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Microwave Absorption and Molecular Structure in Liquids. LXIX. Atomic Polarization and Relaxation in Several Siloxanes and Hexamethyldisilazane[1]

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Abstract: The dielectric constants and losses of hexamethyldisiloxane, hexaethyldisiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and hexamethyldisilazane have been measured over a range of temperature at 2.2 mm wavelength and at centimeter wavelengths. The data have been used to calculate the dielectric relaxation times, the atomic polarizations, and the dipole moments. Use of the very large values found for the atomic polarizations in the calculation of the dipole moments gives much smaller moment values than those previously reported in the literature which did not take account of the atomic polarization. The large atomic polarizations and the short relaxation times found are consistent with the great flexibility which has been ascribed to the Si–O–Si bonds. They are discussed in terms of the structures of the molecules.

An anomalously low value for the dielectric relaxation time of hexamethyldisiloxane obtained from centimeter wavelength measurements[2] indicated the desirability of higher frequency measurements to establish the low value more exactly. The unexpectedly small dipole moment,[2,3] the large atomic polarization,[2,3] the wide Si–O–Si valence angle,[4] and the frequency of occurrence of the silicon–oxygen bond give additional reasons for the extension of the measurements to 2.2 mm wavelength. Four other silicon compounds have also been measured in the hope of throwing additional light upon the problems involved.

Measurements and Calculations

Hexamethyldisiloxane, hexamethyldisilazane, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane were obtained from the General Electric Co. in very pure form. Hexaethyldisiloxane of similar purity (99.5%) was obtained from the Dow-Corning Corp. Measurements of dielectric constant ϵ' and loss ϵ'' were made at wavelengths of 0.22, 1.25, 3.22, 10.01, and 25.00 cm at 21, 40, and 60°, using the methods already described.[5–9] The ϵ' value at 25 cm, or at an even shorter wavelength, depending on the loss, was indistinguishable from the so-called static dielectric constant ϵ_0 obtained with a heterodyne beat apparatus.[10] For hexamethylcyclotrisiloxane, the loss ϵ'' was so low that the dielectric constant ϵ' at 3.22 cm was used for ϵ_0. The values for these quantities given in Table I have been used for Cole–Cole[11] analysis in the IBM 7094 computer. The values of ϵ_∞, the infinite-frequency or optical dielectric constant, τ_0, the most probable re-

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Table I. Dielectric Constants and Losses

Temp, °C	ϵ_0	λ_0, cm	ϵ'	ϵ_∞	ϵ''
		Hexamethyldisiloxane			
2.0	2.223	0.216	2.185	2.102	0.046
20.0	2.179	0.216	2.152	2.098	0.042
40.0	2.130	0.216	2.108	2.056	0.033
		Hexaethyldisiloxane			
25.0	2.259	0.22	2.224	2.198	0.013
		1.25	2.246		0.013
		3.22	2.253		0.011
		10.01	2.257		0.005
40.0	2.229	0.22	2.194	2.172	0.012
		1.25	2.221		0.011
		3.22	2.225		0.008
		10.01	2.229		0.004
60.0	2.195	0.22	2.163	2.150	0.011
		1.25	2.189		0.009
		3.22	2.192		0.007
		10.01	2.194		0.003
		Hexamethylcyclotrisiloxane			
70.0	2.139	0.22	2.132	2.131	0.006
		1.25	2.138		0.003
		3.22	2.139		0.001
		Octamethylcyclotetrasiloxane			
23.0	2.390	0.22	2.350	2.318	0.030
		1.25	2.383		0.017
		3.22	2.388		0.009
		25.00	2.390		0.003
40.0	2.346	0.22	2.316	2.285	0.028
		1.25	2.343		0.016
		3.22	2.345		0.006
		25.00	2.347		0.002
60.0	2.298	0.22	2.267	2.245	0.025
		1.25	2.291		0.012
		3.22	2.295		0.005
		25.00	2.300		0.002
		Hexamethyldisilazane			
21.0	2.273	0.22	2.205	2.190	0.029
		1.25	2.265		0.027
		3.22	2.273		0.014
		10.01	2.274		0.005
40.0	2.232	0.22	2.165	2.156	0.027
		1.25	2.219		0.021
		3.22	2.230		0.010
		10.01	2.232		0.004
60.0	2.184	0.22	2.128	2.116	0.025
		1.25	2.177		0.017
		3.22	2.184		0.008
		10.01	2.184		0.003

laxation time, α, the distribution parameter, and C_2, the amplitude or relative weight of the contribution of the second relaxation process, if one exists, thus obtained are tabulated in Table II. ϵ_∞ is used to calculate the induced polarization $P_E + P_A = M(\epsilon_\infty - 1)/d(\epsilon_\infty + 2)$ where M is the molecular weight and d the density. The total polarization P is obtained similarly from ϵ_0. The electronic polarization P_E is calculated from n_∞, the refractive index at infinite wavelength. The refractive indices n are measured at at least two wavelengths, the sodium D-line and the H_α or H_β line, to calculate[12] n_∞ from

$$n_\infty = \frac{\lambda_1^2 n_1 - \lambda_2^2 n_2}{\lambda_1^2 - \lambda_2^2}$$

