indicated by X-ray analysis of octamethylspiro[5.5]pentasiloxane. However, electron diffraction has given 130 ± 10° for the Si–O–Si valence angle,[9] a value consistent with those found for cyclic siloxanes,[10] which, however, could be some-

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[2] This paper represents a part of the work submitted by Mr. R. S. Holland to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Procter and Gamble Fellow in Chemistry, 1953–1954.

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[10] E. H. Aggarwal and S. H. Bauer, *ibid.*, **18**, 42 (1950).

what different. Symmetry considerations make it evident that, with an oxygen valence angle of 130°, the molecule would have to possess a dipole moment unless the sum of the H–C, C–Si and Si–O bond moments were zero. Consequently, the measurements of dielectric constant and loss described in the following section were undertaken in an attempt to resolve the dilemma.

Experimental Measurements

The sample of hexamethyldisiloxane used was kindly given us by Dr. J. D. Hoffman of the General Electric Company. Having a stated purity of better than 99.5%, it was used without further purification; n^{20}_D 1.3776, lit. n^{20}_D 1.3772–1.3774.

Microwave measurements of dielectric constant ϵ' and loss ϵ'' were made at wave lengths of 1.24, 3.22, 6.17 and 10.2 cm., over a temperature range of −60 to +40°, using methods previously described.[11-14] The so-called static dielectric constant ϵ_0 was measured at a frequency of 525 kc. with a heterodyne beat apparatus.[15] Temperatures below the ice point were obtained with an acetone–Dry Ice bath, and all temperature measurements were made with a thermistor and resistance bridge. The thermistor was calibrated against a previously calibrated platinum resistance thermometer.

The specific volume was determined over a temperature range of −80 to +40°, using both a dilatometer and a pycnometer, the former having an approximate volume of 0.19 ml., and the latter a volume of 16.9 ml. Both were calibrated with *n*-heptane and agreement between the two methods was excellent. The empirical equation obtained for the specific volume of the liquid hexamethyldisiloxane as a function of temperature, $t°$, is $v = 1.2752\,(1 + 1.304 \times 10^{-3}t + 9.06 \times 10^{-7}t^2)$. At the melting point, −67.5°, the specific volume rises from 1.1193 to 1.1685 cc./g. The experimental data are shown in Table I.

TABLE I

DIELECTRIC CONSTANTS, LOSSES AND SPECIFIC VOLUMES OF HEXAMETHYLDISILOXANE

t, °C.	v (cc./g.)	ϵ_0	λ_0 (cm.)	ϵ'	ϵ''
−80(solid)	1.118	2.33 ± 0.05			
−60(liquid)	1.180	2.422	1.24	2.368	0.0430
			3.22	2.404	.0200
−40	1.210	2.353	1.24	2.324	(.0274)
			3.22	2.343	(.0152)
−20	1.242	2.290	1.24	2.279	.0205
			3.22	2.285	.0111
2	1.279	2.227	1.24	2.220	.0154
			3.22	2.224	.0075
			10.22	2.221	.0006
20	1.309	2.179	1.24	2.178	.0123
			3.22	2.179	.0050
			6.17	2.180	.0014
			10.22	2.178	.0004
40	1.344	2.130	1.24	2.132	.0091
			3.22	2.130	.0031
			10.22	2.130	.0003

The data in Table I have been used to calculate several quantities which are given below in Table II. At each of the temperatures listed Cole and Cole arc plots[16] were constructed, plotting ϵ'' against ϵ'. The values of ϵ_∞ obtained from these plots are tabulated, together with induced polarizations $P_A + P_E$ and total molar polarization P, which are calculated from the relations

$$P_A + P_E = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \times Mv \quad \text{and}$$

$$P = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \times Mv$$

As will be seen shortly, the average value of $P_A + P_E$ from this and other methods is 55.5 cc. This value was the basis for a new set of ϵ_∞ values which were used in the construction of a new set of arc plots. This procedure minimizes individual errors in the original data. The values of critical wave length, λ_m, and distribution coefficient, α, shown in Table II are calculated from the second set of arc plots. The average value of $P_E + P_A$ disregards the value of 58.2 obtained at −40°, which deviates from the mean of the other four values by eight times the average deviation of 0.4.

TABLE II

CRITICAL WAVE LENGTHS, DISTRIBUTION COEFFICIENTS, OPTICAL DIELECTRIC CONSTANTS AND POLARIZATIONS

t, °C.	λ_m(cm.)	α	ϵ_∞	$P_E + P_A$ (cc.)	P (cc.)
−60	0.15–0.36	0.4	2.21	55.1	61.60
−40	.10– .16	.2	2.26	(58.2)	61.04
−20	.13	.2	2.14	55.4	60.61
2	.11	.2	2.06	54.4	60.25
20	.14	0	2.06	55.5	59.93
40	.10	0			59.69

Av. = 55.1 ± 0.4 cc.

Discussion of Results

The increase of the molar polarization P of the liquid with decreasing temperature, the sharp drop in the static dielectric constant with solidification despite the drop in specific volume, and the not inconsiderable dielectric loss show that the hexamethyldisiloxane molecule possesses a dipole moment. The accurate calculation of the moment is made difficult by its small size and the considerable atomic polarization, P_A. Since the moment is small, a value for the total induced polarization, $P_E + P_A$, may be obtained by plotting P against the reciprocal of the absolute temperature, $1/T$. The value 55.8 thus obtained differs by approximately its probable error from the value 55.1 obtained from the arc plots. In an attempt to determine $P_E + P_A$ as the polarization of the solid, which gave no evidence of molecular rotation, the dielectric constant of the solid was measured several times. The value obtained depended somewhat on the rate of cooling and on the extent of void formation, but a fairly satisfactory value gave $P_E + P_A = 55.5 \pm 1$. In Table III are shown these polarization values, together with dipole moments, calculated by various methods.

TABLE III

POLARIZATIONS AND CALCULATED DIPOLE MOMENTS

t, °C.	Method	$P_E + P_A$ (cc.)	μ (× 10^{18})
−60–+40	Arc plots	55.1	
−80	ϵ of solid	55.5	
−60–+40	$P - 1/T$ slope	55.8	0.45
−60–+40	Onsager eq.		0.45–0.46
20–40	λ_m and ϵ''		0.45– .48
30	Benzene soln.		0.54
47–247	Vapor		0.66 ± .05

Although a calculation of moment by means of the Debye equation from the slope of the P–$1/T$ curve for a pure polar liquid must be somewhat approximate, the value 0.45 thus obtained is identical with the value obtained by means of the Onsa-

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ger equation at all the temperatures within the wide range measured.

The dielectric loss gives a means of obtaining the dipole moment without use of the induced polarization. The Debye equations may be put in the form[17]

$$\mu^2 = \frac{27kT\epsilon''(1 + \omega^2\tau^2)}{4(\epsilon' + 2)^2 Nc\pi\omega\tau}$$

where $c = 1/Mv$, k is the Boltzmann constant, ω is the angular frequency used in the measurement, τ is the relaxation time, N is Avogadro's number, and T is the absolute temperature. Values of μ have been calculated by means of this equation from the experimental values of ϵ' and ϵ'' at 20 and 40°, using both 1.24 and 3.22 cm. data. Corresponding calculations cannot be made at other temperatures because the above equation is not applicable if a distribution of relaxation times exists. The values thus obtained are indistinguishable from those obtained by the other methods. It may be concluded, therefore, that the molecule of hexamethyldisiloxane in the pure liquid possesses a moment of 0.46×10^{-18}.