The dipole moment μ has been calculated by means of the Onsager equation[13] with ϵ_∞ used instead of n^2.

Table II. Polarization (cc) and Dipole Moment (D.) Values

Temp, °C	P	P_A	Temp, °C	P	P_A
Hexamethyldisiloxane			Octamethylcyclotetrasiloxane		
2.0	60.42	9.4	23.0	98.11	22.1
20.0	60.25	9.6	40.0	97.80	22.2
40.0	60.04	9.5	60.0	97.34	22.1
Hexaethyldisiloxane			Hexamethyldisilazane		
25.0	86.61	11.0	21.0	62.27	9.9
40.0	86.37	11.0	40.0	62.12	9.9
60.0	86.10	10.9	60.0	61.86	9.9
Hexamethylcyclotrisiloxane					
70.0	65.84	9.7			

Compound	P_E	μ_{lit}	μ_n	μ
Hexamethyldisiloxane	47.60	0.46[a] 0.74[b] 0.80[c]	0.73	0.38
Hexaethyldisiloxane	72.85		0.72	0.38
Hexamethylcyclotrisiloxane	55.82	0.0[c]	...	(0.14)
Octamethylcyclotetrasiloxane	74.55D 72.5 (est)	0.67[c] 1.09[b]	1.00	0.42
Hexamethyldisilazane	49.40		0.74	0.37

[a] Reference 2. [b] R. O. Sauer and D. J. Mead, *J. Am. Chem. Soc.*, **68**, 1794 (1946). [c] Reference 3.

Table III. Relaxation Times, Distribution and Weight Parameters, and Energy of Activation

Temp, °C	α	τ_0[a]	τ_1[a]	τ_2[a]	C_2	ΔF, kcal/mole
		Hexamethyldisiloxane				
2.0	0.14	0.74	2.1	0.5	0.60	2.5
20.0	0.00	0.27	...	0.3	1	
40.0	0.00	0.21	...	0.2	1	
		Hexaethyldisiloxane				
25.0	0.44	2.4	11.4	0.6	0.54	2.4 (τ_2)
40.0	0.44	1.6	10.7	0.4	0.62	0.7 (τ_1)
60.0	0.38	1.1	10	0.4	0.67	
		Hexamethylcyclotrisiloxane				
70.0	0.04	(2.7)				
		Octamethylcyclotetrasiloxane				
23.0	0.00′	1.9				1.3
40.0	0.00	1.7				
60.0	0.00	1.6				
		Hexamethyldisilazane				
21.0	0.05	2.7				1.2
40.0	0.00	2.4				
60.0	0.00	2.0				

[a] 10^{-12} sec.

For comparison, values calculated with n_∞^2 are listed as μ_n in Table III. As the measurements were made at three different temperatures, the free energies of activation $\Delta F^{\ddagger}$ could be calculated in the usual manner.[14]

Discussion of Results

Dipole Moments. The dipole moments in Table II tend to be much lower than those in the literature, in which the effects of the large atomic polarizations are neglected. When n^2 is used in the moment calculation instead of ϵ_∞, the moment value μ_n obtained is almost twice as large and in satisfactory agreement with previous literature values calculated in this way. The values of $P_E + P_A$ and P for hexamethylcyclotrisiloxane differ by no more than the total probable error, and

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(12) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 405.

(13) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

(14) C. P. Smyth, ref 12, p 63.

the very small apparent moment value in Table II is indistinguishable from zero. This zero moment is consistent with the planar structure of the molecule indicated by electron diffraction[15] and X-ray analysis[16] and taken correctly by Kurita and Kondo[3] as indicating zero dipole moment. With zero dipole moment Kurita and Kondo took the total polarization $P = P_E + P_A$ and thus obtained a value of 10.9 for P_A, which is a little larger than the value 9.7 in Table II because their value of P was 66.7 as compared to 65.8 in Table II. Their estimated atomic polarization for hexamethyldisiloxane was only 4.9 and that for octamethylcyclotetrasiloxane was 14.5, the estimates being made from comparison with hexamethylcyclotrisiloxane. Consequently, their dipole moment values for these two compounds are more than twice as large as those listed for μ in Table II. The presumably correct moments μ for the four unsymmetrical molecules in Table II are almost identical.