The six determinations of the polarization of hexamethyldisiloxane vapor at temperatures from 47 to 247° by Dr. A. Di Giacomo[18] showed no trend with temperature and differed from a mean value 62.0 by a maximum of 0.7. Four points determined six months later by Dr. Di Giacomo and one of the authors at temperatures from 94 to 238° showed a rough trend with temperature indicating an approximate moment value of 0.6. For this substance the moment is so small that the total variation with temperature of the small orientation polarization is of the same magnitude as the experimental error, a little larger than usual, in the fairly large total polarization. The moment values calculated at each temperature from the differences between the vapor polarizations and the induced polarization, $P_E + P_A = 55.5$, show an average deviation 0.05 and a maximum deviation 0.11 from the mean value 0.66, the difference between the mean values of the two sets of measurements being only 0.01. The moment calculated from the difference between the polarization in benzene solution,[6] 61.4 and 55.5, is 0.54.

An accurate determination of the atomic polarization, P_A, requires that the electronic polarization at infinite wave length be used for P_E in place of the more commonly used molar refraction for the sodium-D line, MR_D. The optical dispersion of the refractivity of hexamethyldisiloxane at 20° was measured, using the sodium-D line and four lines in the mercury vapor spectrum. The value $P_{E_\infty} = 47.6$ cc. was thus obtained, as compared to $MR_D = 48.9$ cc., giving $P_A = 55.5 - 47.6 = 7.9$ cc. The dependence of molar refraction on wave length is shown in Table IV.

TABLE IV

DISPERSION OF MOLAR REFRACTION AT 20°

λ(mμ)	435.9	546.1	578.0	589.3	623.4
MR_λ (cc.)	50.00	49.07	48.90	48.94	48.75

The large atomic polarization value is consistent with the previously mentioned softness of the silicon–oxygen bond which permits an unusually large amount of orientation by bending of the two small resultant dipoles, which make an angle of 130° with each other.

Tetrahedral symmetry causes the moment in each half of the molecule to be the sum of three bond moments

$$m = m(\text{H–C}) + m(\text{C–Si}) + m(\text{Si–O})$$

From the moment value 0.46 found for the liquid and the Si–O–Si angle 130°, m is calculated to be 0.54, while the vapor value 0.66 gives $m = 0.78$. Calculation of the bond moments from the electronegativities of the elements[19] and an extremely approximate relation between electronegativity difference and amount of ionic character in the bond[20] gives[18]

$$m = 0.4 - 1.2 + 2.8 = 2.0$$

This is far higher than the values of m calculated from the moment values. From infrared intensities Wright and Hunter[21] have estimated that both the Si–C and the Si–O bonds are rather polar with the Si–O bond having an amount of ionic character about 2.3 times that of the C–O bond, a ratio in remarkably good agreement with that calculated from the electronegativity differences. The H–C bond moment used in the calculation of m is taken as having its positive end toward the hydrogen, but this is uncertain even when the methyl group is attached to a carbon atom. When attached to silicon, the direction may be reversed. Since Wright and Hunter conclude that the low intensity of the H–C band indicates a considerable lowering of the moment below that of the bond when the methyl is attached to carbon, it seems best to set $m(\text{H–C}) = 0$, which reduces the calculated m to 1.6. The discrepancy between this value and the value 0.78, which would be 0.96 if the Si–O–Si angle had its upper limit 140°, is still large, but no larger than those sometimes observed between observed bond moments and those calculated in this way.[22,23] More modern calculations show[23] that such discrepancies are to be expected because the charge distribution in the molecule is much more complicated than that used in the calculation. The strong infrared intensities do, however, suggest strong polarities for the Si–O bonds, which may be compensated for by a somewhat larger Si–O–Si angle than that indicated by the electron diffraction results. It would seem, therefore, that there are no serious discrepancies in a molecular model with an overall dipole moment of 0.6×10^{-18}, almost negligible polarity in the H–C bonds, considerable polarity in the Si–C bonds, so much ionic character in the Si–O bonds that the bond length is close to that of an ionic bond,[7–9] with the oxygen valence angle widened to a value much greater than that of a covalent oxygen bond angle, and the two oxygen bonds very flexible, giving large atomic polarization and low characteristic bending frequency.

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According to the theory of Coop and Sutton,[24] the determination of P_A should permit a test of the hypothesis that the oxygen bond angle of hexamethyldisiloxane is "soft," *i.e.*, that it is easily deformed. Inserting the value $P_A = 7.9$ cc. and $\mu_i = 0.54 \times 10^{-18}$ into their relation $P_A = 4\pi N\mu_i^2/9V_i$ where V_i is the bending force constant, and treating the molecule as a one-dimensional oscillator, a very weak force constant $V_i = 0.31 \times 10^{-18}$ erg/rad.^{2} is obtained. This is less by a factor of 100 than is usual for bending force constants This calculation assumes that the bending of the oxygen bond angle is the sole contributor to P_A, since, as Coop and Sutton show, contributions from bond stretching vibrations are extremely small, usually of the order of a few tenths of a cc.

An attempt was made to calculate the wave length at which this bending vibration should appear in the absorption spectrum, using the valence force model[25] and considering the trimethylsilyl group to move as a unit. With the force constant for the Si–O stretch[21] taken as 5.0×10^5 dyne/cm. and the bond angle[9] as 130°, the bending absorption was calculated as occurring at 143 μ, and the symmetric stretching absorption at 2.9 μ. The infrared spectrum, obtained in this Laboratory with a Perkin–Elmer Double Beam Infrared Spectrophotometer, showed no strong absorption at 2.9 μ, and in the range 2 to 14 μ there were no absorptions which could be assigned to the symmetric stretching vibration. Wright and Hunter[21] expect the bending vibration to absorb near 25 μ.

When it appeared possible that the hexamethyldisiloxane molecule might have zero dipole moment, the discovery that the liquid exhibited dielectric loss and had an extremely short relaxation time, 0.6×10^{-12} sec., and short critical wave length, 0.12 cm., suggested the possibility of resonance absorption due to the low frequency Si–O–Si bending. Molecular interaction would tend to reduce a resonance absorption peak, making difficult the differentiation between resonance absorption and that due to dipole orientation. The existence of resonance absorption is not disproved, since the nearest measuring frequency, 1.24 cm., is too far from the absorption peak to enable an accurate determination of the shape and height of the absorption curve, but the establishment of a small permanent dipole moment in the molecule provides an adequate explanation of the loss.

The critical wave length is shorter than would be expected for a molecule of this size and its temperature dependence is too small to exceed the considerable experimental error arising from the remoteness of the highest available measuring frequency from the frequency of maximum loss, which is small because of the smallness of the dipole moment. Heptane solutions of ethyl bromide and *t*-butyl chloride, which have molecules smaller than that of hexamethyldisiloxane, show critical wave lengths of 0.3 cm., two and one-half times as large,[26] although the solutions have slightly lower viscosities. Dimethylsiloxanes, in general, have been found[27,28] to possess lower viscosities at 25° than the saturated hydrocarbons of corresponding molecular weight and lower molecular cohesive forces as obtained[28] from vapor pressures and viscosity temperature slopes. The smaller variation of viscosity with temperature gives lower energies of activation for viscous flow for the dimethylsiloxanes than for the hydrocarbons of approximately the same molecular weight. A probable small decrease in the critical wave length of hexamethyldisiloxane with rising temperature is obscured by the relatively large experimental error. The considerable symmetry of the molecule about an axis in the Si–O–Si plane perpendicular to the axis of the molecular dipole, which bisects the Si–O–Si angle, would so facilitate rotational orientation of the molecule around this axis as to make the abnormally short critical wave length or relaxation time and its very small temperature dependence, at least qualitatively, reasonable.

The authors wish to express their indebtedness to Dr. A. Di Giacomo and Dr. R. C. Miller for many helpful discussions and for assistance in some of the measurements.

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