Atomic Polarizations. The atomic polarizations of hexamethyldisiloxane and hexamethyldisilazane are almost equal, indicating that the Si–N bonds have almost the same unusual flexibility that the Si–O bonds have. The atomic polarization of hexaethyldisiloxane is only 1.5 larger than that of the hexamethyl compounds, the small increase coming from the six CH_2 groups in the former compound. The main distortion polarization is evidently associated with the Si–O–Si portion of the molecule. The virtual identity of the atomic polarization of hexamethylcyclotrisiloxane with those of hexamethyldisiloxane and hexamethyldisilazane indicates that the binding of the six Si–O bonds in the planar ring considerably reduces their flexibility. Further indication of this reduction of flexibility by ring formation is given by the fact that the atomic polarization found in this laboratory[17] for the corresponding open-chain compound is 19.0, about twice as large. The available instruments did not cover the range needed for the extrapolation of the refraction of octamethylcyclotetrasiloxane to infinite wavelength. The molar refraction for the sodium D-line marked with D is, therefore, given in Table II, and used to estimate a value of P_E. A reasonable estimate of the extrapolated value P_E is 72.5 ± 0.5, which gives the value 22 for P_A shown in Table II. This value, which is only a little lower than that found in this laboratory for the corresponding open-chain compound, shows much greater flexibility than that of the symmetrical, planar hexamethylcyclotrisiloxane molecule. Kurita and Kondo[3] interpret the moment found for this substance as suggesting the existence of its molecules in a mixture of forms (crown, cradle, and tub) or in a single, slightly polar form intermediate between these. There would seem to be a possibility of shift from one form of the eight-membered ring to another with greater flexibility than that found in the present work for the symmetrical, planar six-membered ring.

Relaxation Times. The most probable relaxation time τ_0 found for hexamethyldisiloxane, 0.7 at 2°, and the value 0.14 of the distribution parameter α agree well within the experimental uncertainty with the values 0.6 and 0.2, respectively, previously obtained[2] with no measurement below 1.2 cm wavelength. However, the values of τ_0 at 20 and 40° show an abrupt drop from the 2° value and the distribution apparent at 2° is absent at the higher temperatures. The data at 2° can be well represented in terms of two relaxation times,[18] the longer of which should be associated with a molecular rotational motion and the shorter with an intramolecular motion. The intramolecular process appears to take over almost entirely at 20 and 40°, where the values of τ_0, presumably τ_2, are consistent with that of τ_2 at 2° as evidenced by the linearity of the plot of log τ_2 against $1/T$. The existence of two relaxation processes at lower temperatures is also suggested by the increase of the distribution parameter to 0.4 at −60° in the earlier measurements.[2] For hexaethyldisiloxane, the large value of the distribution parameter indicates more than one relaxation time, and the data are well represented in terms of two relaxation times. The larger of these is about what might be expected for the rotational relaxation of a molecule of this size. The values of τ_2 for hexaethyldisiloxane are somewhat larger than those for hexamethyldisiloxane as would be expected from the larger size of the ethyl groups as compared to the methyl. Although the values of C_2 show increase in importance of the shorter relaxation process with rising temperature, the shorter process does not dominate completely in this temperature range as it does in the case of the smaller molecules.

Since the molecular dipole moment of hexamethylcyclotrisiloxane has been concluded to be zero, it is evident that the relaxation time obtained for it in Table III cannot be for molecular dipole rotation. Indeed, the dielectric loss 0.006 at 2.1 mm wavelength and 70° is lower than the value 0.0073 found for nonpolar benzene at 20° at the same wavelength—further evidence of the absence of any permanent moment in the molecule. This relaxation time, although of the same order of magnitude as the others in Table III, is presumably associated with a different mechanism and will be considered with those of other nonpolar liquids to be discussed in another paper.

The molecule of octamethylcyclotrisiloxane is large and its dipole moment is small but real. The single relaxation time found for it (Table III) is too small to correspond to simple rotational orientation of a rigid molecule of this size. In spite of the fact that the molecule is a closed ring, it seems probable that sufficient bending and twisting of the flexible Si–O bonds can occur to produce the equivalent of an orientation of the net molecular dipole moment, somewhat like that proposed[19,20] for diphenyl ether and similar molecules, though different in detail. Hexamethyldisilazane, which has a molecule similar in size to that of hexamethyldisiloxane, shows only a single relaxation time in the temperature range investigated here. It is much larger than the τ_0 values found for hexamethyldisiloxane, but not far from the value of τ_1 attributed to the rotational orientation of the molecule of this substance. There is no evidence in these results of the very rapid intramolecular relaxation process indicated for hexamethyl- and hexaethyldisiloxane.

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

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The values of the free energy of activation may be too approximate to have significance. The free energies for the shorter relaxation processes in hexamethyldisiloxane and hexaethyldisiloxane appear unexpectedly to be higher than that for the longer relaxation process in hexaethyldisiloxane and those for the only relaxation process evidenced in octamethylcyclotetrasiloxane and hexamethyldisilazane.

From viscosity measurements on hexamethyldisiloxane and octamethylcyclotetrasiloxane[21,22] values of η have been interpolated by means of the Arrhenius equation to the temperatures corresponding to those of the relaxation times. The ratios τ/η are shown in Table IV. The ratio of τ_2/η for hexamethyldisiloxane is much closer to that of τ_0/η for octamethylcyclotetrasiloxane than is τ_2 to τ_0 in Table III. A considerable part of the difference between the two would appear to be due to viscosity. However, the rapid increase of τ/η with temperature for octamethylcyclotetrasiloxane points also to an intramolecular motion less susceptible to the influence of viscosity than molecular rotation is.

Table IV

Temp, °C	τ, 10^{-12} sec	η, cp	τ/η
	Hexamethyldisiloxane		
	τ_2		
2	0.45	0.659	0.68
20	0.27	0.512	0.53
40	0.21	0.402	0.52
	Octamethylcyclotetrasiloxane		
	τ_0		
23	1.91	2.243	0.85
40	1.72	1.638	1.05
60	1.59	1.180	1.32

The fact that the values of τ/η in Table IV are smaller by a factor not far from 10 than those found for effectively rigid molecules[23] gives further evidence of relaxation by intramolecular motion. In the reference cited the relaxation times are expressed in 10^{-11} sec, instead of 10^{-12} sec as in the present paper.

Conclusions

The low moments of these compounds are due to the reduction of the Si–O and Si–N bond moments by d_π–p_π bonding below those to be expected from the considerable difference between the electronegativities of the bonded atoms.[4,24] In the case of hexamethyldisiloxane, the widening of the Si–O–Si angle[24] to about 150° also reduces the resultant moment.

Lazarev and Tenisheva[25] have concluded from an analysis of infrared data that the oxygen in the Si–O–Si group possesses considerable freedom of displacement in the Si–O–Si plane and perpendicular to it and that the motions involved in such displacements have such low energies as to be substantially excited even at ordinary thermal energies. Analyses of a quasi-linear triatomic molecule[26] and of disiloxane[27] have shown that, if the potential function for siloxane has minima at angles not far from 180° (150° may be near enough), the vibrational spectroscopic properties of the molecule may be indistinguishable from those of a linear molecule (180° angle). The motion may be that of a bent molecule with rotational motion superimposed on the bending vibration about the minimum of potential energy.[26] It would appear that the very short relaxation time τ_2 for hexamethyl- and hexaethyldisiloxane in Table III may be associated with dipole orientation by bending of the Si–O–Si angle from 150° through a maximum at 180° to another minimum at 150°, while the slower relaxation is molecular rotation, which, in the case of the almost linear, nearly symmetrical hexamethyldisiloxane molecule encounters little hindrance.

In octamethylcyclotetrasiloxane the Si–O–Si angle is found[28] by X-ray analysis to be 142.5°, probably wide enough to permit frequent bending through the potential maximum at 180° to reverse the direction of the dipole and thus give intramolecular relaxation, which may be too close to the frequency for molecular rotational relaxation to permit of analytical separation of the two processes in our data. The Si–N–Si angle is reported[24] to be 120° with the H and the two Si's coplanar with the N in hexamethyldisilazane. This structure does not give two potential minima separated by a maximum which can be crossed easily to give intramolecular dipole orientation or relaxation. The one relaxation time found for the molecule should, therefore, be that for molecular rotational motion. It should be longer than τ_1 for hexamethyldisiloxane because of the closeness of the latter's shape to that of a cylinder.

The abnormally high atomic polarizations which have received comment evidently arise from infrared absorptions, which have been treated from the spectroscopic point of view in the papers referred to[25–27] and in others. These atomic polarizations are several times larger than the orientation or dipole polarizations which arise from the orientation of the dipoles fixed in the molecules. With these polarizations we are beginning to enter a doubtful territory in which it may be difficult or arbitrary to distinguish between dipole polarization and atomic polarization.

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